



Australian
National
University

Exciton Dynamics in Atomically Thin Organic-Inorganic Semiconductor Materials

Ankur Sharma

June 2019

A thesis submitted for the degree of Doctor of Philosophy
of The Australian National University

Research School of Engineering
College of Engineering and Computer Science
The Australian National University

© Copyright by Ankur Sharma 2019

All Rights Reserved

Declaration

This thesis reports the research I conducted during August 2015 to March 2019, at the Research School of Engineering, College of Engineering and Computer Science, the Australian National University, Canberra ACT, Australia.

I certify that this thesis does not incorporate without acknowledgement any material previously submitted for a degree or diploma in any university, and that, to the best of my knowledge, it does not contain any material previously published or written by another person except where due reference is made in the text. The work in this thesis is my own, except for the contributions made by others as described in the acknowledgment or referenced in an appropriate manner. The thesis is a compilation of 6 manuscripts, all of which I am the first author or equal contributing first author. The manuscript details are given as below.

Manuscript 1 is presented as Chapter 3 in this thesis.

- Title: Highly enhanced many-body interactions in anisotropic 2D semiconductors.
- Authors: Ankur Sharma, Han Yan, Linglong Zhang, Xueqian Sun, Boqing Liu, and Yuerui Lu.
- Current status: published in Accounts of chemical research 51 (5), 1164-1173.
- Contributions: YL and AS conceptualized the manuscript. H.Y., L.Z., X.S., B.L. contributed to schematic making. A.S. and Y.L. co-wrote the manuscript and all authors contributed to the manuscript.
- Declaration signed from a senior author: 

Manuscript 2 is presented as Chapter 4 in this thesis.

- Title: Super-transport of Excitons in Atomically Thin Organic Semiconductors at the 2D Quantum Limit.
- Authors: Ankur Sharma, Linglong Zhang, Jonathan O. Tollerud, Miheng Dong, Yi Zhu, Robert Halbach, Tobias Vogl, Kun Liang, Hieu T. Nguyen, Fan Wang, Shilpa Sanwani, Stuart K. Earl, Daniel Macdonald, Ping Koy Lam, Jeff A. Davis and Yuerui Lu.
- Current status: Under round 2 review in Nature Communications.
- Contributions: Y. L. conceived and supervised the project; A.S., M. D, L. Z, K. L. prepared pentacene samples; A. S. carried out all the optical measurements; A. S, Y. L. and R. H. analysed the data; A. S. took the AFM imaging; J.T., S.S., S.E., and J.D. helped with setup and measurements from TR pump-probe; H. T. N., D. M., T. V., P. K. L., Y. Z. and F. W. contributed to the set up for optical measurements; A. S. and Y. L. drafted the manuscript and all authors contributed to the manuscript.
- Declaration signed from a senior author: 

Manuscript 3 is presented as Chapter 5 in this thesis.

- Title: Quasi-line spectral emissions from high crystalline 1D Organic Nanowires.
- Authors: Ankur Sharma, Ahmed Khan, Yi Zhu, Robert Halbach, Wendi Ma and Yuerui Lu.
 - Current status: Published in Nano Letters 19.11 (2019): 7877-7886.
- Contributions: Y. L. conceived and supervised the project; A.S., A.K. and Y. Z. prepared pentacene samples; A. S. carried out all the optical measurements; A. S, Y. L. and A. K. analyzed the data; A. S. took the AFM imaging; R. H., W. M., Y. Z.

helped with the schematic preparation and sample optimization. A. S. and Y. L. drafted the manuscript and all authors contributed to the manuscript.

- Declaration signed from a senior author:



Manuscript 4 is presented as Chapter 6 in this thesis.

- Title: Engineering the Exciton Dynamics and Transport in Monolayer WS₂.
- Authors: Ankur Sharma, Yi Zhu, Robert Halbach, Linglong Zhang, Bowen Wang and Yuerui Lu
- Current status: Submitted to Nature Communications and under review

Contributions: Y. L. conceived and supervised the project; A.S., Y.Z., B.W and L.Z prepared WS₂ samples and MOS device; A. S. carried out all the optical measurements; A. S, Y. L. and R. H. analysed the data; A. S. took the AFM imaging; A. S. and Y. L. drafted the manuscript and all authors contributed to the manuscript.

- Declaration signed from a senior author:



Manuscript 5 is presented as Chapter 7 in this thesis.

- Title: Defect Engineering in Few-Layer Phosphorene.
- Authors: Ankur Sharma, Bo Wen, Boqing Liu, Ye Win Myint, Han Zhang, and Yuerui Lu.
- Current status: published in Small 14 (16), 1704556.
- Contributions: Y.L. and H.Z. conceived and designed the project. A.S., B.L., B.W prepared phosphorene samples; A. S. and Y.W.M carried out all the optical measurements; A. S and Y. L. analyzed the data; A. S. took the AFM imaging; A. S. and Y. L. drafted the manuscript and all authors contributed to the manuscript.

- Declaration signed from a senior author:



Manuscript 6 is presented as Chapter 8 in this thesis.

Title: Efficient and Layer-Dependent Exciton Pumping across Atomically Thin Organic–Inorganic Type-I Heterostructures.

- Authors: Linglong Zhang*, Ankur Sharma*, Yi Zhu, Yuhan Zhang, Bowen Wang, Miheng Dong, Hieu Nguyen, Zhu Wang, Bo Wen, Yujie Cao, Boqing Liu, Xueqian Sun, Jiong Yang, Ziyuan Li, Arara Kar, Yi Shi, Daniel Macdonald, Zongfu Yu, Xinran Wang, Yuerui Lu.
- Current status: published in Advanced Materials 30 (40), 1803986.
- Contributions: *A.S and L.L.Z. contributed equally to this work. Y.R.L. and X.R.W. conceived and supervised the project; A.S., L.L.Z., Y.H.Z, Y.J.C., B. L, X. S. and A.K. prepared the samples; H. N. and D. M. contributed to the PLE set up; L.L.Z. and B.W.W conducted the measurements; L.L.Z. did the PSI measurements. L.L.Z., A.S. and Y.Z. did the PL measurements; B.W.W., M.H.D., B.W., H.N., D.M., Z.Y.L. and Y.S. contributed to data analysis; Z.W and Z.F.Y did the absorption simulation; Y.R.L, L.L.Z. and A.S. cowrote the paper; all authors discussed the results and commented on the manuscript.
- Declaration signed from a senior author: 



Ankur Sharma

January 2020

Acknowledgement

To the omnipotent and omnipresent-**Shiva**. You are Shakti. You are Shiva. You are everything male and female, light and dark, flesh and spirit. You are the universe, perfectly balanced in one single moment lasting an eternity...

As the great Hellen Keller once said, “Alone we can do so little, together we can do so much.” There are several people whom I would like to acknowledge for helping me achieve great success during my Ph.D. This thesis and the academic success I have had, is dedicated to the immense contribution from the following individuals.

First, I would like to express my deepest gratitude towards my supervisor Dr. Yuerui (Larry) Lu. He was not just a mentor, but a friend, inspiration and a source of inspiration for me during my Ph.D. I would like to thank him for his unfailing enthusiasm and guidance during my Ph.D., and for doing so much to foster my research capabilities. I would also like to thank my supervisory panel Prof. Daniel Macdonald and Prof. Chennupati Jagadish for their constant guidance and technical lab support. The technical team comprising of Prof. Hoe Tan, Prof. Lan Fu, Dr. Ziyuan Li, Dr. Sudha Mokkapati, Dipankar Chugh and Dr. Fan Wang were instrumental to help me train and operate various experimental setups. I would also like to acknowledge the technical staff at ANFF, Dr. Kaushal Vora and at CECS, ANU for their constant support in the labs. This Thesis would not have been complete without their support.

Second, I would like to extend my gratitude towards my colleagues and lab mates Dr. Jiong Yang, Linglong Zhang, Yi Zhu, Chris Zhang, Shuang Zhang, Robert Halbich, Han Yan and Bowen Wang for their constant help and support during my Ph.D. I had several roadblocks and these people were always there to help me overcome them. I would also like to thank all my collaborators round the world for their support with my research over the past three years.

I would like to acknowledge financial support from the ANU PhD Scholarship. I would also like to thank the College of Engineering and Computer Science (CECS) for their scholarship and living expenses support during my Ph.D. which was instrumental for my success. I would like to acknowledge the constant support I received from CECS HDR admin and Engineering School Admin team for my projects. They were the hidden support wheels, which made my journey bump free and enjoyable.

I would also like to express my gratitude towards the CECS Marketing team. They made me a very popular person on campus. Thank you, Emily O' Hara, Zoe Cornell, Rebecca McHarg, Elise Mallory, Kendall Power, Johan Arnberg, Ash Gosili and Akeel Feroz for giving me an opportunity to explore a world outside of my research. I have the best memories of my Ph.D. working and learning with them. Ph.D. was more fun because of them.

Most importantly, I would like to thank my friends. They were more like a family here in Canberra for me. Thank you, Preetha Iyer and Dr. Mahesh Venkataraman for treating me like your family. Guiding, loving and feeding me through the toughest times and being with me to share a smile through the best. Raktima Dey for invaluable suggestions, which helped me make the toughest decisions. You made me realize my strengths and weaknesses and made me a better human being. Anukriti Mathur and Astha Sharma for being with me in all my madness and showering me unconditional love and for respecting me. Meenu Kejriwal, Bikash Aggarwal and Aarav for not just taking me into your home but taking me into your hearts. Thank you, Anita Soldic, for being more than a friend- a mentor, a movie companion and more importantly being a strong believer in me.

Thank you, Elise J. Mallory, for existing. She saw something in me, which no one ever did, not even me. She was there in my best moments, without me even realizing it and she was there in my toughest without complaining about (about) it. Her support and guidance were instrumental during the most critical time of my Ph.D. and I benefitted immensely from her suggestions and zero-nonsense approach. The completion of my thesis is dedicated to her perseverance, care and unflinching trust in my abilities.

Finally, I would like to thank my parents Kusum Lata Sharma and Sunil Kumar Sharma, my grandfather Capt. (Retd.) S.N. Lal, grandmother Shanti Devi and my sister Ankita Sharma for making me every bit of a person I am today. Their unconditional love and support during my Ph.D. have been the key factors for my success. I have no words that could explain my sincere most gratitude for their sacrifices and love that they have showered me with. They say family is the backbone of one's success. In my case they are the backbone and the heart of my success. All my achievements, academic success and this thesis are dedicated to them. It is a testimony to the values and principles with which they raised me, that have made me the person I am today.

Maa and Papa this thesis and all my research is owed to your strong will, commitment and sacrifices that you made to make me fly high and reach the sky.

Abstract

Two-dimensional (2D) semiconductor nanomaterials have recently gathered significant attention due to their remarkable optical and electrical properties. Quantum confinement as resultant of reduced dimensions results in exciting optoelectronic phenomenon, which have never been reported before. This makes them promising candidates for future optoelectronics and photonics device applications. Many body interactions between fundamental particles in 2D semiconductors are strongly enhanced compared with those in bulk semiconductors, because of the reduced dimensionality and thus reduced dielectric screening. These enhanced many body interactions lead to the formation of robust quasi-particles, such as excitons, trions and bi-excitons, which are extremely important for the optoelectronics device applications of 2D semiconductors, such as light emitting diodes, lasers and optical modulators, *etc.* This thesis focusses on experimentally demonstrating properties of these many body interactions/quasi-particles and engineering them for future device optoelectronic device applications.

After the discovery of graphene, similar other inorganic 2D materials such as transition metal dichalcogenides (TMDCs) have been extensively researched. But the research is still in its early stages and there have been few attempts to study and develop organic 2D materials. First half of this thesis focusses on the interesting optical properties and exciton dynamics from a new class of organic 2D materials grown through low-temperature vapor deposition process. I observed an exciting phenomenon of superradiance/supertransport experimentally from organic 2D materials which has several potential applications in ultrafast excitonic circuits, OLEDs, high-efficiency solar cells, quantum circuits and exciton-polariton devices such as Bose-Einstein condensates at room temperature. The thesis also explores the dynamics and spatial transport mechanism of excitons and trions in inorganic TMDC materials using near-field and time-resolved PL imaging. In the thesis, I have demonstrated an external

engineering control for the exciton transport in monolayer TMDCs using back gate voltage, substantiating their use for faster long-range exciton transport applications such as excitonic transistors, quantum logic gates. The thesis further explores the dimensionality defect engineering of excitons in inorganic 2D materials such as phosphorene to 1D and quasi-0D space to enhance their properties for suitable optoelectronic device applications. This thesis demonstrates an experimental approach to generate a 2D-1D-0D hybrid system of excitons. The properties demonstrated have tremendous applications in future optoelectronic devices.

The thesis further demonstrates a 1D organic nanowire with exciting optical properties that has potential applications in organic display screens, OFETs and lasers. The exciton dynamics have been studied and reported at various temperatures to understand the nature of excitons as the dimensionality changes from 2D to 1D. The thesis reports the first demonstration of Shpol'skii spectra and zero phonon lines from a solid state system. This was achieved through high crystalline and an ordered growth of organic molecules over hBN adsorbent surfaces. The thesis also demonstrates a functional FET device made incorporating organic 1D wire to demonstrate external engineering control of the Shpol'skii spectra valuable for future nanowire based device applications.

Finally, the thesis demonstrates a first of its kind 2D organic-inorganic hybrid semiconductor heterojunction, which has high efficiency for light to electricity conversion ratio. The organic 2D material reported earlier in the thesis were used to form a heterojunction with inorganic 2D TMDC material to report interesting optical properties. The organic and inorganic part are both atomically thin and that resulted in exciting optical properties that have not been demonstrated before.

In sum, this thesis is focused on exploring the fundamental excitonic dynamics and properties in novel 2D/1D organic, inorganic atomically thin semiconductor materials for their applications in next generation miniaturized optoelectronic, electronic and photonics devices.

Publications

Journal Papers

- [1] **Sharma A**, Zhang L, Zhu Y, Zhang Y, Wang B, Dong M, Nguyen HT, Wang Z, Wen B, Cao Y, Liu B. et al. Efficient and Layer-Dependent Exciton Pumping across Atomically Thin Organic–Inorganic Type-I Heterostructures. **Advanced Materials**. 2018 Oct;30(40):1803986.
- [2] **Sharma A**, Yan H, Zhang L, Sun X, Liu B, Lu Y. Highly enhanced many-body interactions in anisotropic 2D semiconductors. **Accounts of chemical research**. 2018 Apr 19;51(5):1164-73.
- [3] **Sharma A**, Wen B, Liu B, Myint YW, Zhang H, Lu Y. **Defect Engineering in Few-Layer Phosphorene**. *Small*. 2018 Apr;14(16):1704556.
- [4] **Sharma A**, Zhang L, Tollerud J., Dong M, Zhu Y, Halbich R, Vogl T, Nguyen H, Wang F, Liang K, Sanwani S, Earl S, MacDonald D, Lam PK, Davis J and Lu Y. “Super-transport of Coherent Excitons in Atomically Thin Organic Semiconductors at the 2D Quantum Limit”. (Under Round-2 Review at **Nature Communications**, 2019.
- [5] **Sharma A**, Khan A, Zhu Y, Halbich R, Ma W and Lu Y. “Quasi-line spectral emissions from high crystalline 1D Organic Nanowires.” **Nano Letters** **19.11 (2019): 7877-7886**.
- [6] **Sharma A**, Zhu Y, Halbich R, Zhang L, Wang B and Lu Y. “Engineering the Exciton Dynamics and Transport in Monolayer WS₂.” Under review in **Nature Communications**, 2019.
- [7] Vogl, T.; Sripathy, K.; **Sharma, A.**; Reddy, P.; Sullivan, J.; Machacek, J. R.; Zhang, L.; Karouta, F.; Buchler, B. C.; Doherty, M. W.; Lu, Y.; Lam, P. K., **Nature Communications** 2019, *10* (1), 1202. DOI 10.1038/s41467-019-09219-5.
- [8] Zhang L, Yan H, Sun X, Dong M, Yildirim T, Wang B, Wen B, Neupane GP, **Sharma A**, Zhu Y, Zhang J. Modulated interlayer charge transfer dynamics in a monolayer TMD/metal junction. **Nanoscale**. 2019;11(2):418-25.
- [9] Wang X, Yildirim T, Si KJ, **Sharma A**, Xue Y, Qin Q, Bao Q, Cheng W, Lu Y. An Adaptive Soft Plasmonic Nanosheet Resonator. **Laser & Photonics Reviews**. 2019 Feb 15:1800302.

Oral Conference Presentations

- [1] Ankur Sharma. **Graphene 2017**-7th edition of Europe’s Largest International conference on Nanomaterials and 2D materials. “Dimensionality Engineering in monolayer phosphorene.”
- [2] Ankur Sharma. **ICON-2DMAT**-4th International conference on 2D Nanomaterials and Technology, Melbourne, Organized by Monash University, December 2018.

- [3] Ankur Sharma. **ICONN-2018**- 2nd International Conference on Nanoscience and Nanotechnology, Wollongong, Australia. “Defect Engineering in Few-layer phosphorene.”, February 2018.

Publications not included in this thesis

- [1] **Sharma A**, Varshney U, Lu Y. ‘Electronic applications of Graphene Mechanical Resonators’ - **IET Circuits Devices System**, (2016).
- [2] **Sharma A** et al. Extraction of Nickel Nanoparticles from Electroplating Waste & their application in production of Bio-Diesel from Biowaste’- **International Journal of Chemical Engineering and Applications**, Vol. 6, No.3, June 2015.
- [3] **Sharma A**, Ahmad N, Khan W. Zinc Oxide Nanoparticle Fuel Additives for Improved Efficiency and Emissions of Internal Combustion Engines. *Advanced Science, Engineering and Medicine*. 2016 Feb 1;8(2):135-9.

Table of Contents

Declaration	iv
Acknowledgement	viii
Abstract	xi
Publications.....	xiv
Journal Papers	xiv
Conference Papers	xv
Table of Contents	xvi
List of Abbreviations and Acronyms.....	xix

CHAPTER 1: Introduction..1

1.1 Excitons in atomically thin inorganic 2D materials and their applications.....	4
1.1.1 Transition metal dichalcogenides (TMDC).....	4
1.1.2 Phosphorene	8
1.2 Excitons in atomically thin organic 2D materials.....	10
1.2.1 Organic 2D nanomaterials.....	11
1.2.2 Excitons in organic 2D materials.....	12
1.3 Van der Waals heterostructures and their applications.....	15
1.4 Thesis Outline.....	19
1.5 References.....	23

CHAPTER 2: Experimental Techniques..... 36

2.1 Chemical vapor deposition (CVD).....	37
2.2 Atomic force microscopy (AFM)	39
2.3 Phase-shift interferometry	39
2.4 Raman and PL spectroscopy.....	41
2.4.1 Low temperature Raman and PL spectroscopy	42
2.4.2 Polarization resolved Raman and PL spectroscopy	43
2.5 Time-Resolved PL Spectroscopy	43
2.6 Pump-probe transient reflectivity measurements for lifetime	45
2.7 Near and Far-Field Scanning Optical Microscope	46
2.7.1 Diffusion length measurements	47
2.8 Device Fabrication.....	48

2.8.1 Plasma enhanced chemical vapor deposition (PECVD).....	48
2.8.2 Photolithography.....	49
2.8.3 Electron-beam evaporation	50
2.8.4 Inorganic TMDC sample preparation	51
2.8.5 Scanning electron microscope equipped with focused ion beam	52
2.9 Summary.....	52
2.10 References	53
 CHAPTER 3: Highly enhanced many-body interactions in anisotropic 2D semiconductors	 55
 CHAPTER 4: Super-transport of Excitons in Atomically Thin Organic Semiconductors at the 2D Quantum Limit.....	 68
 CHAPTER 5: Quasi-line spectral emissions from high crystalline 1D Organic Nanowires	 130
 CHAPTER 6: Engineering the Exciton/Trion Dynamics and Transport in Monolayer WS₂	 172
 CHAPTER 7: Defect Engineering in Few-Layer Phosphorene.....	 216
 CHAPTER 8: Efficient and Layer-Dependent Exciton Pumping across Atomically Thin Organic–Inorganic Type-I Heterostructures.....	 234
 CHAPTER 9: Conclusion and Future Work	 260
9.1 Key Outcomes	262
9.1.1 Superradiance and Supertransport of Frenkel Excitons in an organic 2D material	262
9.1.2 Quasi-line spectra from 1D Organic Nanowires and Shpol' skii spectra	263
9.1.3 Engineering Exciton Dynamics in inorganic 2D materials	264
9.2 Future Prospects	266
9.2.1 Exciton polaritons from organic 2D and 1D materials	266
9.2.2 High speed excitonic circuits and transistors.....	267
9.2.3 Highly efficient light emitting diodes, lasers and transistors.....	269

List of Abbreviations and Acronyms

PL	photoluminescence
2D	two-dimensional
TMD	transition metal dichalcogenide
hBN	hexagonal boron nitride
1L	monolayer
AFM	atomic force microscope
2L	bilayer
NbSe ₂	niobium diselenide
MoS ₂	molybdenum disulphide
FET	field-effect transistor
MoSe ₂	molybdenum diselenide
WS ₂	tungsten disulphide
DBR	distributed Bragg reflector

WSe ₂	tungsten diselenide
SWG	sub-wavelength reflector
SEM	scanning electron microscope
CHQ	calix[4]hydroquinone
MoTe ₂	molybdenum ditelluride
PSI	phase-shifting interferometry
OPL	optical path length
FIB	focused ion beam
SiO ₂	silica
AFM	atomic force microscopy
TRPL	time-resolved PL
FTIR	Fourier transform infrared
SOM	scanning optical microscope

PECVD	plasma-enhanced chemical vapour deposition
MOS	metal-oxide-semiconductor
CCD	charge-coupled device
LED	light-emitting diode
OPD	optical path difference
TCSPC	time-correlated single photon counting
SPAD	single photon avalanche diode
SiH ₄	silane
N ₂ O	nitrous oxide
N ₂	nitrogen
RF	radio frequency
UV	ultra-violet
4L	four-layer

5L	five-layer
15L	fifteen-layer
TEM	transmission electron microscope
STM	scanning tunnelling microscope
3L	tri-layer
QW	quantum well
PLE	photoluminescence excitation
Quasi-1D	quasi-one-dimensional
FWHM	full width at half maximum
DFT	density functional theory
0D	zero-dimensional
9L	nine-layer
NA	numerical aperture

6L	six-layer
8L	eight-layer
RCWA	rigorous coupled wave analysis
CVD	chemical vapour deposition
3D	three-dimensional
Al_2O_3	aluminium oxide
ZnO	zinc oxide

CHAPTER 1

Introduction and Thesis Outline

Introduction of the 2D materials^{1, 2, 3, 4, 5} after the advent of graphene⁸ opened up opportunities in the domain of semiconductor nanomaterials to explore the light matter interactions at the atomic limit. Recently, these 2D materials have gathered significant research attention due to their outstanding optical, electrical and optoelectrical properties^{5, 9, 10, 11, 12, 13, 14} making them ideal candidates for various device applications such as lasers^{15, 16, 17, 18}, light emitting diodes (LEDs)^{19, 20, 21}, photodetectors^{22, 23, 24} and photovoltaic devices and solar cells^{25, 26, 27}. Optoelectronic devices are electronic devices that can use electric charge to convert into electricity or vice versa.

2D materials are from the crystalline family of materials which have a single or few layers which can have zero-wide energy band gap.^{8, 28} This thesis restricts to study of 2D materials with middle-bandgap or semiconducting materials in both inorganic and organic categories. This thesis will focus exclusively on transition-metal dichalcogenides (TMDCs), phosphorene^{29, 30, 31, 32} and organic 2D materials which have band gap in the visible and near infrared regimes. To maximize the conversion ratio of photons into electrons/hole or electron hole pairs, absorbance and transmittance are the key parameters.³³ The integration of 2D materials into photonic devices is critical due to their ability to absorb significant number of photons per layer. Graphene for example, has a broadband light absorption of 2.3% below 3 eV. This scales linearly with the number of layers. The absorbance depends on the fine structure constant, given by equation (1) as follows

$$\alpha = \frac{e^2}{\hbar c} \quad (1)$$

where, c is the speed of light, e is the charge of an electron and $\hbar$ is the Planck's constant divided by 2π . Thus, the transmittance can be described by equation (2) as follows

$$T = (1 + 2\pi G_0/c)^{-2} \quad (2)$$

where, G_0 is the conductance of the material. The TMDC material show much higher absorption in the visible and near infrared regimes and their optical band gap makes them suitable for making thinnest photo-active materials.^{33, 34} The band structure of these semiconducting materials dramatically changes from single to multi-layer samples involving a direct band gap in monolayer to indirect band gap in multi-layer samples.^{1, 2,}

³ This makes them ideal candidates for next generation miniaturized and nano material based semiconducting and optoelectronic applications.

Due to reduced dimensionality and atomically thin structure, excitonic effects are especially relevant in these materials. The existence of neutral and charges excitons

makes them interesting for both experimental and theoretical studies. An exciton is a quasi-particle which consists of one electron and one hole and a trion is a negatively/positively charged exciton with an additional charge.^{12, 35, 36} Due to optically or laser excitation, electrons are inelastically excited from the valence band to the conduction band in the 2D semiconducting materials. These quasiparticles are quite stable due to the coulombic attraction between them and reduced dielectric screening in the 2D state. Inelastic light matter interactions involve this energy transfer between photons and electrons and phonons.³⁷ Photon-electron and phonon-phonon interactions result in two widely studied phenomenon known as photoluminescence (PL) and Raman shift. This thesis aims to utilize PL and Raman spectroscopy to characterize organic and inorganic classes of 2D materials.

Due to the reduced dimensionality and highly strong quantum confinement excitons in these 2D semiconducting materials are quite stable and have much higher binding energies, as explained in detail in chapter 3. Various optoelectronic applications based on inorganic and organic semiconducting 2D materials including integrated circuits and transistors depend on excitonic and trionic recombination. Thus, it is important to study the dynamics and properties of excitons and other quasi-particles in these 2D semiconducting materials at the atomic limit. This thesis aims to study the properties such as carrier recombination mechanisms, optical and energy band gaps, thermal properties and atomic bonds of the atomically thin semiconducting materials, especially under external influences such as temperature, excitation methods, electric field and direct optical injection intensities *etc.* Further, the thesis explores the possibility of using these properties to fabricate devices based on the studied low dimensional semiconducting materials. The thesis finally establishes organic and inorganic 2D materials for their respective nano device applications based on experimentally demonstrated excitonic properties and subsequent engineering modulations.

1.1 Excitons in atomically thin inorganic 2D materials and their applications

This thesis does not intend to include all 2D materials in the premise of discussion. It intends to only discuss semiconducting 2D materials with band gaps in visible or near infrared regime making them suitable for future optoelectronic and photonics device applications. This section aims at introducing the inorganic 2D materials classes, namely TMDCs and phosphorene, which have been recently discovered and are being researched extensively in this field. The most widely studied semiconductor has been graphene since its discovery in 2004 by Novoselov and Geim, et al.^{8, 38} Recently, TMD semiconductors rose up due to their intrinsic bandgap and the direct bandgap nature when thinned down to a monolayer.^{7, 39} And recently, phosphorene has attracted attention due its highly anisotropic nature and direct bandgap in the infrared range.⁴⁰ In this section, we will briefly introduce the excitonic and electrical properties of these classes of 2D semiconductors.

1.1.1 Transition metal dichalcogenides (TMDC)

The TMDC are a group of 60 materials which have been realized in 2D states with mechanical cleavage technique recently.^{36, 41} Figure 1.1 shows the broad categories in which inorganic 2D materials are classified.⁵ They are stable at room temperature and have an indirect band gap in few layer stages which changes in to direct band gap in the monolayer regime.³⁴ The Coulomb interaction in TMDC monolayers also determines the valley polarization dynamics of excitons and determines spin character and orbital selection rules.^{33, 34} The promotion of an electron from the filled valence band to the empty conduction band leaves an empty electron state in the valence band.

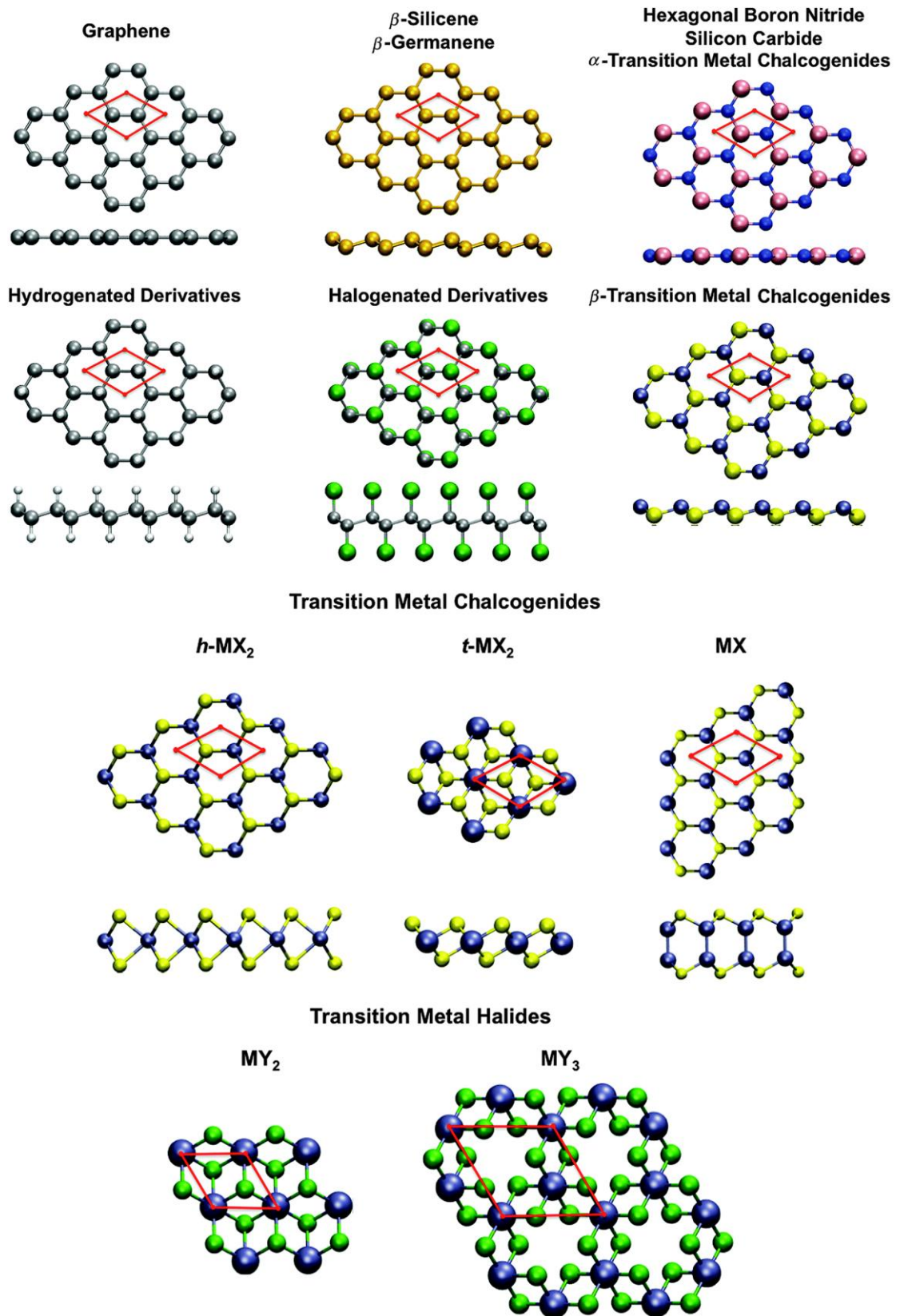


Figure 1.1 Structure of atomically thin 2D materials. Unit cells are depicted in red.

Adapted with permission from ref.⁵

The demonstration of a many-body system like an exciton can be reduced to the two-particle problem of the negatively charged conduction electron interacting with a positively charged valence hole.⁴² The direct Coulomb interaction describes the interaction of positive and negative charge distributions related to the electron and the hole. The long-range part of the direct interaction is determined mainly by the envelope function of the electron-hole pair being slightly sensitive to the form of the Bloch functions, i.e., valley and spin states; It depends on the dimensionality (which is highly reduced to 2D state here) and dielectric properties of the material.^{1, 38} The long-range direct interaction thus corresponds to attractive Coulomb forces between opposite charges. Thus, an electron and a hole can form a bound state, the neutral exciton, with strongly correlated relative positions of the two constituents in real space, as schematically shown in Figure 1.2.

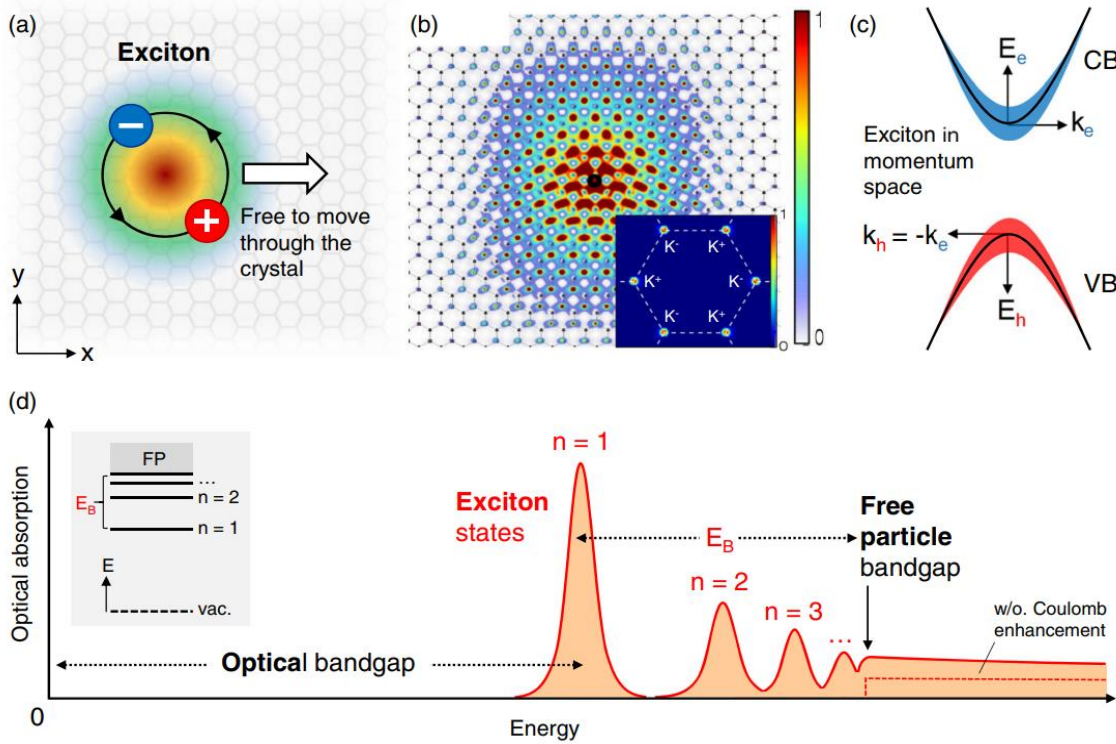


Figure 1.2(a) Schematic representation of an exciton in real space. (b) A typical exciton wavefunction calculated for monolayer MoS₂. (c) Exciton representation in reciprocal space with conduction and valence bands. (d) Illustration of optical absorption of an ideal 2D semiconductor. Inset shows atomlike energy levels. Adapted from ref¹ with permission.

Graphene does not have a bandgap, making it difficult to study electronic properties. Whereas TMDC materials own a bandgap of ~ 2 eV in the visible range and are ideal for optoelectronic applications. They can be represented by MX_2 (M represents the transition metal elements such as Mo and W and X represents the chalcogenide atoms such as S, Se and Te). They are covalently bonded in a single layer or multiple layers which are stacked over each other with weak van der Waals forces as shown in Figure 1.2.

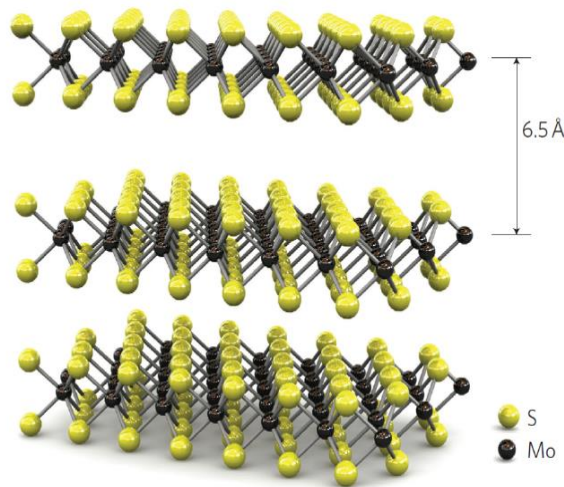


Figure 1.3 Schematic plot of MoS_2 , a typical member of TMD semiconductor. Adapted with permission from ref⁷.

In 2010, Castellanos-Gomez *et al.*⁴³ identified optically the thin TMDC crystals, including NbSe_2 and MoS_2 , which proved that monolayer MoS_2 is a direct band gap semiconductor, supported by theoretically calculating the band diagram and PL absorption and emission spectra. After that FET devices based on MoS_2 ⁷ were also demonstrated. The demonstrated carrier mobilities and high values of on/off ratio catapulted these materials into device applications. Raman and PL spectroscopy is used extensively to study the layer dependent electronic band structures and different lattice vibrations. Polarization, temperature and time-resolved spectroscopy has been subsequently used to study the excitons, trions and other high-order complexes in TMDC materials. Exciton, trion and biexciton binding energy of 1L TMDCs were measured to

be ~ 0.5 eV, ~ 30 meV and ~ 60 meV, respectively making them ideal for device applications. This thesis explores the spatial and temporal diffusion of these high order many body particles in TMDC materials using direct CCD imaging technique and time-resolved PL spectroscopy in Chapter 7.

1.1.2 Phosphorene

Phosphorene⁴⁴ (black phosphorus) is a new addition to the family of inorganic 2D materials and has shown highly anisotropic excitonic properties as compared to the TMDCs.^{29, 30, 31, 32, 45} The schematic is shown in Figure 1.4, demonstrating its puckered structure and alignment of excitons in quasi 1D space. Similar to TMDC materials, the phosphorus atoms are bonded by covalent bonds to form a continuous single layer of phosphorene and the different layers are stacked with weak van der Waals forces.⁴⁴ Recently, it was demonstrated that the electron mobility is very high in phosphorene and has layer dependent band gap, making it extremely useful for various optical and near infrared device applications.^{29, 31, 45, 46}

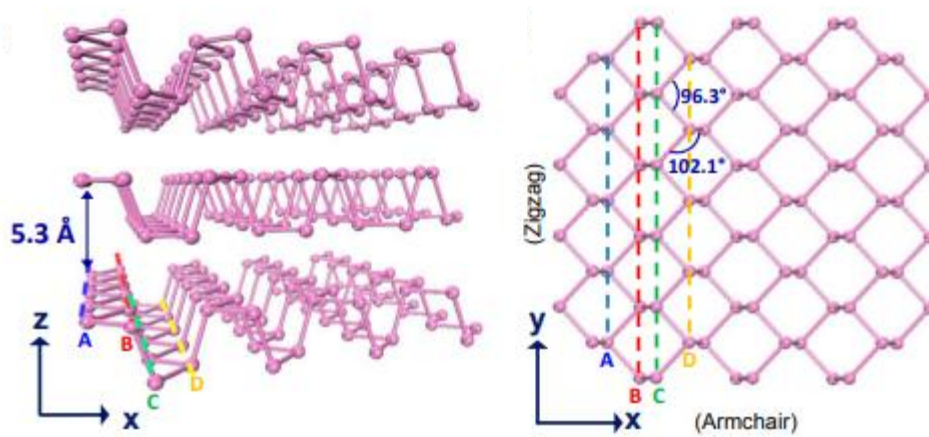


Figure 1.4: Side and top view of the crystal structure of monolayer phosphorene. Adapted from ref⁴⁴ with permission.

Owning a direct bandgap from visible to near-infrared range in 1L to few-layer phosphorene, thin-layer phosphorene can bridge the zero-bandgap graphene and comparatively large bandgap TMDs. Its direct bandgap varies with layer number, from ~ 2 eV for 1L phosphorene gradually down to ~ 0.3 eV for bulk black phosphorus.^{47, 48} With direct bandgap in the visible to near-infrared range, phosphorene can serve as the foundation material for optical and optoelectronic applications in the infrared range as shown in Figure 1.5. This thesis explores the defect excitonic emission from 1-3-layers of phosphorene using external defect induction, which is discussed in detail in chapter 7 and is focussed on highly efficient excitonic emissions from phosphorene in the NIR regime.

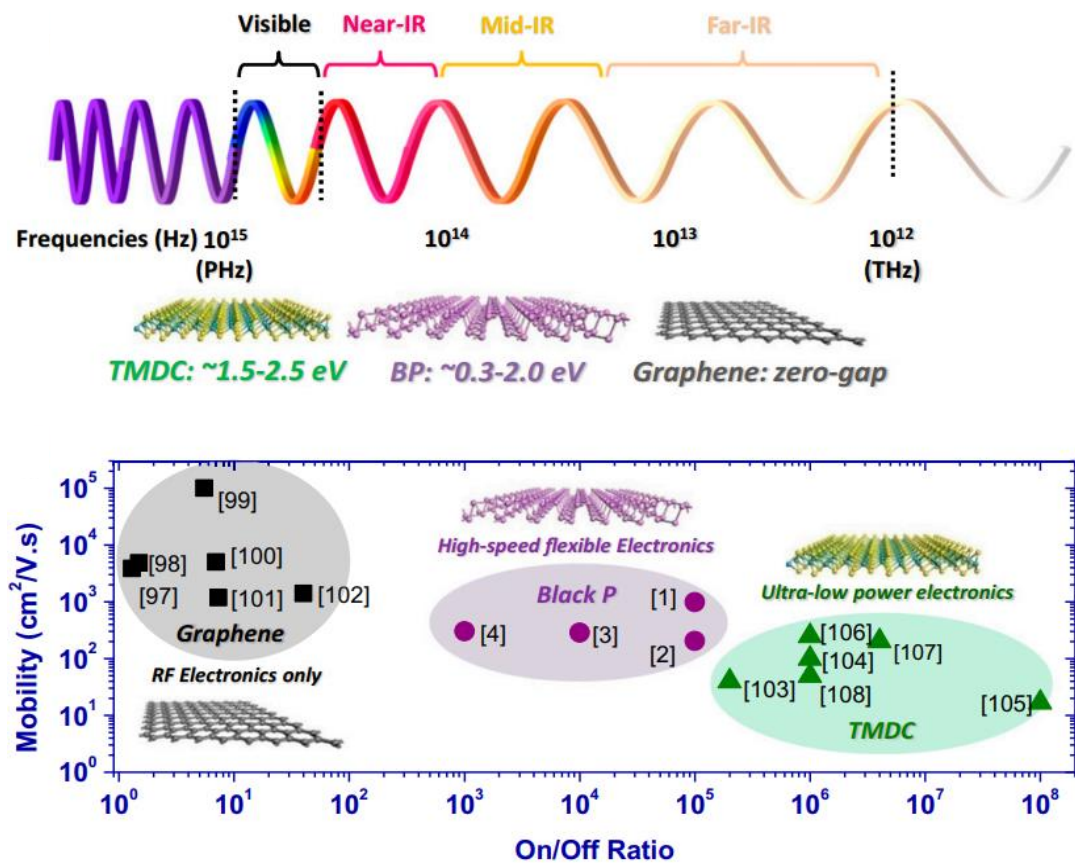


Figure 1.5: The electromagnetic wave spectrum and the band gap ranges of various types of 2D materials. The “electronics spectrum,” i.e., the mobility/on–off ratio spectrum, of nanomaterials with corresponding performance regions. Adapted from ref.⁴⁴ with permission.

1.2 Excitons in atomically thin organic 2D materials

In inorganic elemental and crystalline semiconductors, the arrangement of elements in the lattice results in delocalized electronic states and the band gaps. As a result, these inorganic semiconducting materials hence can be susceptible to impurities, defect sites and deformed crystalline boundaries which might affect their semiconducting electrical and optical properties. Another approach to solve this challenge can be to use materials which are intrinsic in nature, whose semiconducting properties are defined by each molecule and its orientation rather than their arrangement in the crystal lattice. Organic semiconductors are those intrinsic semiconductors which offer this distinct advantage. The electronic properties of molecular semiconductors are largely ‘hard-wired’ into each molecule, and do not rely on a crystal structure being formed. This renders them significantly more tolerant to impurities, packing defects or grain boundary effects and so allows far greater scope for low-cost processing. Decoupling electronic and physical structure also casts bandgap engineering as a problem of molecular design, rather than crystal composition. In particular, the tremendous flexibility of organic (carbon-based) chemistry has led to the dominance of organic molecules within molecular semiconductor technology. Figure 1.6 shows the broad classification of organic semiconductor materials. This thesis focusses on development and testing excitonic properties of a new class of 2D organic nanomaterials for various optoelectronic device applications.

1.2.1 Organic 2D nanomaterials

As discussed in the earlier sections atomically thin 2D layered materials have emerged as promising candidates for future electronic and optoelectronic devices^{7, 23, 27, 49}. Compared with bulk materials, those atomically thin layers provide an ideal platform to investigate the strong many-body interactions arising from the highly enhanced quantum confinement and reduced dielectric screening in atomic layers^{9, 14, 50, 51, 52}. But, most of

those 2D materials studied so far—which include semi-metallic graphene⁵³, insulating hexagonal boron nitride (h-BN)⁵⁴, semiconducting transition metal dichalcogenides (TMDs)^{7, 23, 49}, and phosphorene^{6, 7, 32}—are inorganic crystals with strong in-plane covalent chemical bonds. On the other hand, organic molecular crystals, which are bound by the weak van der Waals cohesive forces between small molecules, are an important class of materials for future electronic, optoelectronic, and photonic devices.^{55, 56, 57}

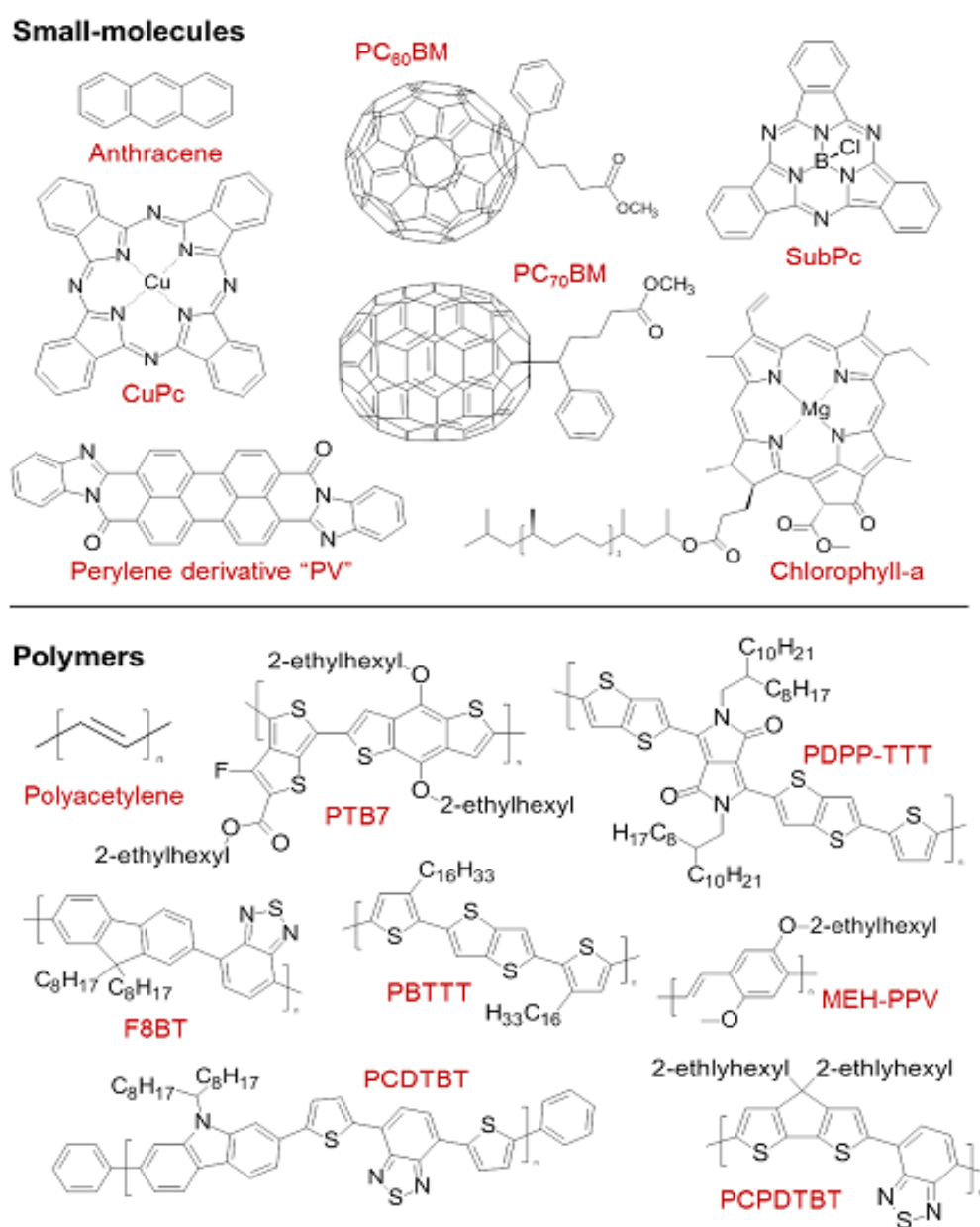


Figure 1.6 Chemical structures for a range of commonly used small-molecule and polymer semiconductors. CuPc=Copper phthalocyanine, SubPc=boron subphthalocyanine chloride. Adapted with permission from ref.⁶

1.2.2 Excitons in organic 2D materials

The excitonic nature of organic crystals plays an important role in determining their optoelectronic properties⁵⁷. In organic semiconductors, there are typically two types of excitons: Frenkel and charge-transfer (CT) excitons^{57, 58} (details mentioned in chapter 4). The Frenkel exciton is a neutral excited state in which the electron and hole are placed on the same molecule. Frenkel excitons show the characteristic of large short-range Coulombic interactions and high radiative efficiencies, enabling potential applications in organic light-emitting diode (OLED) and laser devices^{57, 59}. Whereas, the CT exciton consists of a pair of charge carriers localized at different molecules. CT excitons exhibit long-range Coulombic interactions and low recombination rates, which makes them suitable for organic solar cells and singlet exciton fission applications^{57, 59}. As soon as the energy difference between CT and Frenkel excitons becomes small, both excitons can interact and form new Frenkel–CT mixed states^{58, 60}. The mixed states are observed in most bulk and thin film organic semiconductors due to the lack of high crystallinity and the presence of disorders and interfacial states^{61, 62, 63}. The strong Frenkel–CT coupling results in the lack of feasibility of organic bulk thin film semiconductors to be potentially used specifically either as highly efficient OLED/lasers or solar cells as mentioned above, which has been a long-standing challenge for bulk thin film organic semiconductors. On the other hand, the characterization of excitons in bulk organic crystals such as polymers is particularly complicated and challenging because of the large amount of disorders and interfacial states in bulk samples^{61, 62, 63}.

In order to reduce the Frenkel-CT mixing and study the complex excitonic characters in organic semiconductors, we need to precisely control the crystallinity and molecular aggregation into H- (CT exciton dominated aggregation) and J-type (Frenkel exciton dominated molecular aggregation), as theoretically predicted by Spano *et al.*⁶⁴.

However, very limited experimental evidence exists to identify the nature of intrinsic excitons in organic semiconductors because a direct measurement of absorption is challenging due to difficulties in growing high quality ordered optically transparent single crystal samples⁵⁷. Fluorescence spectroscopic results from bulk thin film organic semiconductors are distorted due to high self-absorption, wave guiding from total internal reflection and depolarization due to crystal birefringence⁵⁷. It is therefore important to study the nature of low lying excitonic states in organic 2D materials, in order to understand the nature of excitonic transitions and the nature of their optical properties, to enhance the isolated charge generation for enhanced efficiencies in solar cells^{65, 66} and several other similar applications. Several groups have attempted to understand the excitonic nature of transitions in thin film organic materials. Initially they were predicted to comprise mostly of tightly bound Frenkel excitons⁶⁷ but Schuster et al⁶⁸ predicted the contribution of Charge transfer (CT)⁶⁹ excitons to explain the dispersion of the lowest lying states in pentacene. CT excitons in oligoacenes crystals though have been shown in the 80s by Sebastian et al^{70, 71} and very recently by Zhu et al^{69, 72}. But none of these included the contribution of vibronic coupling into their estimation. Recently, Spano et al^{64, 66, 73} used Frenkel-Holstein Hamiltonian theoretical quantum-chemical calculations to describe the contributions of CT states and vibronic coupling in low lying states of anthracene and pentacene. They have discussed the effect of CT excitation on the shape, sign and magnitude of Davydov Splitting⁷⁴ in tetracene and pentacene.

This thesis in chapter 4 and 5, for the first time deterministically reports the effect of molecular packing on optical properties of low-lying states in crystal and 2D and 1D states or organic nanomaterials. We used few layers of pentacene grown using van der Waals epitaxy on hBN surface over a silicon substrate⁷⁵ and observed strong photoluminescence (PL) emission from the few layers, which behaved differently

according to the orientation of stacking of the molecules in each layer and the incident polarization angle of excitation light which was in coherence to the theoretical calculations.^{64, 66}

From our temperature-dependent and angle-resolved photoluminescence (PL) measurements, wetting layer (WL) pentacene samples, which had H-type molecular aggregation, showed in-plane isotropic emissions that were dominated by CT excitons. In contrast, monolayer (1L) pentacene samples, which had J-type molecular aggregation, showed one sharp and strongly anisotropic PL emission peak and four isotropic PL peaks. The anisotropic and isotropic peaks were attributed to be dominated by Frenkel and CT excitons, respectively. The observed dichroic ratio (*DR*) of the anisotropic PL peak from Frenkel excitons in 1L pentacene was even slightly higher than that from the anisotropic 2D phosphorene^{6, 7, 32}. The *DR* values of isotropic PL peaks from CT excitons in WL and 1L pentacene were close to 1, which is comparable with the *DR* values found for isotropic TMD monolayers^{7, 23, 49}. Our simulation results from time-dependent density functional theory (TDDFT) quantum calculations matched very well with our experimental findings. The strongly aggregation-sensitive intrinsic excitonic emissions (H and J-type) discovered in 2D organic semiconductors in this work coupled with clear understanding of nature of excitons (Frenkel and CT) will enable the exploration of novel optoelectronic and excitonic devices that can be designed and fabricated for a specific application ranging from OLEDs to solar cells.

1.3 Van der Waals heterostructures and their applications

In the previous section this thesis has individually discussed inorganic and organic 2D materials and their interesting properties, which makes them ideal candidates for various electronic device applications. Combining two or more atomically thin materials to utilise the weak interaction between the layers resulted in a new paradigm in 2D semiconductors which are referred to as van der Waals heterostructures^{28, 76}. These vdW heterostructures have in-plane covalently bonded atomic layers which facilitates the formation of well-defined interfaces with absence of any dangling bonds⁷⁷. Figure 1.7 shows the schematic representation of the Van der Waals heterostructures.

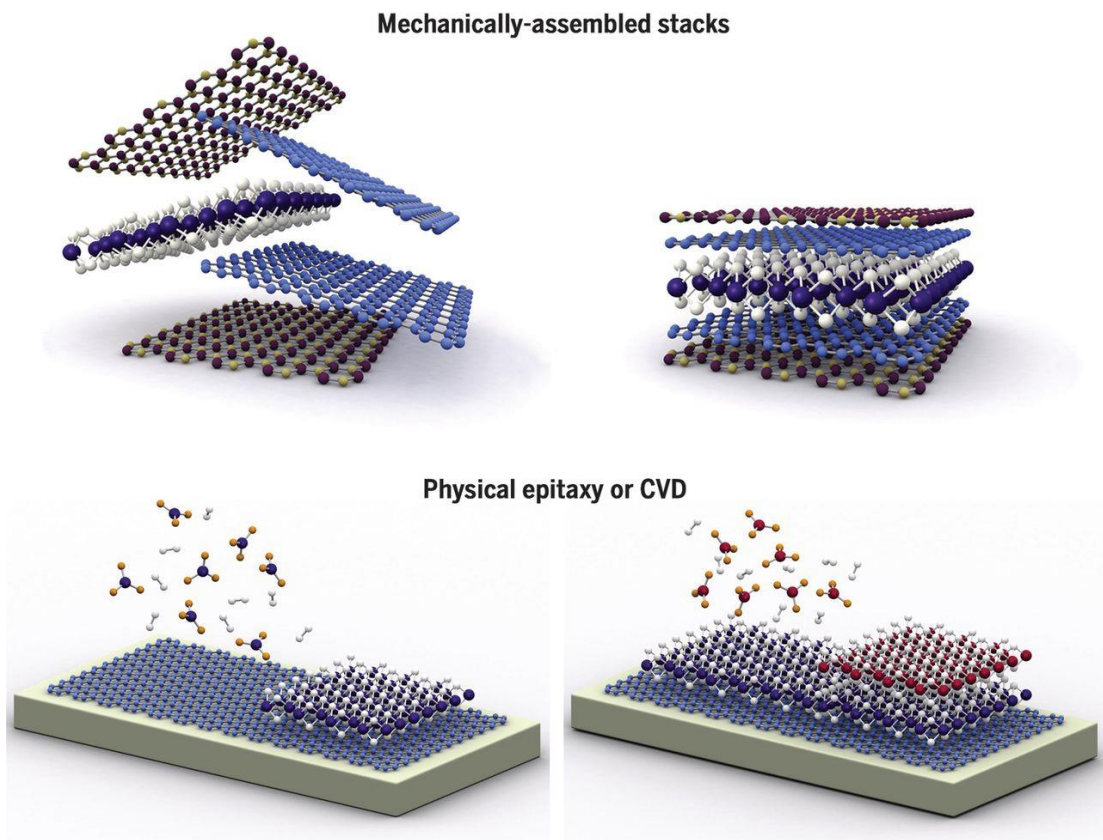


Figure 1.7: Schematic representation of mechanically stacked and epitaxially grown van der Waals heterostructures possible with 2D semiconductor nanomaterials. Adapted from ref.⁷⁸ with permission.

The constituent layers interact weakly with out of plane layers and this weak vdW interaction enables the stacking of these atomically thin layers over each other with precision. This results in interesting electronic and optical properties of these heterostructures and has resulted in demonstration of opto-electronic devices based on tuneable band gap such as photodiodes, light emitting diodes, resonant tunnelling diodes and solar cells^{79, 80, 81, 82, 83, 84}. Several combinations of 2D materials have been used to synthesize vdW heterostructures recently, but it started with the use of specific materials such as hBN and graphene to create functional interfaces between two different materials^{85, 86}. Since then various vdW heterostructures have been synthesized and reported. Specifically, junctions of various TMDC (inorganic-inorganic) have been demonstrated extensively to quantify ultra-fast charge transfer across the interacting layers and long lived dissociated charges^{87, 88, 89, 90, 91, 92, 93, 94}.

Most of these heterostructures were observed to be of Type-II nature (excitonic pair residing on different layers), based on theoretical band gap calculations and experimental observations. They reported a quenched PL spectrum from heterojunction as compared to a monolayer TMD attributing it to the fast charge movement across the layers and fast exciton dissociation. Similar ultrafast charge transfer has been established in organic-organic vdW coupled junctions^{95, 96, 97, 98} but they did not show sharp crystalline atomic interfaces and comparatively slower charge transfer and dissociation. Conversely, Type-I heterostructures have opposite behaviour with both hole and electron in an excitonic pair existing in conduction/valence bands of same material. These type-I heterostructures have been demonstrated in TDMs where photo-induced excitonic pairs are transferred from one layer to other^{99, 100, 101} with applications in light emitting devices.

Interestingly, Lee et al.⁷⁷ predicted that organic-inorganic interfaces can also combine to give such heterojunctions with epitaxially grown materials such as graphene or hBN¹⁰².

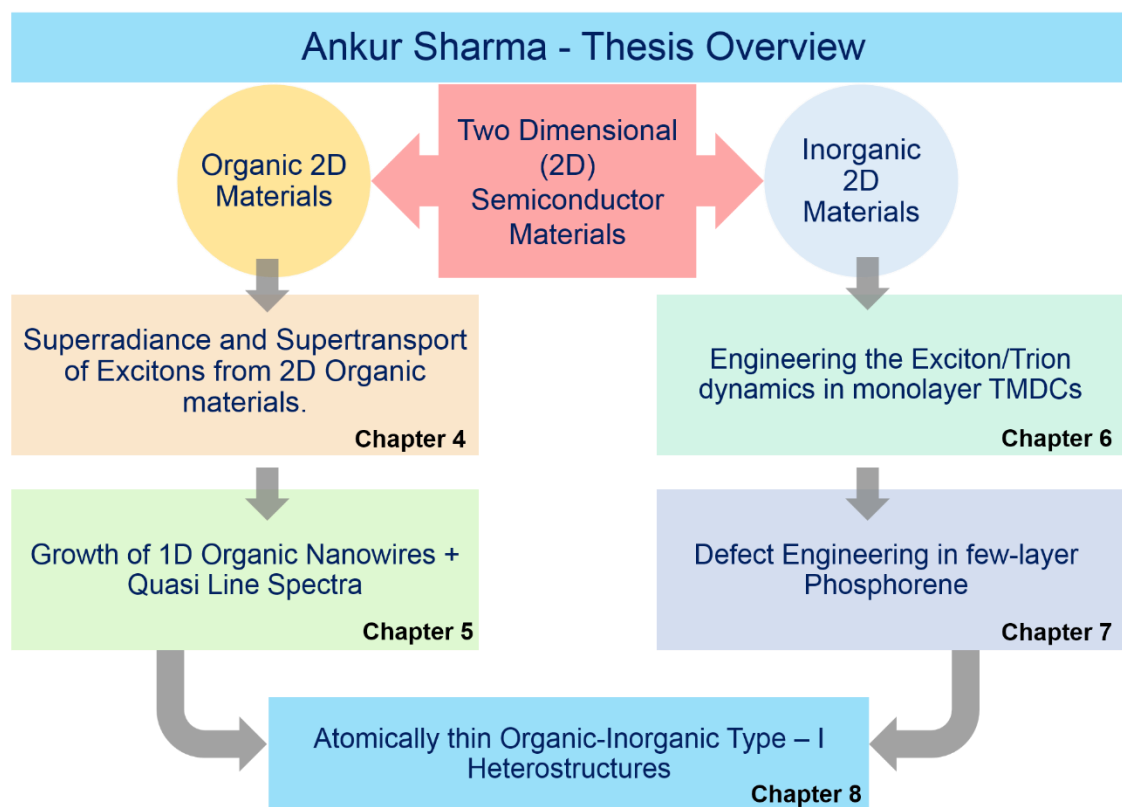
Recently, a combination of organic-inorganic (O-I) vdW heterostructure was reported with deposition of thin layer pentacene (p-type) over MoS₂ (n-type)^{103, 104} which established that such O-I interface can also facilitate ultrafast charge transfer and long lived excitons with exciton pair residing in different layers of the heterojunction. (type-II). This pentacene-MoS₂ interface hence showed PL quenching and was suited better for p-n junction photovoltaics as it had long lived separated charges. This heterojunction proved that TMDs (MoS₂ in this case¹⁰⁴) can work as acceptors/donors with the organic 2D materials to facilitate fast and efficient (50%) charge transfer across the O-I interface. But since they are type-II in nature they cannot be used for selective broadband absorption and light emitting device applications. Whereas, Type-I band alignments can be used in various optical devices due to their ability to confine electrons and holes spatially so they can combine radiatively and efficiently¹⁰⁵. There are no studies available at present that demonstrate the charge transfer across any type-I organic-inorganic heterojunctions. Thus, the subsequent challenge obviously will be to design an O-I heterostructure with Type-I band alignment and clean atomic interface grown using van der Waals epitaxy which explains the fundamental charge transfer mechanism and once the band alignment is re-engineered at the interface these junctions offer functionalities that are not achievable using single layer alone.

This thesis demonstrates in chapter 8, epitaxially grown single crystal pentacene (various thickness) over hBN surface stacked under a monolayer MoSe₂ to realize a hetero-epitaxial organic-inorganic type-I vertical vdW heterostructure. Epitaxially grown single crystal pentacene⁷⁵ provides a atomically sharp and clean interface with no dangling bonds and impurities over which a TMD MoSe₂ could be deposited to study the fundamental charge transfer mechanisms across the O-I interface^{106, 107}. The thesis reports three different heterostructures based on different thickness of pentacene layers used in

the heterostructure and observe a three times PL enhancement from the MoSe₂-PEN as compared to the monolayer MoSe₂ suggesting a type-I band alignment. This MoSe₂-PEN based heterostructure offers a distinct advantage of PL enhancement (type-I) opposite to the previously demonstrated MoS₂-pentacene heterostructure^{103, 104} (type-II) which showed a quenched PL. In further contrast to that, we have used mono/bi layer single crystal epitaxially grown pentacene (compared to thin layer polycrystalline pentacene) which provides a much sharper atomic surface free of any dangling bonds to demonstrate the fundamental charge transfer mechanism at this O-I interface. This chapter opens up new avenues for material and heterostructure fabrication based on 2D materials, which are designed specifically to achieve certain applications and objectives.

1.4 Thesis outline

This thesis is classified in to 9 chapters. This chapter (#1) has introduced the fundamental concepts about properties and structure of 2D atomically thin semiconducting materials in both organic and inorganic classes and their heterostructures. The dissertation will explore in detail the excitonic dynamics and engineer their properties to achieve optoelectronic device applications. Chapter 2 will discuss all the related experimental techniques, we have used to experimentally demonstrate the exciton properties and engineering methods used to fabricate 2D materials and devices. Chapter 3-8 explore the excitonic properties divided in to 5 segments as shown in Figure 1.8



In chapter 3, an overview of excitonic properties will be provided in the 2D materials with focus on dimensionality of excitons and how it affects the binding energy and stability of excitons and other higher order quasi particles. This chapter will talk about

the role of reduced dielectric screening, reduced dimensionality and quantum confinement in the 2D materials which gives them their interesting optical, electrical properties and the direct band gap structure. The chapter then talks about phosphorene as an example to explain anisotropic excitonic properties and how similar TMDC materials and other 2D material can be explored for device applications. The chapter finally describes various device applications based on excitonic properties such as tunable LEDs, exciton-polariton devices and defect assisted excitonic emissions for single-photon sources. This chapter was published as an article in the journal *Accounts of Chemical Research* (Impact factor = 22).

Chapter 4 introduces the concept of organic 2D materials coupled with molecular orientation dependent excitonic properties. The chapter reports a superradiant excitonic emission from monolayer pentacene 2D material, which has never been reported before on organic solid state system. The chapter then further explores the spatial and temporal diffusion of excitons in organic 2D system using a direct near-field imaging and time-resolved PL spectroscopy. We report a very high value of exciton diffusion from organic 2D material attributed as a phenomenon called supertransport of excitons. This firmly establishes the 2D organic material as a suitable candidate for applications in fast excitonic circuits and exciton polariton cavities. This chapter clearly differentiates the layer dependent optical properties we observed in monolayer to multilayer organic 2D material samples. The properties in 2D materials vary significantly as the layer number changes. This chapter characteristically studies the layer dependent optical properties from 0L-2L samples and identifies the physics behind the varying optical properties through a series of experiments. The band gap in this regime appears to be still direct as opposed to TMDCs where it changes to indirect when the layer number increases. This

chapter has been submitted as manuscript to Nature Photonics (Impact factor = 37) and is under round 2 review.

Chapter 5 further explores the growth mechanism of organic material into 1D crystalline phase for high ordered and crystalline growth. Though the thesis focusses on 2D materials and the study of their properties, but I have focused on studying these unique properties from 1D organic nanowires for the following reasons. First, growth of low dimensional organic 1D structures has been particularly challenging up to now. It is difficult to control their morphology and maintain a defect free interface. Second, the optical properties in a 1D (or a quasi 1D system) such a nanowire, can significantly enhance the quantum confinement effects and result in enhanced binding energies of the quasi-particles such as excitons leading to interesting optoelectronic properties not observed before. Thus, in this chapter, I discuss the growth of first light-weight organic nanowire system made from pentacene. We were able to grow them using the same CVD technique we used to grow 2D pentacene structures. Also, we observed a very clear vibronically resolved PL spectra from these nanowires, which has interesting applications as discussed in Chapter 5. We report the first highly ordered solid state growth of organic nanowires on hBN substrate. The optical emission from organic nanowires is vibronically well resolved even at room temperature as compared to the bulk and thin film pentacene. At low temperatures, due to reduced phonon-charge coupling and reduced degrees of freedom we report a quasi-line, zero phonon line spectra with a width of only 2-3 nm, which has never been reported from 1D organic nanowires. We attribute this to the Shpol'skii effect. Polarization resolved and time-resolved PL measurements have been used to characteristically determine the molecular orientation in 1D organic nanowires and establish the high order of crystallinity in the 1D state. The thesis further demonstrates a MOS device based on 1D nanowire to demonstrate the electrical tunability of Shpol'skii spectra for applications

in Nano lasers, Tunable LEDs and chemical sensor applications. This chapter has been published in Nano Letters.

Chapter 6 focusses on studying the exciton dynamics in inorganic TMDC materials which have been discussed in detail in chapter 1. The chapter will talk about incorporating the monolayer TMDC into a MOS device to manipulate the exciton recombination lifetime and spatial diffusion, measured using TRPL and near-field imaging techniques. We report external modulation of exciton diffusion coefficient using back gate static electric field, which has never been reported before. We further engineer the substrate by making a suspended monolayer TMDC MOS device to demonstrate the highest value of diffusion coefficient in an inorganic 2D system which is comparable to its organic counterparts. This chapter has been submitted as a manuscript to Nature Communications (Impact factor = 12.3) and is under review.

Chapter 7 further explores another inorganic 2D material-phosphorene. We use defect engineering using a PECVD grown substrate to include external defects in the puckered structure of phosphorene. We observe a highly efficient excitonic emission from defect states in phosphorene at 1430 nm, which is in the near infrared (NIR) regime. We use power dependent and temperature dependent PL measurements to establish the defect nature of these excitonic emissions. The chapter further experimentally determines the activation energy of these defect emissions to be 77.2 meV, which makes them quite stable even at room temperatures, which contrasts with what has been reported from other TMDC materials. This chapter has been published as an article in the journal Small (Impact factor = 8.2)

Chapter 8 finally combines the organic and inorganic 2D material to demonstrate a first of its kind 2D Van der Waals organic-inorganic (O-I) heterostructure. We report an ultra-highly efficient exciton pumping from the organic interface (due to its higher quantum efficiency) to the inorganic side which enhances the PL emission from monolayer TMDC by a factor of 3 times. We attribute this to superfast exciton pumping across the O-I interface supported by fast charge transfer as observed from TRPL measurements. We confirmed it to be a Type-I heterostructure using PLE measurements, which has never been reported before. We further demonstrate how the trion binding energies in the TMDC material can be modulated by changing the thickness of the organic material underneath by making a MOS device based on this heterostructure. This opens avenues for 2D heterostructures based on organic-inorganic components to be designed for specific purposes and device applications. The O-I 2D heterostructure demonstrated in this chapter has key applications in tunable LEDs, high efficiency solar cells and photodetectors.

Finally, chapter 9 summarizes all the key research findings of this dissertation and comments on future research and device prototyping prospects.

References

1. Wang G, *et al.* Colloquium: Excitons in atomically thin transition metal dichalcogenides. *Reviews of Modern Physics* 2018, **90**(2): 021001.
2. Xiao J, Zhao M, Wang Y, Zhang X. Excitons in atomically thin 2D semiconductors and their applications. *Nanophotonics* 2017, **6**(6): 1309-1328.
3. Schneider C, *et al.* Two-dimensional semiconductors in the regime of strong light-matter coupling. *Nature Communications* 2018, **9**(1): 2695.
4. Yang J, *et al.* Self-organized growth and self-assembly of nanostructures on 2D materials. *FlatChem* 2017, **5**: 50-68.
5. Miró P, Audiffred M, Heine T. An atlas of two-dimensional materials. *Chemical Society Reviews* 2014, **43**(18): 6537-6554.
6. Yamada H, Okujima T, Ono N. Organic semiconductors based on small molecules with thermally or photochemically removable groups. *Chemical Communications* 2008(26): 2957-2974.
7. Radisavljevic B, *et al.* Single-layer MoS₂ transistors. *Nat Nano* 2011, **6**(3): 147-150.
8. Geim AK, Novoselov KS. The rise of graphene. *Nat Mater* 2007, **6**(3): 183-191.
9. Mak KF, *et al.* Tightly bound trions in monolayer MoS₂. *Nat Mater* 2013, **12**(3): 207-211.

10. Mak KF, He K, Shan J, Heinz TF. Control of valley polarization in monolayer MoS₂ by optical helicity. *Nat Nano* 2012, **7**(8): 494-498.
11. Novoselov KS, *et al.* Two-dimensional gas of massless Dirac fermions in graphene. *Nature* 2005, **438**(7065): 197-200.
12. Ramasubramaniam A. Large excitonic effects in monolayers of molybdenum and tungsten dichalcogenides. *Physical Review B* 2012, **86**(11): 115409.
13. Ross JS, *et al.* Electrical control of neutral and charged excitons in a monolayer semiconductor. *Nature Communications* 2013, **4**: 1474.
14. Shang J, *et al.* Observation of Excitonic Fine Structure in a 2D Transition-Metal Dichalcogenide Semiconductor. *ACS Nano* 2015, **9**(1): 647-655.
15. Bao Q, *et al.* Atomic-Layer Graphene as a Saturable Absorber for Ultrafast Pulsed Lasers. *Advanced Functional Materials* 2009, **19**(19): 3077-3083.
16. Lu J, Liu H, Tok ES, Sow C-H. Interactions between lasers and two-dimensional transition metal dichalcogenides. *Chemical Society Reviews* 2016, **45**(9): 2494-2515.
17. Wu S, *et al.* Monolayer semiconductor nanocavity lasers with ultralow thresholds. *Nature* 2015, **520**(7545): 69-72.
18. Ye Y, *et al.* Monolayer excitonic laser. *Nat Photon* 2015, **9**(11): 733-737.
19. Ross JS, *et al.* Electrically tunable excitonic light-emitting diodes based on monolayer WSe₂ p-n junctions. *Nat Nano* 2014, **9**(4): 268-272.

20. Salehzadeh O, *et al.* Exciton Kinetics, Quantum Efficiency, and Efficiency Droop of Monolayer MoS₂ Light-Emitting Devices. *Nano Letters* 2014, **14**(7): 4125-4130.
21. Zimmler MA, Voss T, Ronning C, Capasso F. Exciton-related electroluminescence from ZnO nanowire light-emitting diodes. *Applied Physics Letters* 2009, **94**(24): 241120.
22. Liu C-H, Chang Y-C, Norris TB, Zhong Z. Graphene photodetectors with ultra-broadband and high responsivity at room temperature. *Nat Nano* 2014, **9**(4): 273-278.
23. Lopez-Sanchez O, *et al.* Ultrasensitive photodetectors based on monolayer MoS₂. *Nat Nano* 2013, **8**(7): 497-501.
24. Wang X, *et al.* High-responsivity graphene/silicon-heterostructure waveguide photodetectors. *Nat Photon* 2013, **7**(11): 888-891.
25. Gregg BA. Excitonic Solar Cells. *The Journal of Physical Chemistry B* 2003, **107**(20): 4688-4698.
26. Pospischil A, Furchi MM, Mueller T. Solar-energy conversion and light emission in an atomic monolayer p-n diode. *Nat Nano* 2014, **9**(4): 257-261.
27. Tsai M-L, *et al.* Monolayer MoS₂ Heterojunction Solar Cells. *ACS Nano* 2014, **8**(8): 8317-8322.
28. Geim AK, Grigorieva IV. Van der Waals heterostructures. *Nature* 2013, **499**(7459): 419-425.

29. Liu H, *et al.* Phosphorene: An Unexplored 2D Semiconductor with a High Hole Mobility. *ACS Nano* 2014, **8**(4): 4033-4041.
30. Xu R, *et al.* Extraordinarily Bound Quasi-One-Dimensional Trions in Two-Dimensional Phosphorene Atomic Semiconductors. *ACS Nano* 2016, **10**(2): 2046-2053.
31. Yang J, *et al.* Optical tuning of exciton and trion emissions in monolayer phosphorene. *Light Sci Appl* 2015, **4**: e312.
32. Zhang S, *et al.* Extraordinary Photoluminescence and Strong Temperature/Angle-Dependent Raman Responses in Few-Layer Phosphorene. *ACS Nano* 2014, **8**(9): 9590-9596.
33. Bablich A, Kataria S, Lemme M. Graphene and two-dimensional materials for optoelectronic applications. *Electronics* 2016, **5**(1): 13.
34. Roldán R, *et al.* Electronic properties of single-layer and multilayer transition metal dichalcogenides MX₂ (M= Mo, W and X= S, Se). *Annalen der Physik* 2014, **526**(9-10): 347-357.
35. Rodin AS, Carvalho A, Castro Neto AH. Excitons in anisotropic two-dimensional semiconducting crystals. *Physical Review B* 2014, **90**(7): 075429.
36. Thilagam A. Exciton complexes in low dimensional transition metal dichalcogenides. *Journal of Applied Physics* 2014, **116**(5): 053523.
37. Weiner J, Ho P-T. *Light-matter interaction, Fundamentals and applications*, vol. 1. John Wiley & Sons, 2008.

38. Novoselov KS, *et al.* Two-dimensional atomic crystals. *Proceedings of the National Academy of Sciences of the United States of America* 2005, **102**(30): 10451-10453.
39. Mak KF, *et al.* Atomically Thin MoS_2 : A New Direct-Gap Semiconductor. *Physical Review Letters* 2010, **105**(13): 136805.
40. Qiao J, *et al.* High-mobility transport anisotropy and linear dichroism in few-layer black phosphorus. *Nature Communications* 2014, **5**: 4475.
41. Tan C, Zhang H. Two-dimensional transition metal dichalcogenide nanosheet-based composites. *Chemical Society Reviews* 2015, **44**(9): 2713-2731.
42. Gupta A, Sakthivel T, Seal S. Recent development in 2D materials beyond graphene. *Progress in Materials Science* 2015, **73**: 44-126.
43. Castellanos-Gomez A, Agraït N, Rubio-Bollinger G. Optical identification of atomically thin dichalcogenide crystals. *Applied Physics Letters* 2010, **96**(21): 213116.
44. Ling X, *et al.* The renaissance of black phosphorus. *Proceedings of the National Academy of Sciences* 2015, **112**(15): 4523-4530.
45. Lu J, *et al.* Light–Matter Interactions in Phosphorene. *Acc Chem Res* 2016, **49**(9): 1806-1815.
46. Kim J-S, *et al.* Toward air-stable multilayer phosphorene thin-films and transistors. *Scientific Reports* 2015, **5**: 8989.

47. Li L, *et al.* Direct observation of the layer-dependent electronic structure in phosphorene. *Nat Nano* 2017, **12**(1): 21-25.
48. Andres C-G, *et al.* Isolation and characterization of few-layer black phosphorus. *2D Materials* 2014, **1**(2): 025001.
49. Zeng H, *et al.* Valley polarization in MoS₂ monolayers by optical pumping. *Nat Nano* 2012, **7**(8): 490-493.
50. Yang J, *et al.* Optical tuning of exciton and trion emissions in monolayer phosphorene. *Light: Science & Applications* 2015, **4**(7): e312.
51. Xu R, *et al.* Exciton Brightening in Monolayer Phosphorene via Dimensionality Modification. *Advanced Materials* 2016: n/a-n/a.
52. Ugeda MM, *et al.* Giant bandgap renormalization and excitonic effects in a monolayer transition metal dichalcogenide semiconductor. *Nat Mater* 2014, **13**(12): 1091-1095.
53. Bonaccorso F, Sun Z, Hasan T, Ferrari AC. Graphene photonics and optoelectronics. *Nat Photon* 2010, **4**(9): 611-622.
54. Constantinescu G, Kuc A, Heine T. Stacking in Bulk and Bilayer Hexagonal Boron Nitride. *Physical Review Letters* 2013, **111**(3): 036104.
55. Sirringhaus H, Tessler N, Friend RH. Integrated Optoelectronic Devices Based on Conjugated Polymers. *Science* 1998, **280**(5370): 1741-1744.
56. Rogers JA. Toward paperlike displays. *Science* 2001, **291**(5508): 1502-1503.

57. Bardeen CJ. Excitonic processes in molecular crystalline materials. *MRS Bulletin* 2013, **38**(01): 65-71.
58. Hoffmann M, *et al.* The lowest energy Frenkel and charge-transfer excitons in quasi-one-dimensional structures: application to MePTCDI and PTCDI crystals. *Chemical Physics* 2000, **258**(1): 73-96.
59. Yamagata H, *et al.* HJ-Aggregate Behavior of Crystalline 7,8,15,16-Tetraazaterrylene: Introducing a New Design Paradigm for Organic Materials. *The Journal of Physical Chemistry C* 2014, **118**(49): 28842-28854.
60. Hestand N, *et al.* Polarized Absorption in Crystalline Pentacene: Theory vs Experiment. *The Journal of Physical Chemistry C* 2015, **119**(38): 22137-22147.
61. Lee K, *et al.* Interfacial Trap Density-of-States in Pentacene-and ZnO-Based Thin-Film Transistors Measured via Novel Photo-excited Charge-Collection Spectroscopy. *Advanced Materials* 2010, **22**(30): 3260-3265.
62. Chua L-L, Zaumsell J, Chang J-F, Ou EC. General observation of n-type field-effect behaviour in organic semiconductors. *Nature* 2005, **434**(7030): 194.
63. Podzorov V, *et al.* Intrinsic charge transport on the surface of organic semiconductors. *Physical Review Letters* 2004, **93**(8): 086602.
64. Hestand NJ, *et al.* Polarized Absorption in Crystalline Pentacene: Theory vs Experiment. *The Journal of Physical Chemistry C* 2015, **119**(38): 22137-22147.
65. Bardeen CJ. Triplet excitons: Bringing dark states to light. *Nat Mater* 2014, **13**(11): 1001-1003.

66. Beljonne D, *et al.* Charge-Transfer Excitations Steer the Davydov Splitting and Mediate Singlet Exciton Fission in Pentacene. *Physical Review Letters* 2013, **110**(22): 226402.
67. Frenkel J. On the Transformation of Light into Heat in Solids. II. *Physical Review* 1931, **37**(10): 1276-1294.
68. Schuster R, Knupfer M, Berger H. Exciton Band Structure of Pentacene Molecular Solids: Breakdown of the Frenkel Exciton Model. *Physical Review Letters* 2007, **98**(3): 037402.
69. Zhu XY, Yang Q, Muntwiler M. Charge-Transfer Excitons at Organic Semiconductor Surfaces and Interfaces. *Accounts of Chemical Research* 2009, **42**(11): 1779-1787.
70. Sebastian L, Weiser G, Bässler H. Charge transfer transitions in solid tetracene and pentacene studied by electroabsorption. *Chemical Physics* 1981, **61**(1): 125-135.
71. Sebastian L, Weiser G, Peter G, Bässler H. Charge-transfer transitions in crystalline anthracene and their role in photoconductivity. *Chemical Physics* 1983, **75**(1): 103-114.
72. Yang Q, Muntwiler M, Zhu XY. Charge transfer excitons and image potential states on organic semiconductor surfaces. *Physical Review B* 2009, **80**(11): 115214.
73. Yamagata H, *et al.* The nature of singlet excitons in oligoacene molecular crystals. *The Journal of Chemical Physics* 2011, **134**(20): 204703.

74. Davydov A. Theory of molecular excitations. *Plenum press, New York* 1971, **7**: 387-394.
75. Zhang Y, *et al.* Probing Carrier Transport and Structure-Property Relationship of Highly Ordered Organic Semiconductors at the Two-Dimensional Limit. *Physical Review Letters* 2016, **116**(1): 016602.
76. Novoselov KS, Neto AHC. Two-dimensional crystals-based heterostructures: materials with tailored properties. *Physica Scripta* 2012, **2012**(T146): 014006.
77. Lee G-H, *et al.* Heterostructures based on inorganic and organic van der Waals systems. *APL Materials* 2014, **2**(9): 092511.
78. Novoselov KS, Mishchenko A, Carvalho A, Castro Neto AH. 2D materials and van der Waals heterostructures. *Science* 2016, **353**(6298): aac9439.
79. Lin Y-C, *et al.* Atomically thin resonant tunnel diodes built from synthetic van der Waals heterostructures. *Nature communications* 2015, **6**.
80. Lee C-H, *et al.* Atomically thin p–n junctions with van der Waals heterointerfaces. *Nat Nano* 2014, **9**(9): 676-681.
81. Wang QH, *et al.* Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. *Nat Nano* 2012, **7**(11): 699-712.
82. Bernardi M, Palummo M, Grossman JC. Extraordinary Sunlight Absorption and One Nanometer Thick Photovoltaics Using Two-Dimensional Monolayer Materials. *Nano Letters* 2013, **13**(8): 3664-3670.

83. Yu WJ, *et al.* Highly efficient gate-tunable photocurrent generation in vertical heterostructures of layered materials. *Nat Nano* 2013, **8**(12): 952-958.
84. Furchi MM, *et al.* Photovoltaic Effect in an Electrically Tunable van der Waals Heterojunction. *Nano Letters* 2014, **14**(8): 4785-4791.
85. Wang L, *et al.* One-Dimensional Electrical Contact to a Two-Dimensional Material. *Science* 2013, **342**(6158): 614-617.
86. Dean CR, *et al.* Boron nitride substrates for high-quality graphene electronics. *Nat Nano* 2010, **5**(10): 722-726.
87. Massicotte M, *et al.* Picosecond photoresponse in van der Waals heterostructures. *Nat Nano* 2016, **11**(1): 42-46.
88. He J, *et al.* Electron transfer and coupling in graphene–tungsten disulfide van der Waals heterostructures. *Nature communications* 2014, **5**: 5622.
89. Rivera P, *et al.* Observation of long-lived interlayer excitons in monolayer MoSe₂–WSe₂ heterostructures. *Nature communications* 2015, **6**: 6242.
90. Ceballos F, Bellus MZ, Chiu H-Y, Zhao H. Probing charge transfer excitons in a MoSe₂-WS₂ van der Waals heterostructure. *Nanoscale* 2015, **7**(41): 17523-17528.
91. Gong Y, *et al.* Vertical and in-plane heterostructures from WS₂/MoS₂ monolayers. *Nat Mater* 2014, **13**(12): 1135-1142.
92. Kozawa D, *et al.* Evidence for fast interlayer energy transfer in MoSe₂/WS₂ heterostructures. *arXiv preprint arXiv:150901875* 2015.

93. Shim GW, *et al.* Large-area single-layer MoSe₂ and its van der Waals heterostructures. *ACS nano* 2014, **8**(7): 6655-6662.
94. Ceballos F, Bellus MZ, Chiu H-Y, Zhao H. Ultrafast Charge Separation and Indirect Exciton Formation in a MoS₂–MoSe₂ van der Waals Heterostructure. *ACS nano* 2014, **8**(12): 12717-12724.
95. Grancini G. Hot exciton dissociation in polymer solar cells. *Nature materials* 2013, **12**(1): 29-33.
96. Jailaubekov AE. Hot charge-transfer excitons set the time limit for charge separation at donor/acceptor interfaces in organic photovoltaics. *Nature materials* 2013, **12**(1): 66-73.
97. Kaake LG. Coherence and Uncertainty in Nanostructured Organic Photovoltaics. *The journal of physical chemistry letters* 2013, **4**(14): 2264-2268.
98. eacute, linas SS. Ultrafast long-range charge separation in organic semiconductor photovoltaic diodes. *Science (New York, NY)* 2014, **343**(6170): 512-516.
99. Tosun M, *et al.* Mos₂ heterojunctions by thickness modulation. *Scientific reports* 2015, **5**: 10990.
100. Bellus MZ, *et al.* Type-I van der Waals heterostructure formed by MoS₂ and ReS₂ monolayers. *Nanoscale Horizons* 2017, **2**(1): 31-36.
101. Hui C, *et al.* Exciton pumping across type-I gallium chalcogenide heterojunctions. *Nanotechnology* 2016, **27**(6): 065203.

102. Lee C-H, *et al.* Epitaxial Growth of Molecular Crystals on van der Waals Substrates for High-Performance Organic Electronics. *Advanced Materials* 2014, **26**(18): 2812-2817.

103. Bettis Homan S, *et al.* Ultrafast Exciton Dissociation and Long-Lived Charge Separation in a Photovoltaic Pentacene–MoS₂ van der Waals Heterojunction. *Nano Letters* 2017, **17**(1): 164-169.

104. Jariwala D, *et al.* Hybrid, Gate-Tunable, van der Waals p–n Heterojunctions from Pentacene and MoS₂. *Nano Letters* 2016, **16**(1): 497-503.

105. Nakamura S, Senoh M, Iwasa N, Nagahama S-i. High-brightness InGaN blue, green and yellow light-emitting diodes with quantum well structures. *Japanese Journal of Applied Physics* 1995, **34**(7A): L797.

106. Lee G-H, *et al.* Flexible and Transparent MoS₂ Field-Effect Transistors on Hexagonal Boron Nitride-Graphene Heterostructures. *ACS nano* 2013, **7**(9): 7931-7936.

107. Kang SJ, *et al.* Organic Field Effect Transistors Based on Graphene and Hexagonal Boron Nitride Heterostructures. *Advanced Functional Materials* 2014, **24**(32): 5157-5163.

CHAPTER 2

Experimental Techniques

This chapter describes all the key experimental techniques used in this thesis to probe different electrical and opto-electronic properties of organic and inorganic 2D materials.

Section 2.1 will introduce the chemical vapor deposition (CVD) growth technique used extensively for the growth of 2D organic materials (Chapter 4) and for 1D organic nanowires (Chapter 5). Section 2.2 will introduce atomic force microscope imaging, used to determine the thickness of 2D materials. Section 2.3 will discuss the Phase-shift interferometry (PSI), which is a non-invasive method to profile the surface of the 2D materials. Section 2.4 will talk about the optical characterization tools. Raman and photoluminescence (PL) spectroscopy used to determine the chemical composition and optical bandgap of the nanomaterials respectively will be discussed in this thesis. Section 2.5 will introduce the homemade setup for time-resolved PL imaging (TRPL) used extensively in this thesis for determining the carrier lifetime of the excitons in the

nanomaterials. Section 2.6 will talk about and also the pump-probe transient reflectivity measurements used in chapter 4 to determine the lifetime from organic 2D materials. Section 2.7 will introduce the near and far-field imaging using CCD detectors used to determine the diffusion length of excitons in this thesis. Section 2.8 will talk about all the techniques, I have used to make devices incorporating 2D materials in this thesis. In addition, each chapter in this thesis has a methods section catering to individual preparation and testing experimental methods that have been used to characterize samples for that chapter.

2.1 Chemical vapor deposition (CVD)

Chemical vapor deposition is a well demonstrated process used extensively to grow organic and epitaxial 2D materials in a wide temperature range. It is generally carried out under vacuum to produce high quality thin films of solid materials.¹ Typically, the wafer or the substrate in a CVD process will be exposed to volatile precursor materials which further react or decompose at a higher temperature on the substrate or wafer. A gas is generally used a carrier to transfer the volatile compounds to the desired positions. It is categorized into various formats depending on how the chemical reaction is initiated, operating conditions, type of substrate heating and cooling mechanism.² It is typically used to deposit uniform and conformal thin films that are atomically thin.³ This is the reason this technique was used in this thesis for the deposition of atomically thin organic material over hBN surface. However, in this thesis we did not use any precursor or catalyst to obtain the organic material. Instead we used the material-pentacene purchased from a commercial supplier in its powder form and used it to deposit over the hBN flakes.

Hence the process in this thesis is also referred to as physical vapor deposition (PVD) process.

Figure 2.1 shows a typical CVD setup which was used in this thesis to grow 2D and 1D organic nanomaterials. hBN flakes were mechanically exfoliated onto a thermally grown 285 nm thick SiO₂ layer deposited over silicon substrate. Before physical vapour deposition (PVD), optical microscope was used to characterize the topological information.

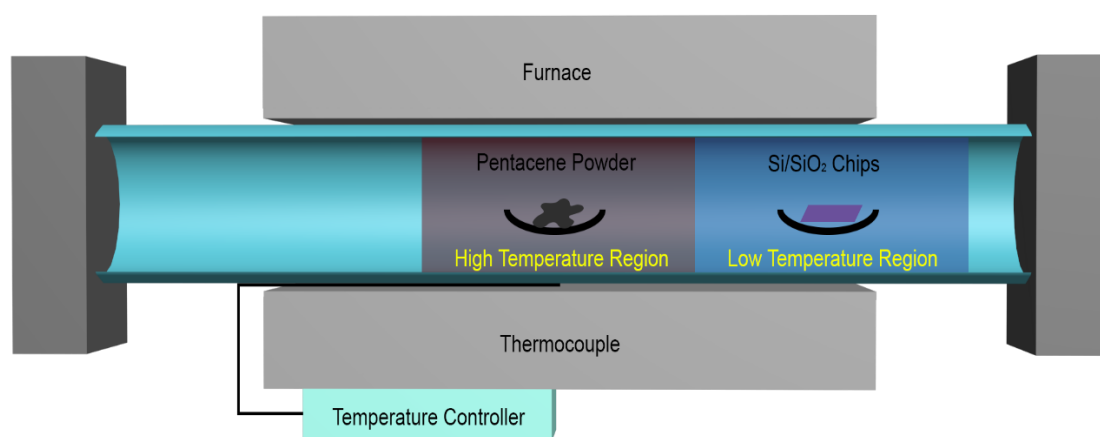


Fig 2.1: Schematic representation of the CVD furnace used for organic nanomaterial growth.

The pentacene (purchased from Chem Supply: P0030-1G) was then deposited over the h-BN flakes, kept centred in a vacuum tube in the furnace. h-BN sheet on SiO₂/Si substrate was placed around 15 cm downstream and a molecular pump was used to evacuate the quartz tube to $\sim 10^{-4}$ mbar. The furnace was heated up to 130~180°C for 15~30 mins to grow pentacene. Then, the whole system was naturally cooled down to room temperature under vacuum. The number of layers were optimized by controlling source temperature, growth time and substrate position. The length of the wires was

controlled by the source temperature, the substrate position and growth time. When the growth was finished, we turned off the furnace and let the sample cool down to room temperature under vacuum.

2.2 Atomic Force Microscopy (AFM)

AFM is a type of scanning probe microscope.^{4, 5} It collects information by touching the surface and hence the resolution can be of the order of a fraction of few nanometres much better than the optical diffraction limit.⁶ It consists of a small spring like cantilever beam hanging from a support with the tip of few angstrom thickness. A piezoelectric element generally oscillates the cantilever in combination with a laser to collect the feedback from the tip surface as it moves over the topography of the sample. With sufficient sensitivity in the spring deflection sensor, the tip can reveal surface profiles with atomic resolution.^{4,}

5

A Bruker MultiMode VIII AFM in ScanAsyst mode was employed in this thesis to determine the thickness of thin-layer 2D semiconductors. The cantilever used is NT-MDT CSG30 with force constant of 0.6 Nm^{-1} so that the cantilever is flexible enough and does not damage the sample surface during the probe.

2.3 Phase shift interferometry (PSI)

PSI is an established measurement technique for surface characterization.⁷ It uses digitization of surface data acquired via a controlled phase shift. It acquires a sequence of images using an objective lens and precisely controlled phase change between the various images.⁸ The phase shifting is generated by mechanical motion of the interference

objective which allows non-contact mapping of the surface. This thesis uses the Veeco NT9100 which operates with a green LED source centred around 535 nm and uses a 10 nm bypass filter. The schematic plot and working principle as obtained from Yang et al.⁷ is shown in Figure 2.2.

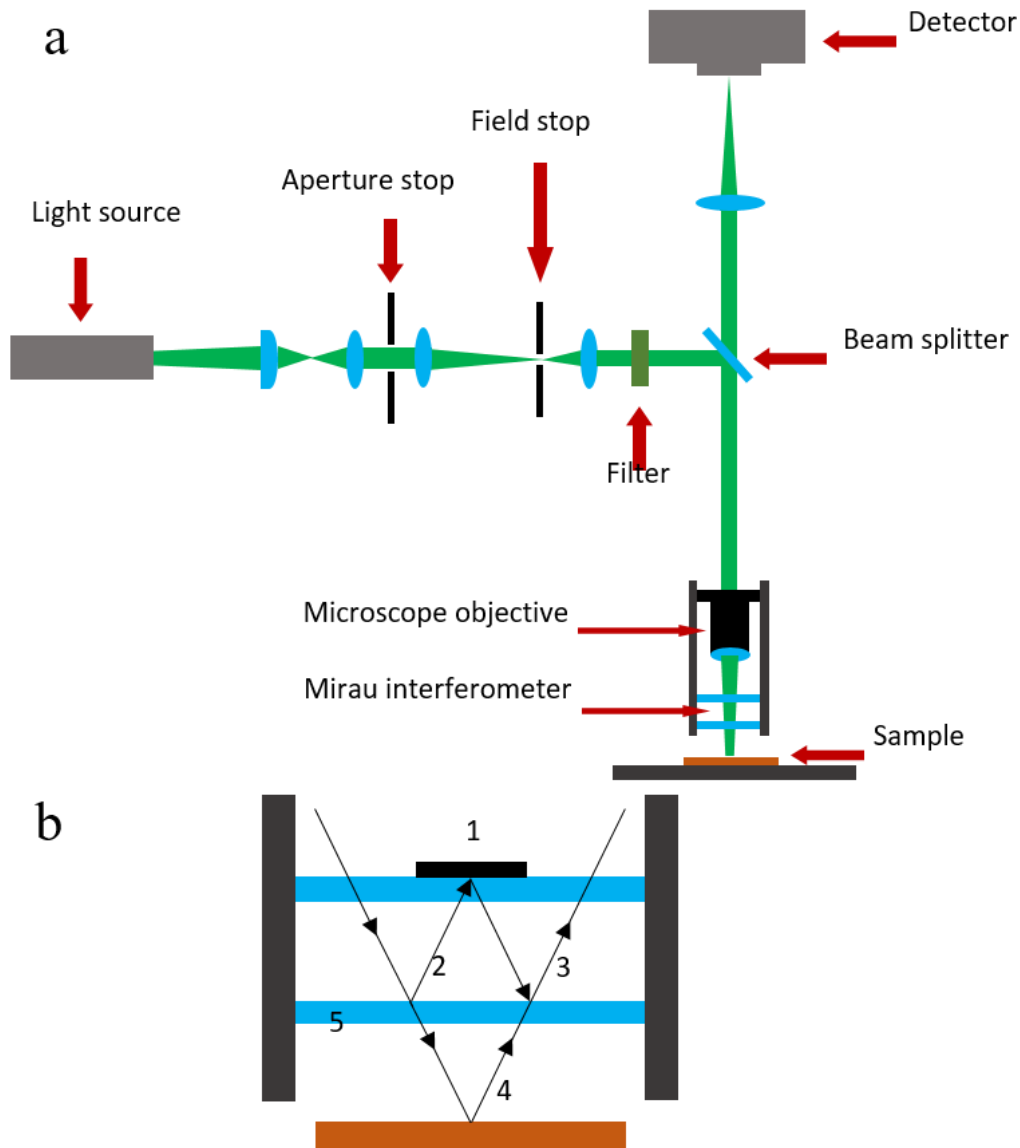


Figure 2.2: Schematic plot of the PSI system. a, Schematic plot of the PSI system. b, Zoomed view of the Mirau interferometer. 1. Reference mirror; 2. First reflection of the reference beam; 3. Third reflection of the reference beam; 4. Reflection of the

test/objective beam; 5. Semi-transparent mirror. 2-1-3 represents the reference beam and 2-4-3 represents the test/objective beam. Adapted with permission from ref 7.

2.4 Raman and PL Spectroscopy

In this thesis, PL spectra are captured using a micro-PL spectroscopy system equipped with confocal optics yielding an on-sample spot size of about 05 μm in diameter. Samples are excited with a laser light. The emitted PL signal is focused through a focusing mirror, and then directed into a double-monochromator and captured by an InGaAs/CCD-Si detector. A standard lock-in technique is employed in order to improve the signal-to-noise ratio. This system allows us to capture the luminescence signal from silicon wafers with a dynamic range of up to five orders of magnitude. However, due to the large illuminated spot size, the spatial resolution of this system is limited and the properties of features smaller than one micrometre are often confounded with those of surrounding regions. Raman and PL measurements are conducted using a HORIBA Jobin Yvon T64000 micro-Raman system equipped with both charge-coupled device (CCD) and InGaAs detectors, along with a 532nm Nd:YAG laser and a SuperK EXTREME supercontinuum laser as the excitation source. Also, another system was used to determine the optical response of the 2D materials. PL measurements at room temperature and 77 K were conducted using a Horiba LabRAM system equipped with a confocal microscope, a charge-coupled device (CCD) Si detector, and a 532 nm diode-pumped solid-state (DPSS) laser as the excitation source. For temperature-dependent (above 77 K) measurements, the sample was placed into a microscope-compatible chamber with a low temperature controller (using liquid nitrogen as the coolant). In the experiment, the incident polarization angle was controlled by an angle-variable half-wave plate and was fixed, and the polarization angle of the

emission (θ) was determined by using an angle-variable polarizer located in front of the detector.

The micro-Raman system is equipped with two gratings, with grating parameter of 150 gr/mm and 900 gr/mm, and another 2400 gr/mm grating can also be installed if necessary. 150 gr/mm grating is used for PL measurements, and 900 gr/mm and 2400 gr/mm gratings are used for Raman measurements.

2.4.1 Low-temperature Raman and PL spectroscopy

For low-temperature Raman and PL measurements, the sample is placed into a Linkam THMS 600 chamber, which can fit into the sample stage of the HORIBA Jobin Yvon T64000 micro-Raman system, and the sample is cooled down to cryogenic temperature by liquid nitrogen circulated with the Linkam TP 94 liquid nitrogen controller. For Raman and PL measurements of phosphorene, a slow flow of nitrogen gas is circulating in the chamber to prevent sample degradation.

2.4.2 Polarization-resolved Raman and PL spectroscopy

In the setup of the polarization-resolved Raman and PL spectroscopy, as shown in Figure 2.3, a linearly polarized Nd:YAG laser with a wavelength of 532 nm is used.

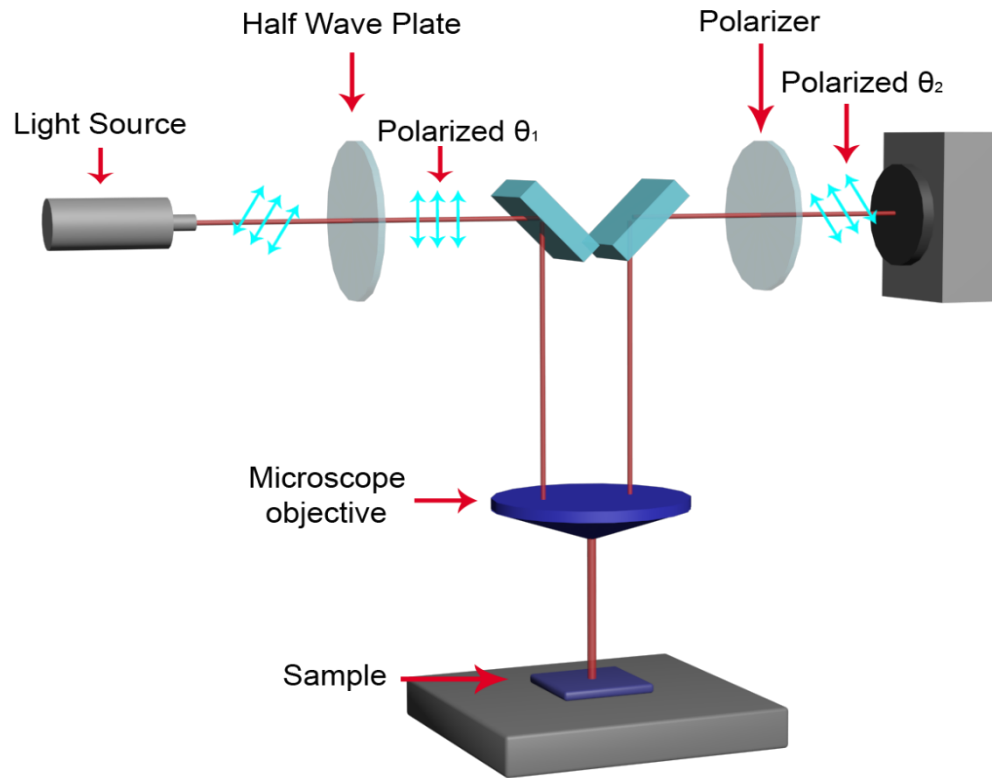


Figure 2.3 Schematic plot of the setup for polarization-resolved Raman and PL spectroscopy.

2.5 Time-Resolved PL Spectroscopy

TRPL spectroscopy can give important information of materials, which is the minority carrier lifetime, t_{mc} .⁹ Carrier lifetime measures the average time that carriers can stay in excited state after the electron-hole generation and before the recombination. It can be defined as:

$$\frac{1}{\tau_{mc}} = \frac{1}{\tau_{nr}} + \frac{1}{\tau_r} \quad (2.1)$$

where τ_{nr} is the non-radiative carrier lifetime and τ_r is the radiative carrier lifetime. τ_{mc} can be obtained by fitting the TRPL decay curve.⁹ Figure 2.4 shows the experimental setup¹⁰ that incorporates micro-PL spectroscopy and a time-correlated single photon counting (TCSPC) system. Time resolved PL measurements were conducted in a setup

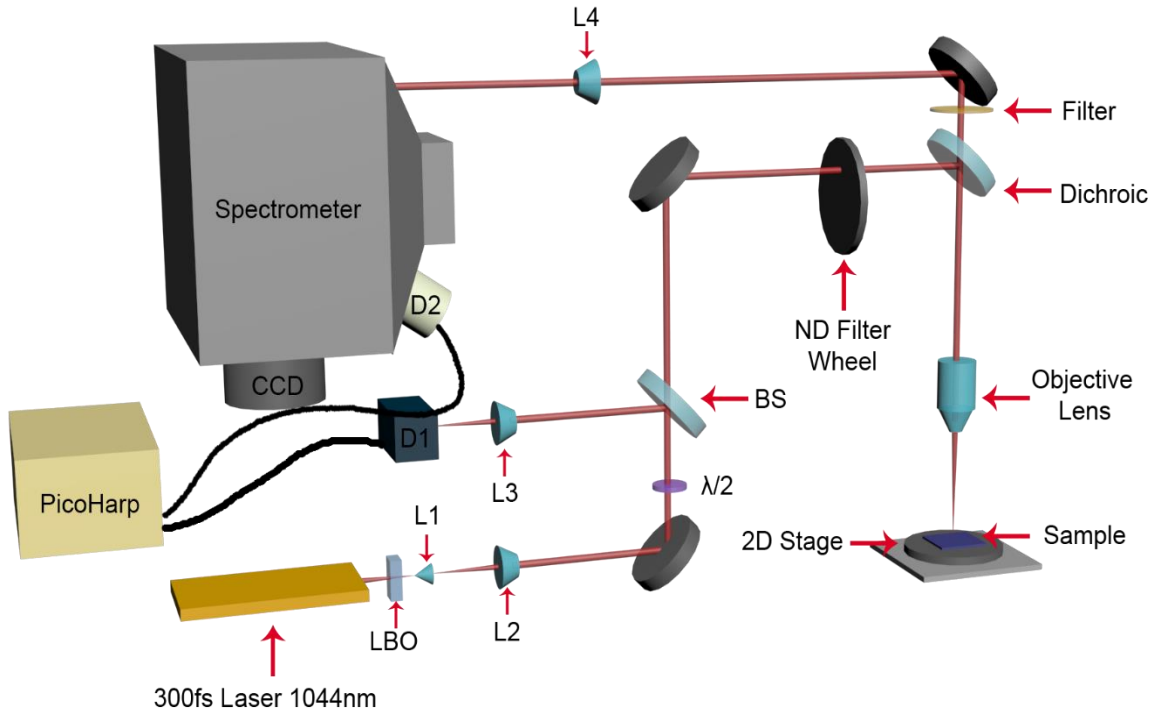


Figure 2.4 Experimental setup of the time-resolved PL system.

which incorporates μ -PL spectroscopy and a time-correlated single photon counting TCSPC system. A linearly polarized pulse laser (frequency doubled to 522 nm, with 300 fs pulse width and 20.8 MHz repetition rate) was directed to a high numerical aperture (NA= 0.7) objective (Nikon S Plan 603). PL signal was collected by a grating spectrometer, thereby either recording the PL spectrum through a charge coupled device

(CCD; Princeton Instruments, PIXIS) or detecting the PL intensity decay by a Si single-photon avalanche diode (SPAD) and the TCSPC (PicoHarp 300) system.

2.6 Pump-probe transient reflectivity measurements for lifetime

Transient reflectivity measurements were performed with a home-built pump-probe setup. Degenerate, linearly polarized pump and probe pulses were produced by splitting ~ 200 fs pulses from a non-collinear optical parametric amplifier (Light Conversion Orpheus-2N) tuned to 680 nm. A half-wave plate in the probe line rotated the polarization to be orthogonal to that of the pump. The pump was delayed using a motorized delay stage to control the pump-probe timing. Pump and probe pulses were recombined to be nearly spatially overlapped and focussed onto the sample with a 25.4 mm focal length lens. Telescopes in the pump and probe lines were used to tune the divergence/waist size of the pump and probe beams. The focal spot size and fluence of the pump and probe were $30\text{ }\mu\text{m}$, $90\text{ }\mu\text{J}/\text{cm}^2$ and $15\text{ }\mu\text{m}$, $12\text{ }\mu\text{J}/\text{cm}^2$ respectively.

The probe pulses were spectrally resolved across a fast CMOS array detector (Andor Zyla) by an imaging spectrometer (Andor Kymera). The detector recorded spectra at 5.21 kHz, synced to the laser repetition rate of 20.83 kHz. A data analysis technique based on lock-in detection was used to isolate only the component of the probe modulated at the same frequency as the chopper in the pump beam, which was also synced to the laser output. A polarizer was used to filter out the pump signal coupled with an iris. The residual pump still appears minimally both as a background signal and as interference fringes between the pump and the probe. The interferometric pump contributions were removed using a Fourier filter with a width of 400 fs, and the static background was

removed by subtracting the signal observed at negative pump-probe delays (i.e. probe arriving before the pump).

2.7 Near and Far-Field Scanning Optical Microscope

The light path of the Horiba Jobin Yvon T64000 micro-Raman system is exploited to set up a near and far-field SOM. The schematic plot of its working principle is shown in Figure 2.5. The SOM uses a green laser at wavelength of 532 nm which is focused by an Olympus 50X (NA = 0.25, depth of focus 18 μm) objective lens.

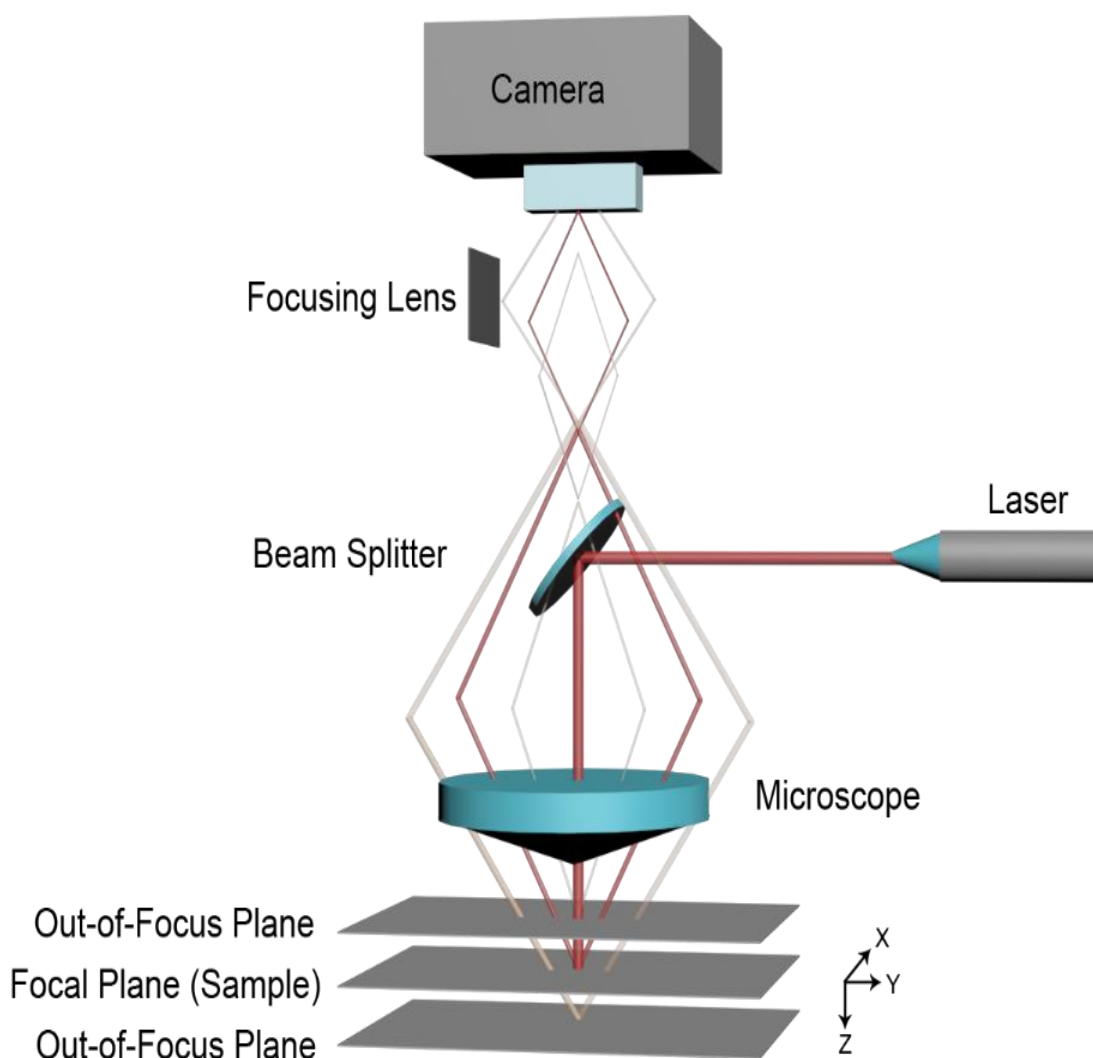


Figure 2.5 Schematic plot of the scanning optical microscope.

2.7.1 Diffusion Length Measurements

Exciton diffusion measurements were carried out using the same PIXIS CCD detector coupled with a X100 (NA= 1.49, oil suspended) objective lens. The pulsed 522 nm laser was used for excitation with a beam diameter ~ 500 nm (confirmed by CCD imaging) with collection time of 1s per measurement. The diffusion mapping direction was well aligned with the polarization of the excitation laser. The collected light was spectrally filtered to remove the pump laser wavelength. Spectral measurements were made using a grating spectrometer (Acton, SpectraPro 2750). The focal plane of the sample was imaged using the zeroth order of the grating and the spectrometer CCD, giving a spatial resolution of about 200×200 nm in space, corresponding to a pixel ($20 \mu\text{m} \times 20 \mu\text{m}$) on the CCD. The PL intensity at a particular excitonic emission energy was plotted as a function of the distance from the excitation centre ($x = 0$). The spatial extent of exciton diffusion (diffusion length L_D) was found by taking the square root of the difference between the variances of the emission image and of the passive laser spot.

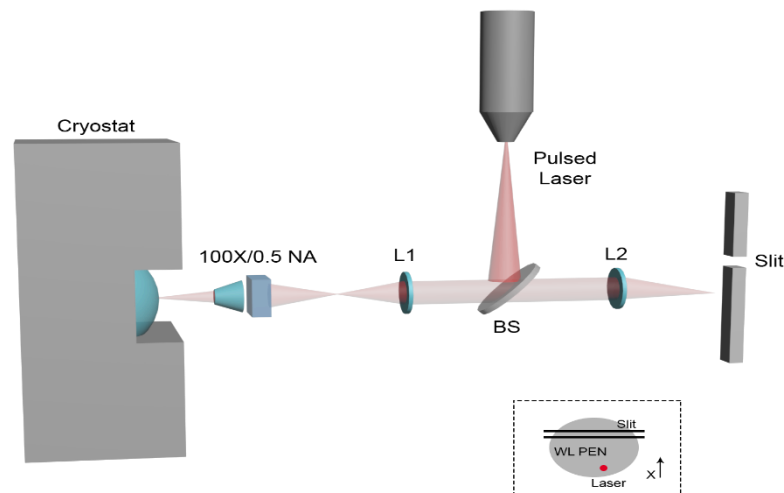
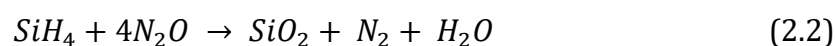


Figure 2.6 The schematic shows the basic representation of the CCD imaging setup coupled with TRPL system use in this thesis to obtain exciton diffusion lengths at cryogenic temperatures .

2.8 Device Fabrication

2.8.1 Plasma-enhanced chemical vapour deposition

Plasmalab 100 Dual Frequency PECVD as used to prepare defect-rich silicon oxide substrate, a 223 nm of silicon oxide layer is deposited on gold substrates (100 nm of gold thin film on silicon substrate). The thickness of silicon oxide layer is calculated to maximize the optical path length to maximise the interaction with PSI system to determine the layer numbers of 2D material deposited on top. In the PECVD system, two power generators (13.56 MHz and 50 kHz - 450 kHz) are connected through a matching network to the top electrode of the reactor; the bottom electrode is grounded and acts as a sample holder.¹¹ The reacting gases silane (SiH_4), nitrous oxide (N_2O) and nitrogen (N_2) are sent into the reactor and the plasma is created by radio frequency (RF) electronic oscillations between the two electrodes. The chemical reaction occurs after the creation of plasma of reacting gases, which can be expressed as:



The flow of SiH_4 , N_2O and N_2 are 9, 710 and 161 sccm, respectively. N_2 is used to dilute the pure SiH_4 and improve the uniformity of the deposition performance. The deposition processes are performed using 20 watts of RF power at 100 °C for 315 s. The total pressure during the deposition process is maintained at a constant value of 650 mTorr.

2.8.2 Photolithography

Photolithography is a commonly used technique in semiconductor research and industry.¹² It consists of substrate cleaning, photoresist spin-coating, mask alignment, ultra-violet (UV) light exposure and development. In our experiment, the SiO₂/Si substrate (275 nm thermal oxide on n⁺-Si) is firstly cleaned with acetone and isopropanol and baked on a hotplate for 2 min at 100 °C. For photoresist spin-coating process, LOR 3A lift-off resist and AZ MIR 701 positive photoresist are spin-coated subsequently. LOR 3A is spin-coated onto the clean substrate at 500 rpm for 5 s and 5000 rpm for 45 s, followed by prebake of 2 min at 180 °C with a UniTemp GmbH HPP-155-L hotplate; and then AZ MIR 701 positive resist is spin-coated at 500 rpm for 5 s and 6000 rpm for 1 min, followed by prebake of 2 min at 85 °C with the same hotplate. Photolithography

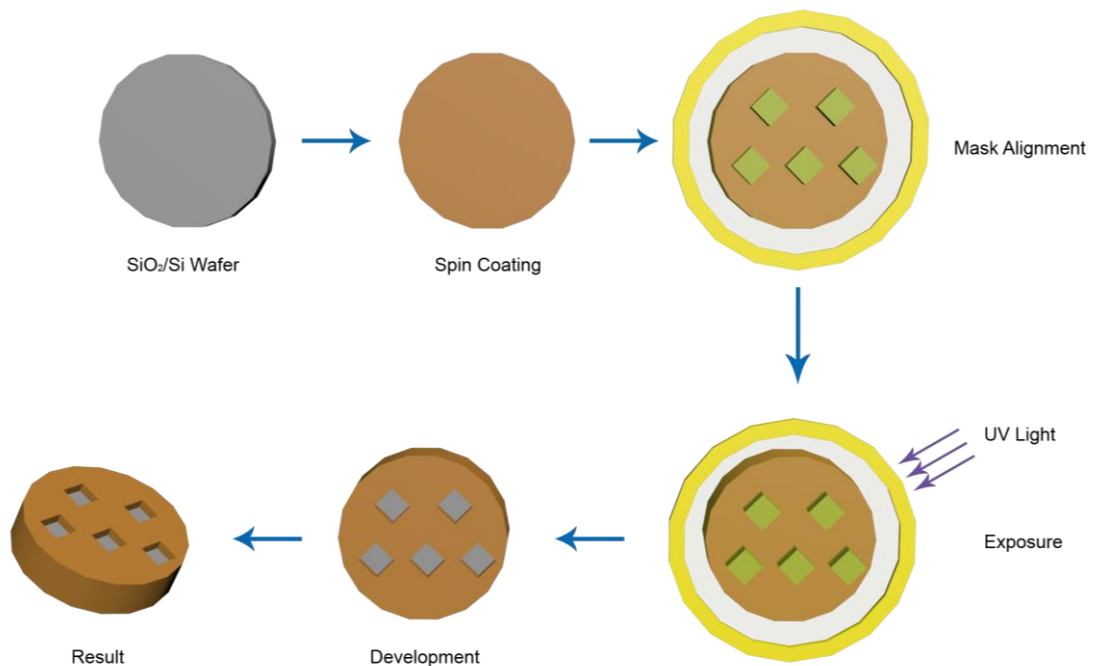


Figure 2.7 Schematic plot of the photolithography process.

mask is aligned with the substrate using a Karl Suss MA6/BA6 mask aligner and the gap between mask and substrate is 20 µm. After mask alignment, the substrate coated with

LOR 3A and AZ MIR 701 is exposed for 35 s in soft contact mode with UV light in the wavelength range of 280-350 nm. And finally, the exposed substrate is developed in AZ 726 MIF developer for 45-60 s, depending on the development results. After development, the wafer is checked with an optical microscope for the outcome of the photolithography process. The whole photolithography process can be illustrated as the schematic plot in Figure 2.7.

2.8.3 Electron beam evaporation

After photolithography, SiO_2/Si substrates with photoresist patterns are loaded into a Temescal BJD-2000 electron beam thermal evaporator to deposit 5 nm of Ti and 100 nm of Au thin film. Ti thin film acts as an adhesion layer. Electron beam evaporation is a high vacuum deposition technique where electron beam is used to bombard and heat the target metal to above its melting point, resulting in its deposition as thin film on substrates. In our experiment, the deposition rate for Ti and Au thin film is 0.5 Å/s and 2 Å/s, respectively. The deposition happens at room temperature, and the filament current is 30 A and the emission current is 338 mA. The schematic is shown in Figure 2.8.

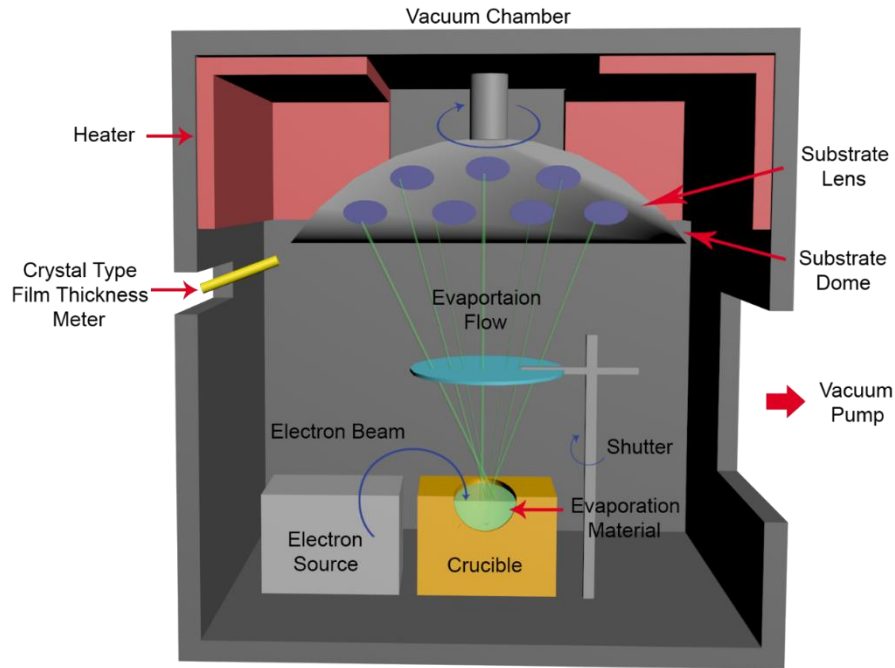


Figure 2.8 Schematic plot of the electron beam evaporation process.

2.8.4 Inorganic TMDC Sample preparation

We use mechanical exfoliation to prepare thin-layer TMDs and phosphorene, and we drily transfer them onto other substrates using Gel-Pak gel films. For MOS device fabrication, we will firstly pattern Au electrodes on SiO₂/Si substrates (275 nm thermal oxide on n⁺-doped silicon) by conventional photolithography, metal deposition and lift-off processes, and then transfer thin-layer TMD samples onto the SiO₂/Si substrate near a pre-patterned Au electrode. Another thick graphite flake can be similarly transferred to electrically bridge the TMD flake and the Au electrode, forming a MOS device. The schematic plot of a MOS device is shown in Figure 2.9.

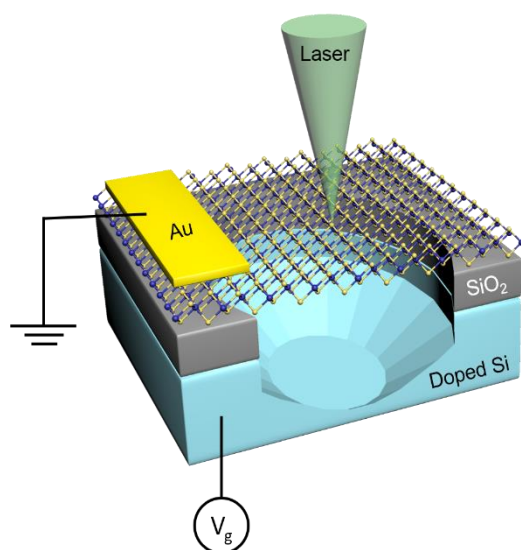


Figure 2.9 Schematic diagram of a MOS device using a monolayer 2D TMD semiconductor.

2.8.5 Scanning electron microscope equipped with focused ion beam

Scanning electron microscopy uses electrons rather than photons to image objects. Because of the small diffraction limit of an electron wave, electron microscopes will have high resolution in imaging nanoscale materials. The 1D organic nanowires and other samples were imaged using a FEI Helios 600 Nanolab dual beam FIB/SEM system with Gallium ion source using pre-calibrated dosage, optimized beam voltage (30 kV) and beam current (9.7 pA). This dual beam SEM/FIB system can reach atomic resolution in the vertical direction and sub-20 nm resolution in lateral direction in ion milling, and we can check the milled pattern instantly with the SEM.

2.9 Summary

In this chapter, I have established in brief all the measurement and experimental techniques that I have used in this thesis to demonstrate various results and their physical significance. CVD method was used to grow organic samples (both 2D and 1D), whereas

PECVD and lithography were used in addition to mechanical exfoliation to make device based on inorganic 2D materials. AFM and PSI were used to determine the layer thickness and obtain topographical information from the prepared samples. Raman and PL spectroscopy were used extensively to determine the optical and opto-electronic properties of all the samples. Polarization and temperature dependent measurements were carried out using external equipment with the PL setup. Time-resolved PL and transient pump-probe reflectivity were used to extensively determine the carrier lifetime of various quasi-particles in this thesis. Near and far field SOM were used to determine the diffusion length of excitons in the 2D materials for both organic and inorganic 2D materials. Finally, the device fabrication techniques used to make MOS and FET device incorporating the 2D and 1D nanomaterials were discussed which utilized, photolithography, electron-beam evaporation and dual beam SEM/FIB system.

2.10 References

1. Stassen I, *et al.* Chemical vapour deposition of zeolitic imidazolate framework thin films. *Nature Materials* 2015, **15**: 304.
2. Tavares J, Swanson EJ, Coulombe S. Plasma Synthesis of Coated Metal Nanoparticles with Surface Properties Tailored for Dispersion. *Plasma Processes and Polymers* 2008, **5**(8): 759-769.
3. Schropp R, *et al.* Hot wire CVD of heterogeneous and polycrystalline silicon semiconducting thin films for application in thin film transistors and solar cells. *Materials Physics and Mechanics* 2000, **1**: 73-82.
4. Binnig G, Quate CF, Gerber C. Atomic Force Microscope. *Physical Review Letters* 1986, **56**(9): 930-933.

5. Cappella B, Dietler G. Force-distance curves by atomic force microscopy. *Surface Science Reports* 1999, **34**(1): 1-104.
6. Rugar D, Hansma P. Atomic force microscopy. *Physics today* 1990, **43**(10): 23-30.
7. Yang J. Inelastic and Elastic Light-Matter Interactions in Two-Dimensional Semiconductors. 2017.
8. de Groot P. Method and system for profiling objects having multiple reflective surfaces using wavelength-tuning phase-shifting interferometry. Google Patents; 2002.
9. Wang F, *et al.* Spatially resolved doping concentration and nonradiative lifetime profiles in single Si-doped InP nanowires using photoluminescence mapping. *Nano Letters* 2015, **15**(5): 3017-3023.
10. Zhang L, *et al.* Efficient and Layer-Dependent Exciton Pumping across Atomically Thin Organic–Inorganic Type-I Heterostructures. *Advanced Materials* 2018, **30**(40): 1803986.
11. Iacona F, Ceriola G, La Via F. Structural properties of SiO₂ films prepared by plasma-enhanced chemical vapor deposition. *Materials Science in Semiconductor Processing* 2001, **4**(1-3): 43-46.
12. Lathrop JW. The Diamond Ordnance Fuze Laboratory's Photolithographic Approach to Microcircuits. *IEEE Annals of the History of Computing* 2013, **35**(1): 48-55.

CHAPTER 3

Highly enhanced many-body interactions in anisotropic 2D semiconductors

Many body interactions in two-dimensional (2D) semiconductors are strongly enhanced compared with bulk semiconductors, because of the reduced dielectric screening. These many body interactions and subsequent bound quasi-particles like excitons, trions and bi-excitons are extremely important for the optoelectronics performance of 2D semiconductors. In particular, anisotropic 2D semiconductors, such as black phosphorus (or termed as phosphorene) and phosphorene-like 2D materials such as GeSe and SnS etc., have shown even stronger many body interactions, because of the lower dimensionality of the quasi-particles and further reduced dielectric screening. This makes anisotropic 2D semiconductors extremely attractive for the fundamental science

and technology development. This field is emerging rapidly and several anisotropic 2D materials have been the center of attraction in the field of 2D semiconductor research in the recent few years, due to their interesting optical and electrical anisotropic performance in the 2D quantum limit. Many body interactions in conventional 2D materials have been heavily investigated but it has not been reported in detail for anisotropic 2D materials. The quasi-particles in anisotropic materials have fractional dimensionality which makes them perfect candidates to serve as a platform to study fundamental particle interactions in fractional dimensional space, enabling novel opto-electronic applications.

Fundamental many-body effects which mainly result from strong electron-hole, electron-electron interactions in environments with reduced dielectric screening, selectively facilitate the experimental study of these fundamental charge particles, leading to their applications in optoelectronics. Stronger interaction within lower dimensional systems leads to larger binding energies, which have already been demonstrated in quasi-2D quantum wells, 1D carbon nanotubes and 0D quantum dots and other 2D TMD materials. Observation and control of excitonic properties is possible due to larger binding energies which has been a long pursued scientific goal. Study of many body interactions in low-dimensional materials can lead to useful scientific information that have great potential in opto-electronic device applications such as light emitters, photodetectors. Phosphorene shows a much larger binding energy of trions in a 2D system, which was only observed earlier in 1D systems like carbon nanotubes, as compared to other 2D counterparts such as TMDs. Higher binding energy provides a platform to study these quasi-particles at room temperature.

This chapter explores the experiments and theoretical simulations related to 2D phosphorene, a 2D system with quasi-one-dimensional (quasi-1D) excitons and trions, due to its unique anisotropic properties provides a unique 2D platform for investigating the dynamics of excitons, trions and bi-excitons in reduced dimensions and fundamental

many-body interactions. Higher binding energy in phosphorene has been experimentally related to the reduced dimensionality, supported by theoretical calculations. High trion binding energy is critical to observe and study these fundamental many-body interactions at room temperature for further investigation into phenomenon such as exciton condensation and Fermi-energy singularity.

This chapter provides a concise and targeted summary on the experimental observation of these fundamental quasi particles (excitons, trions, bi-excitons, etc.) in phosphorene and other anisotropic 2D systems, which are critical to understand excitonic properties discussed subsequently in this thesis. Experimental methods and theoretical models to calculate binding energies will be stressed upon in this chapter., which have been used in successive chapters. The importance of these coulombic interactions and their fundamental significance will be discussed in detail. Also, methods and models to calculate binding energy of these many body particles will be addressed which is consequential for their applications in optoelectronic devices at room temperature. This chapter aims to demonstrate methods to improve fundamental charge interaction in anisotropic 2D materials.

This chapter will provide detailed insights into fundamental behaviour of the quasi-particles in 2D anisotropic materials and further investigation into experimental techniques to study the many body effects and related parameters, critical for future device applications and study of similar fundamental quasi-particles in other low dimensional materials. Anisotropy is a critical phenomenon for optical properties of 2D semiconductors. Chapter 4, 5, 7 and 8 will further explore anisotropic properties of excitons and their applications in detail for both organic and inorganic semiconductor 2D materials. Chapter 2 describes the methods through which I have studied the anisotropic properties of various semiconductor materials using polarized resolved PL spectroscopy.

Highly Enhanced Many-Body Interactions in Anisotropic 2D Semiconductors

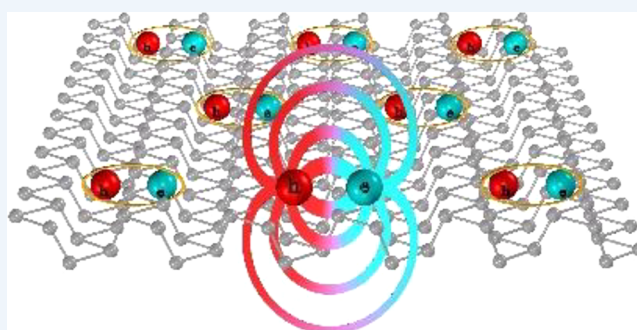
Ankur Sharma,[†] Han Yan,[†] Linglong Zhang,^{†,‡} Xueqian Sun,[†] Boqing Liu,[†] and Yuerui Lu^{*,†}

[†]Research School of Engineering, College of Engineering and Computer Science, The Australian National University, Canberra, Australian Capital Territory 2601, Australia

[‡]National Laboratory of Solid State Microstructures, Collaborative Innovation Center of Advanced Microstructures, School of Electronic Science and Engineering, Nanjing University, Nanjing 210093, People's Republic of China

ABSTRACT: Atomically thin two-dimensional (2D) semiconductors have presented a plethora of opportunities for future optoelectronic devices and photonics applications, made possible by the strong light matter interactions at the 2D quantum limit. Many body interactions between fundamental particles in 2D semiconductors are strongly enhanced compared with those in bulk semiconductors because of the reduced dimensionality and, thus, reduced dielectric screening. These enhanced many body interactions lead to the formation of robust quasi-particles, such as excitons, trions, and biexcitons, which are extremely important for the optoelectronics device applications of 2D semiconductors, such as light emitting diodes, lasers, and optical modulators, etc. Recently, the emerging anisotropic 2D semiconductors, such as black phosphorus (termed as phosphorene) and phosphorene-like 2D materials, such as ReSe₂, 2D-perovskites, SnS, etc., show strong anisotropic optical and electrical properties, which are different from conventional isotropic 2D semiconductors, such as transition metal dichalcogenide (TMD) monolayers. This anisotropy leads to the formation of quasi-one-dimensional (quasi-1D) excitons and trions in a 2D system, which results in even stronger many body interactions in anisotropic 2D materials, arising from the further reduced dimensionality of the quasi-particles and thus reduced dielectric screening. Many body interactions have been heavily investigated in TMD monolayers in past years, but not in anisotropic 2D materials yet. The quasi-particles in anisotropic 2D materials have fractional dimensionality which makes them perfect candidates to serve as a platform to study fundamental particle interactions in fractional dimensional space.

In this Account, we present our recent progress related to 2D phosphorene, a 2D system with quasi-1D excitons and trions. Phosphorene, because of its unique anisotropic properties, provides a unique 2D platform for investigating the dynamics of excitons, trions, and biexcitons in reduced dimensions and fundamental many body interactions. We begin by explaining the fundamental reasons for the highly enhanced interactions in the 2D systems influenced by dielectric screening, resulting in high binding energies of excitons and trions, which are supported by theoretical calculations and experimental observations. Phosphorene has shown much higher binding energies of excitons and trions than TMD monolayers, which allows robust quasi-particles in anisotropic materials at room temperature. We also discuss the role of extrinsic defects induced in phosphorene, resulting in localized excitonic emissions in the near-infrared range, making it suitable for optical telecommunication applications. Finally, we present our vision of the exciting device applications based on the highly enhanced many body interactions in phosphorene, including exciton-polariton devices, polariton lasers, single-photon emitters, and tunable light emitting diodes (LEDs).



1. INTRODUCTION

The discovery of graphene in 2004 opened avenues for a new generation of 2D materials. It was followed by exploration of other 2D semiconductor materials such as transition metal dichalcogenides (TMDs),^{1,2} phosphorene,³ etc. Stronger interaction within lower dimensional systems leads to existence of robust many-body systems^{2,4} and quasi-particles^{5,6} in these atomically thin layered materials. These quasi-particles have been shown to exist in quasi-2D systems (quantum wells),^{7,8} 2D materials,^{4,5,9} and 1D carbon nanotubes (CNTs).¹⁰ The strong interaction is measured by “binding energy” of these

quasi-particle systems. High binding energies allow these many body interactions between electrons and holes to be experimentally detected in various combined forms, such as excitons (electron and hole pair),¹¹ trions (charged excitons),¹² and biexciton (quantum combination of two-excitons: steady state or a trion and free charge: excited state).¹³ Binding energies of excitons (trions) have been theoretically and experimentally demonstrated to be in the range of 5–35 (1–5)

Received: October 9, 2017

Published: April 19, 2018

Table 1. Experimental and Theoretical Binding Energy Values (meV) for Various Quasi-Particles in Different Materials^a

system			quasi-2D	2D				anisotropic 2D					1D
material			quantum wells	1L MoS ₂	1L MoSe ₂	1L WS ₂	1L WSe ₂	1L phosphorene	1L ReSe ₂	1L ReS ₂	1L GeS	1L GeSe	CNT
exciton	exp		8.7–9.2	550 ¹⁶	500 ¹⁶	660 ⁶	380 ¹⁶		860 ⁵⁴				410
													1000
trion	theory		6.6–33.6	540 ¹⁵	470 ¹⁵	500 ¹⁵	450 ¹⁵	830 ³⁴	870 ⁵⁴	1070 ⁵⁶	1200 ⁵¹	400 ⁵¹	210–1100
	exp		1.1–5.5	18 ⁴	30 ⁵⁷	36 ⁵⁷	30 ³¹	162 ^{b24}					140–170
biexciton	theory		1.4–8.9	34 ⁵⁷	31 ⁵⁷	31 ⁵⁷	29 ⁵⁷	100 ²⁵					36–200
	exp	T + C	1.0–2.0	70 ⁵⁸	60 ¹³	65 ⁵⁹	52 ⁶⁰	200 ²⁴					130
		X + X											
	theory	T + C	2.13–2.24	69 ¹³	58 ¹³	67 ¹³	59 ¹³						40–56
		X + X		22 ⁵⁸	23 ⁵⁷	24 ⁵⁸	20 ⁵⁸	41 ³²					

^aNote: T is trion, C is charge, and X is exciton. This distinction has been made to identify excited state (T + C) and steady state (X + X) biexcitons. This distinction has not been made for biexciton values from quantum wells and CNT. References for binding energies of CNTs and quantum wells have been cited in-text because of the large number of references. ^bThe value is from 3L phosphorene sample.

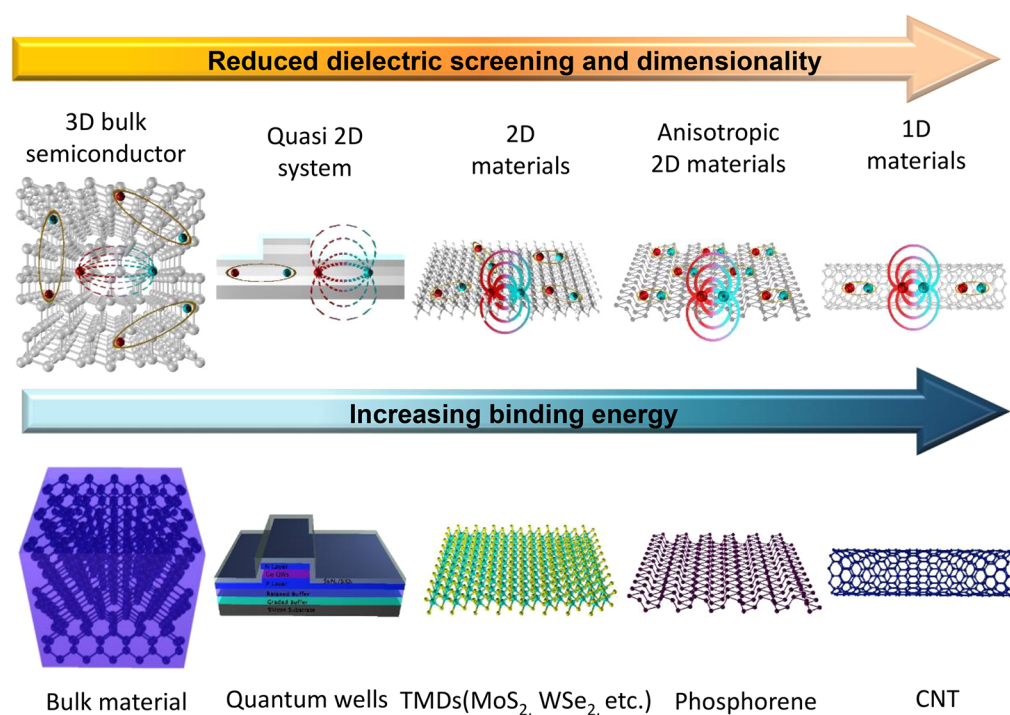


Figure 1. From 3D state (left) to truly 1D state (right) as the dimensionality decreases the dielectric screening decreases while the binding energy or the interaction of many body quasi-particles increases. In 3D state, electric field lines interacting between two fundamental particles are screened by the material. This screening reduces as the particles are further confined dimensionally in quantum wells (quasi-2D systems). 2D materials allow even stronger Coulombic interactions due to absence of any dielectric materials and results in even stronger in-plane many body systems spread across a single plane. In phosphorene, due to puckered configuration of the molecules the many body systems are confined along a quasi-1D space resulting in even higher interactions and binding energies, like a true 1D system, such as a CNT.

meV in quantum wells,¹⁴ 400–550 (20–34) meV in TMD monolayer,^{15,16} and 210–1100 (36–200) meV in CNTs.^{17–20} Detailed values of exciton, trion, and biexciton binding energies from various material systems from theoretical and experimental work have been summarized in Table 1.

However, the relatively low values of binding energies in quasi-2D and 2D systems only allow the exciton and trion photoluminescence (PL) peaks to segregate at cryogenic temperatures, barely resolvable at room temperature compared to their emission bandwidth.²¹ On the other hand, excitons and trions in 1D confined space (such as CNTs) exhibit much higher binding energies and the complete separation of exciton and trion PL peaks at room temperature because of further

dimensionality reduction and reduced screening.^{1,10} However, the utilization of 1D CNTs for practical optoelectronic applications is critically limited by their small cross-sectional area.²² It is extremely difficult to assemble large-sized and optically uniform films composed of CNTs because of the varied distribution of chirality and other issues such as conversion of homogeneous templates into long-chain CNTs at low temperatures.^{22,23} It has been a long-standing scientific challenge to optimize this trade-off between enhanced binding energies at confined dimensionalities and reduced cross-sectional areas, limiting the development of useful excitonic/trionic devices.

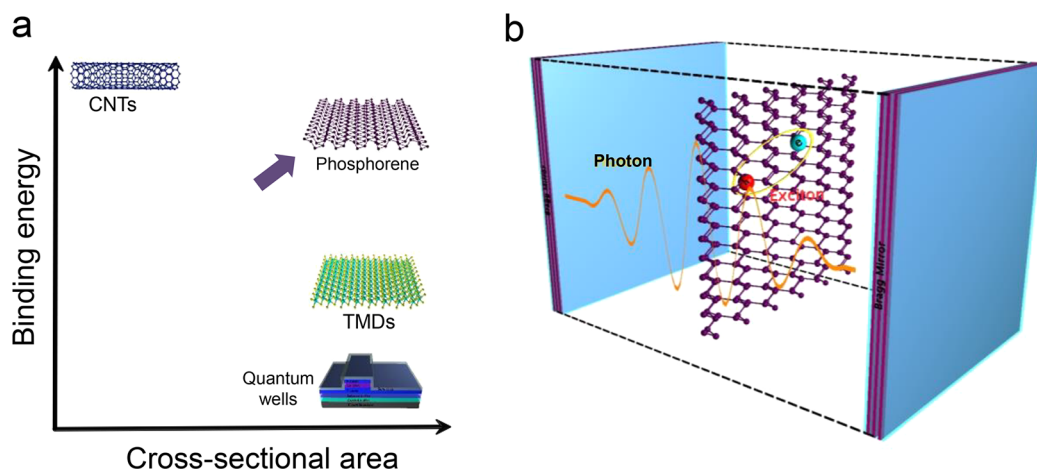


Figure 2. (a) Phosphorene provides high binding energies similar to a true 1D system with a large 2D cross-sectional area. (b) Schematic diagram of an exciton-polariton interaction in a cavity with 2D material.

The recently emerged anisotropic 2D materials, such as phosphorene, provides an elegant way to solve this challenge. Compared with other 2D materials, phosphorene shows strongly anisotropic properties, which results in quasi-1D excitons and trions in a 2D system.^{9,24,25} In this Account, we use the example of phosphorene to demonstrate the role of enhanced many body interactions in anisotropic 2D semiconductors, as compared to other 2D materials, such as TMDs. This enables a system that addresses the above-mentioned problem of the trade-off. High binding energies with large cross-section grant opportunities to use phosphorene in future optoelectronic devices, such as exciton-polariton devices, polariton lasers, tunable LEDs, and other excitonic devices based on exciton condensation.²⁶ This Account is directed toward highlighting the role of dimensional confinement and emphasizes on various experimental techniques employed by us and other groups to study these many body interactions and quasi particles. At the end, we present our visions and prospect on the potential optoelectronic applications of those anisotropic 2D materials.

2. EFFECT OF DIMENSIONALITY AND DIELECTRIC ENVIRONMENT ON FUNDAMENTAL QUASI-PARTICLES

Many body effects, which result from the Coulombic electron–hole interactions, play a key role in determining their electronic transport and optical properties.¹¹ The strength of electric fields between charged particles in a semiconducting material is determined by the level of Coulombic interaction between charged particles, which are affected by the dimensionality of the material and thus dielectric screening from the surrounding environment.²⁷ The effect of the dielectric environment on the interaction of charges and the binding energy in various dimensionalities of semiconductors have been represented schematically in Figure 1. In a conventional bulk semiconductor, the electron–holes interact with each other with electric field lines passing through the dielectric medium of the material itself, causing significant dielectric screening, resulting in weak interactions among the charges. Thus, the binding energy of these quasiparticle/many-body systems originating from the coulomb interaction is almost negligible. In quasi-2D quantum wells, the interaction enhances as the charges are only confined in a quasi-2D space and the dielectric screening is

diminished to an extent. In truly 2D materials, such as TMD monolayers, the dielectric screening to the interacting charges is considerably reduced due to the high localization of interacting charges within a single 2D plane²⁸ (Figure 1). The weak intrinsic screening results in enhanced many-body interactions at the 2D quantum limit. This effect is called the ‘dielectric confinement or “image-charge effect”’.¹ The stronger interaction leads to formation of stable excitons, trions, and biexcitons with higher binding energies as compared to quasi-2D systems. These quasi-particles have been demonstrated in various TMD materials, such as MoS₂,^{4,5} WS₂,^{2,6} MoSe₂,^{13,29} WSe₂,^{30,31} with binding energies of excitons as high as ~0.6 eV and are stable at room temperature. Simultaneously, existence of robust charge interactions combined with dimensional confinement lead to formation of higher order excitonic complexes, such as trions⁴ and biexcitons.¹³ Compared with other 2D materials, phosphorene shows strongly anisotropic properties, which results in quasi-1D excitons and trions in the 2D phosphorene (Figure 1). Because of the formation of quasi-1D trions and excitons, 2D phosphorene has ultrahigh binding energies of excitons (~0.8 eV for monolayer phosphorene³²) and trions (~200 meV²⁴), much higher than those values in TMDs. As the dimensionality is further reduced to true 1D with advent of CNTs, the reported binding energies of excitons (>1 eV^{19,20}) and trions (~200 meV^{17,33}) were even higher than 2D systems due to further unidirectional confinement of charges.

However, high binding energies obtained from 1D CNTs are not applicable for widespread photonics devices applications due to the limited cross-section and difficulties in growing optically uniform integrated CNT networks.²² Phosphorene, due to its strong anisotropic optical and electrical properties,^{24,25} offers an alternative to solve aforementioned trade-off challenge. (Figure 2a). Phosphorene is equivalent to a system made from bundles of identical 1D semiconductors, allowing quasi-1D excitonic and trionic behavior in a large 2D area. This allows phosphorene’s optoelectronic integration for various unique applications in optoelectronics and quantum devices harnessing both the high excitonic and trionic binding energies and large cross-sectional area. For instance, phosphorene has promising applications in cavity devices such as exciton polariton devices (Figure 2b) operating at near-infrared (NIR) range, useful for telecommunication applications and integration with silicon photonics.

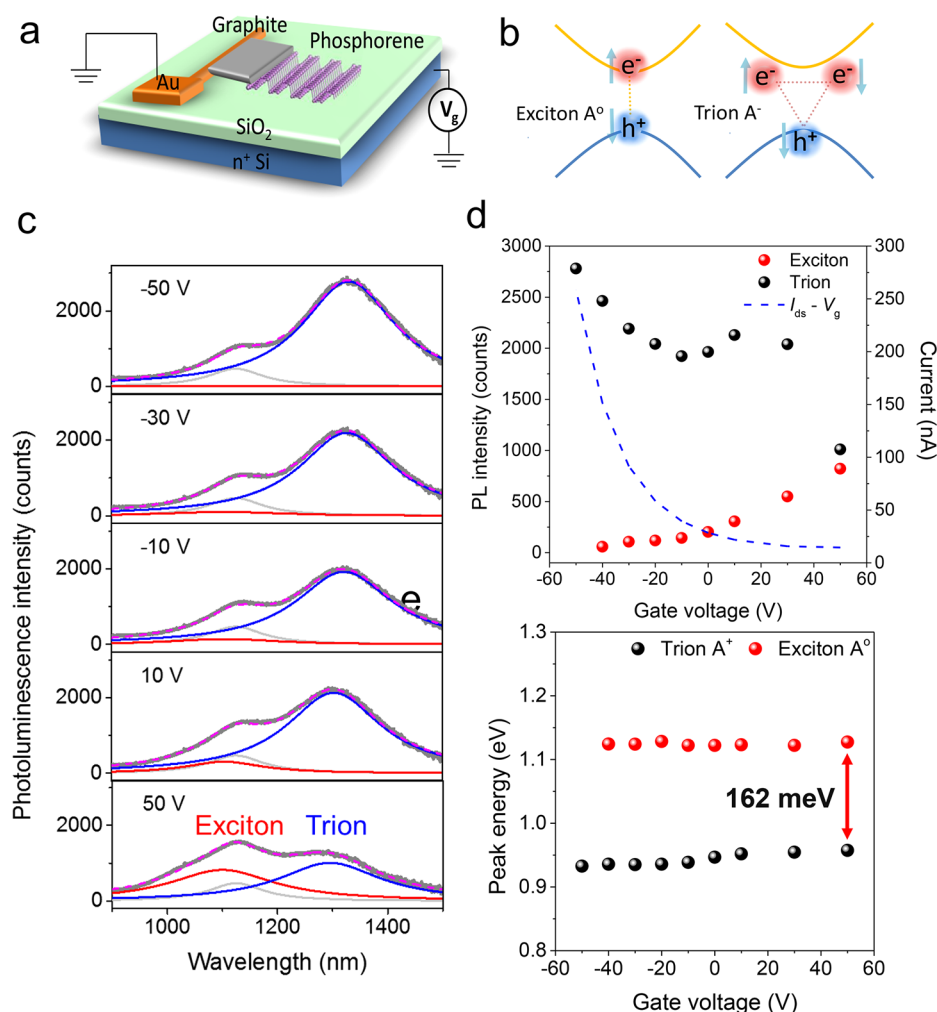


Figure 3. (a) Schematic diagram of the device used for exciton/trion modulation using external back gate voltage. (b) Schematic diagrams of excitons and trions. (c) PL intensity from 3L phosphorene as a function of back gate voltage. (d) Exciton and trion PL intensity variation with change in back gate voltage. (e) Variation in peak energies of exciton and trions as a function of back gate voltage. Figure 3 adapted with permission from ref 24. Copyright 2015 American Chemical Society.

3. TIGHTLY BOUND EXCITONS AND TRIONS IN PHOSPHORENE

Binding energy is the key parameter that defines the extent of interaction between fundamental particles.^{11,28} Several theoretical and experimental techniques have calculated the binding energy of excitons, trions and biexcitons. Table 1 summarizes the values of binding energies for various systems.

We successfully measured the binding energy of trions in a 3L phosphorene sample, using a metal-oxide-semiconductor (MOS) device to tune the PL emissions via controlling the electrostatic doping with applied back gate voltage, as shown in Figure 3a and b. The 3L phosphorene sample showed two emission peaks at ~1100 and ~1300 nm (Figure 3c–e), which were identified to be from excitons and trions, respectively. The relative intensity ratio of exciton/trion is tuned by gate voltage. When negative voltage is applied, positive charges are injected in to the sample and hence the trionic emissions dominated and vice versa. We also demonstrated that optical charge injection can also be controlled with excitation power, to tune the trion density in 1L phosphorene.²⁴ Therefore, binding energy of trions in 3L phosphorene was measured to be ~160 meV, which is much larger than those values in TMD

monolayers and is comparable to that in truly 1D CNTs (Table 1).

High-binding energy is attributed to anisotropic orientation of charged many body complexes in phosphorene, which has been theoretically predicted as well.³⁴ We, confirmed this anisotropic excitonic and trionic emission from phosphorene using angle resolved PL spectroscopy.^{9,24} The PL intensity is highly dependent on the polarization angle of the incident light due to anisotropic absorption in phosphorene attributed to its puckered structure. We also observed that emission of excitonic emissions from phosphorene was also linearly polarized sharply. Thus, the many body complexes are mostly aligned along the armchair direction (as shown in Figure 1). This strong anisotropy results in higher binding energies which can result in several photonics device applications, which will be discussed in the later section.

4. PRODUCING AIR-STABLE MONOLAYER PHOSPHORENE

Degradation of phosphorene has been a long-standing challenge for the scientific community. It is easily oxidized in the presence of oxygen, moisture, and light.³⁵ Several different passivation techniques have been demonstrated including,

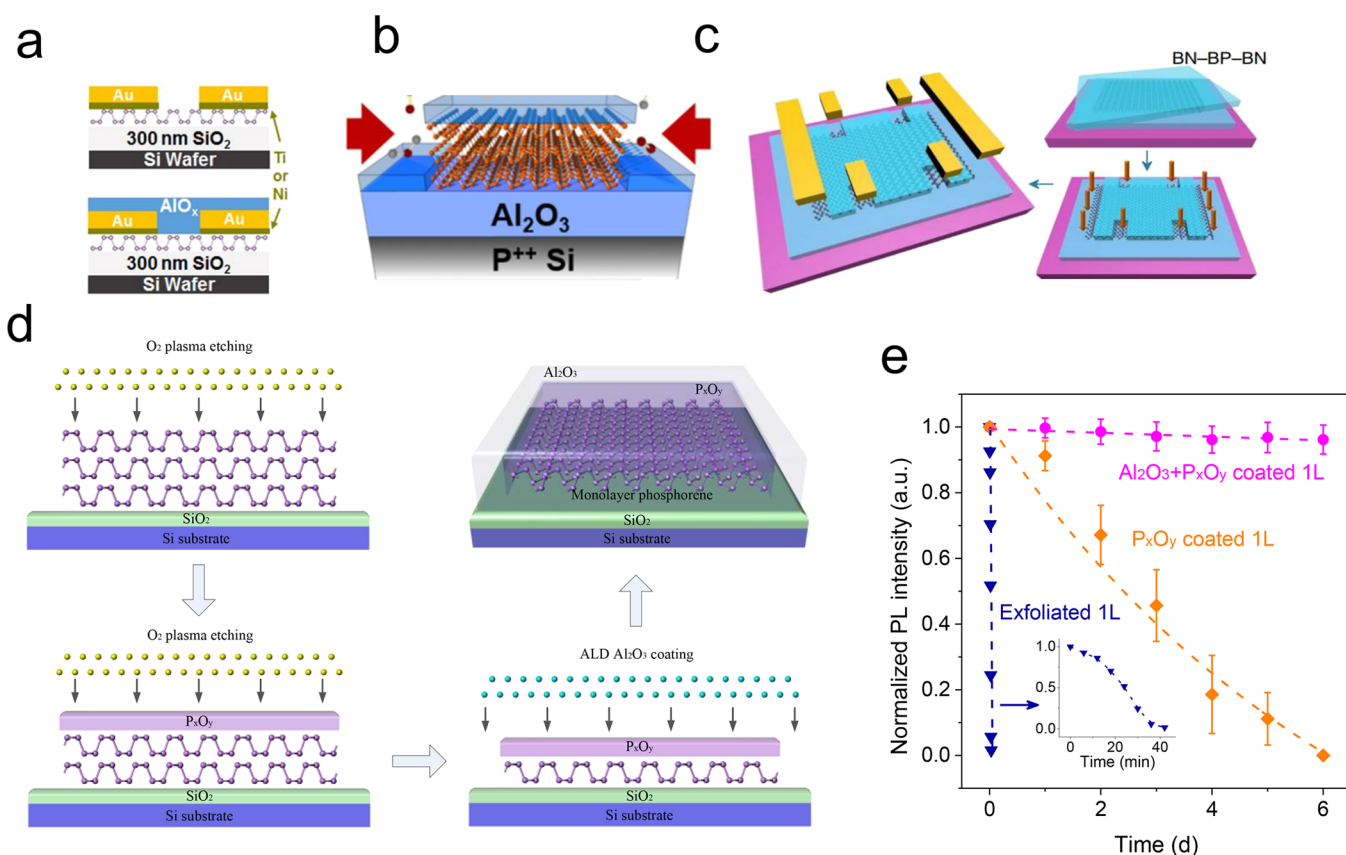


Figure 4. Schematic diagrams showing the passivation of phosphorene using (a) AlO_x , (b) Al_2O_3 , and (c), sandwiching between BN layers. Figure 4a adapted with permission from ref 36. Copyright 2014 American Chemical Society. Figure 4b adapted with permission from ref 37. Copyright 2015, Macmillan Publishers Limited. Figure 4c adapted with permission from ref 38. Copyright 2015 Macmillan Publishers Limited. (d) Passivation of few-layer phosphorene by combining the oxygen plasma treatment and Al_2O_3 encapsulation. (e) PL emission comparison from passivated and unpassivated phosphorene versus time. Panels d and e adapted with permission from ref 39. Copyright 2016 Nature Publishing group.

passivation through coating by Al_2O_3 ³⁶ by atomic layer deposition (ALD) technique³⁷ and sandwiching between h-BN layers³⁸ (Figure 4a–c). But, these techniques have been only partially successful in preserving fast degrading phosphorene flakes in the ambient environment.³⁹ The h-BN encapsulation requires very complicated technique and has a low-throughput. Recently, we developed a novel technique (Figure 4d) combining oxygen plasma etching with subsequent Al_2O_3 deposition to preserve phosphorene flakes in pristine condition in ambient environment. This method has 2-fold advantages. It allows for controlling the thickness of phosphorene very precisely and effective preservation of the phosphorene samples. Oxygen plasma is used to etch through a thick flake of phosphorene. During the treatment, top layers of phosphorene are oxidized to become P_xO_y , which serve as protecting layers for phosphorene underneath. Further plasma etching allows oxygen plasma to penetrate this P_xO_y layer and further oxidize the phosphorene layer underneath. After some time, a dynamic equilibrium is established so that etching rate and thickness of P_xO_y become constant. This allows precise etching down to monolayer. Finally, an additional layer of Al_2O_3 is deposited over the etched phosphorene and P_xO_y to protect it from oxidation. We found that mono- and bilayer samples which were fabricated by O_2 plasma etching can be coated with ALD Al_2O_3 without any further damage to the phosphorene samples under it due to the protective P_xO_y layer on top of it. This technique allows forming a controlled air-

stable few- to monolayered phosphorene samples, enabling its practical applicability in various device applications (Figure 4e).

5. DEFECT ENGINEERING IN PHOSPHORENE

Defect engineering in 2D materials has emerged a sturdy technique to modulate their optical properties for suitable optoelectronic applications. Single-photon emitters have been demonstrated from TMDs⁴⁰ and h-BN⁴¹ recently. The defect states can be realized through oxidation, irradiation, and physical absorption.⁴² Phosphorene and other similar structure based anisotropic materials (ReS_2 , and ReSe_2) offer a distinct advantage for defect engineering due to their puckered sp^3 -like configuration. Defect induction in phosphorene is critical for triggering photon emission at new wavelengths, utilizing the layer dependent band gap in phosphorene from future optoelectronic devices point of view.

We induced defects in monolayer phosphorene using two distinctive methods.^{39,42} First, we used a plasma-enhanced chemical vapor deposition (PECVD) oxide substrate and deposited gold over it followed by phosphorene. PECVD oxide contained a lot of impurities and surface states, which were confirmed with FTIR spectroscopy. These surface states then act as trapping centers for excitons.²¹ Second, we introduced extrinsic oxygen defects in monolayer phosphorene using external oxygen plasma etching.³⁹ Extrinsic defects as dangling “O” bonds are quite common in phosphorene and have been discussed in literature.⁴³ Another form is the diagonal oxygen bridge (Figure 5a), which acts as potential trap state and is

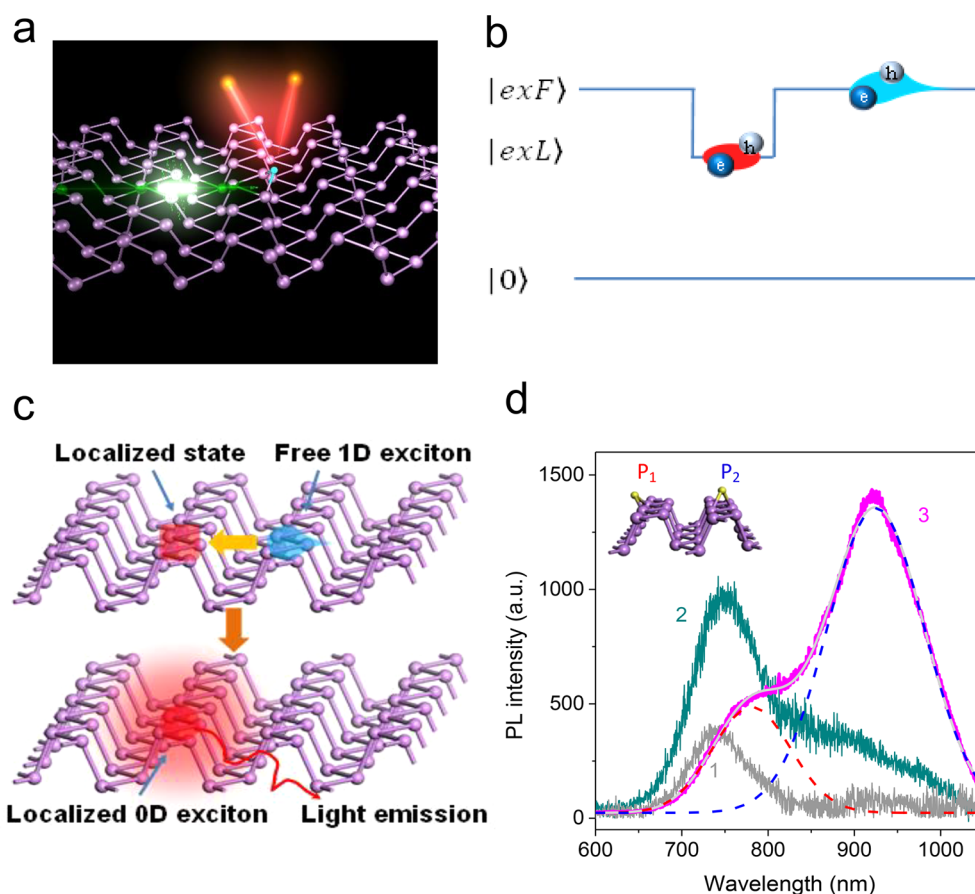


Figure 5. (a) Schematic diagram showing the defect emission from a diagonal bridge type defect in phosphorene. (b, c) Schematic showing the formation of lower energy defect states in phosphorene with respect to the free excitonic energy levels. (d) PL emission from defect engineered phosphorene monolayer with defect shown inset. The green curve represents the free excitonic emission from untreated graphene. The pink curve represents the free and localized excitonic emission from oxygen plasma treated graphene. The dotted curves are Lorentzian fit curves. Figures 5b and c are adapted with permission from ref 42. Copyright 2016 Wiley. Figure 5d adapted from ref 39. Copyright 2016 Nature Publishing group.

quite stable. These surface defects can alter the optical properties of phosphorene and result in defect levels being created in the optical band gap of the materials (Figure 5b), which causes excitonic emissions from these localized states at lower energies than free exciton emission energies (Figure 5c). For defect engineering in monolayer phosphorene, we observed a free exciton emission at ~ 720 nm attributed to the free excitonic emission and low energy emission at ~ 920 nm (Figure 5d). The defect peak shows a sublinear growth in the integrated PL emission with increasing excitation laser power, thus establishing its defect nature.³⁹ The defect emission peaks were observed at room temperature, which is in contrast with defect emissions from TMDs that are only visible at cryogenic temperatures.²¹ The localized excitonic emissions at 920 nm showed much higher PL emission efficiency as compared to the free excitonic state. The overall quantum efficiency was extracted to be ~ 33.6 times higher than free excitonic emission.⁴² The enhanced PL emission yield could be attributed to the longer lifetime-radiative recombination of localized excitons in the trapping states. The defect states can function as quasi-zero-dimensional (quasi-0D) luminescence trapping centers with enhanced PL emission efficiencies. 2D phosphorene, with quasi-1D free excitons and quasi-0D localized excitons forms an interesting 2D–1D–0D hybrid system, which provides us a unique platform to explore the fundamental interactions at multidimensionalities.⁴² As sug-

gested earlier, anisotropic materials due to their specific molecular orientation are ideal candidates for defect engineering using any of the above-mentioned techniques. This is particularly interesting for phosphorene due to its layer dependent band gap, it could possibly lead to defect emissions in the infrared range. Most defect emissions in other TMDs and 1L phosphorene are >1 eV, which is in the visible range. Few-layered phosphorene samples can trigger emissions at much lower energies that are useful for telecommunication device applications.⁴⁴

6. OUR VISION: DEVICES BASED ON STRONG LIGHT MATTER INTERACTIONS IN PHOSPHORENE

The enhanced binding energies of these quasi-particles as discussed earlier is crucial for promising device applications. In this section, we will present our vision for such optoelectronic devices and their working principles based on phosphorene and other similar anisotropic 2D materials. Figure 6a depicts the key domains of device applications based on phosphorene directly linked with the interesting properties we have discussed earlier in this account. For example, high binding energy allows for its integration into a microcavity for electronically pumped exciton-polariton lasers.

In microcavities created by Bragg's mirror on either side of the 2D material (Figure 2b), a strong coupling of excitons and optical fields can be generated. 2D excitons and 2D optical

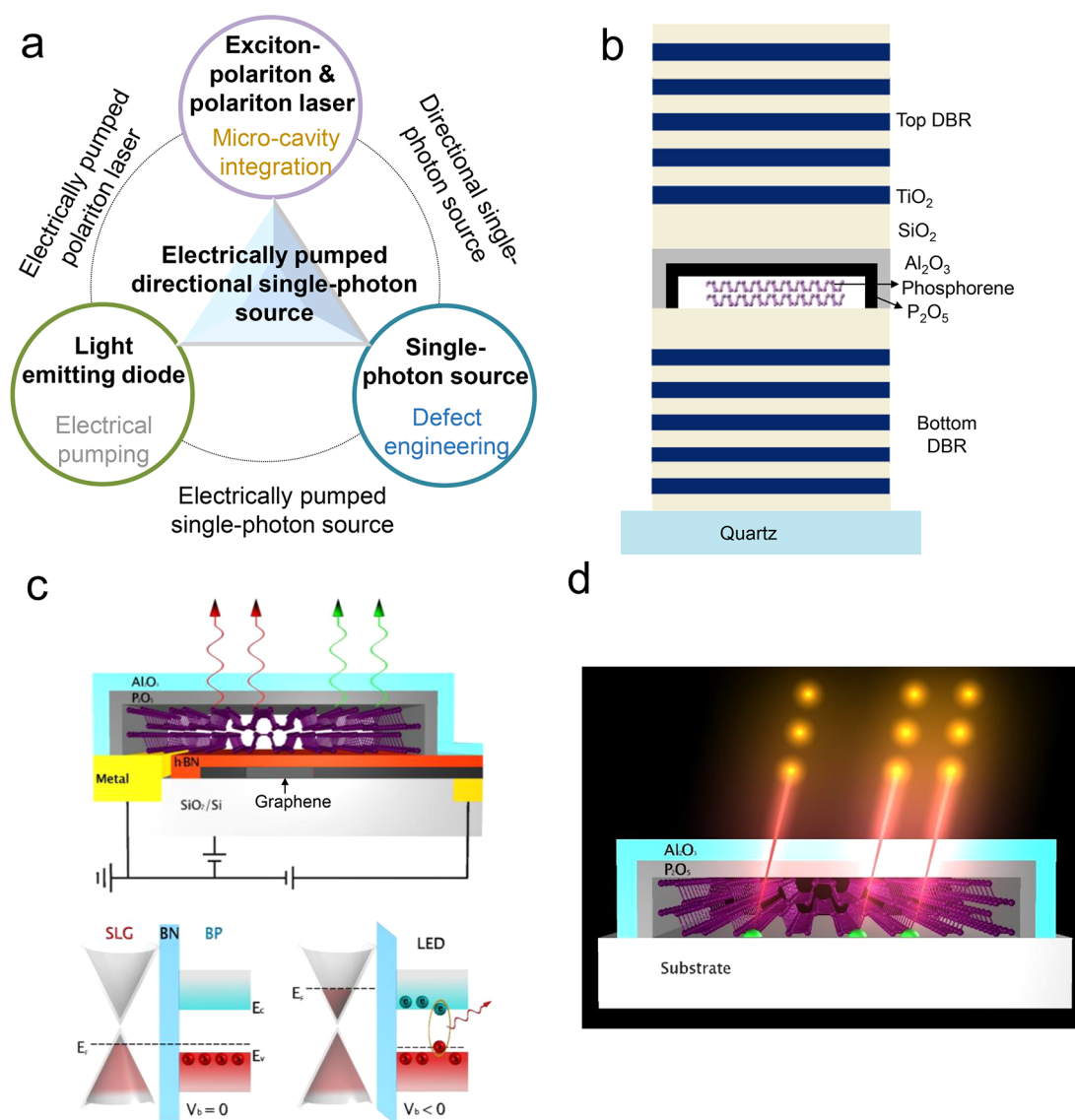


Figure 6. (a) Envisioned research domains with anisotropic materials. (b) Schematic of the structure of planar microcavity composed of dual DBRs with the embedded phosphorene. (c) Schematic plot of the tunable phosphorene LED. Heterostructure band diagram shows the case for zero-bias and the case for a finite negative bias applied to the single layer graphene (SLG). BP: phosphorene. (d) Schematic diagram showing single-photon emissions from defect states in phosphorene.

modes in the strong coupling regime in these cavities gives rise to new eigenmodes called excitons-polaritons.⁴⁵ These can enable study of quantum phenomenon such as Bose–Einstein condensation, quantum vortices, and entangled photon pairs.⁴⁶ Earlier reported exciton-polaritons have been based on quantum wells, where these quasi-particles were only visible at cryogenic temperatures. Recently, they have been reported with TMD based materials⁴⁵ in the microcavities owing to their strong binding energy and direct band gap nature. Exciton-polariton devices operating the infrared region are critical for telecommunication applications and integration with conventional silicon photonics. Recently, NIR exciton-polaritons were reported using single walled CNTs.²² But, CNT-based devices show large performance variation, since it is difficult to control the position, alignment and chirality of the CNTs in the cavity as discussed earlier. Phosphorene thus, provides a high binding energy system, stable, perfectly controllable platform to demonstrate such devices working the NIR region. Layer-dependent band gap⁹ of phosphorene also allows flexibility of

choosing the emission wavelength range. As shown in the Figure 6b, the microcavity consists of atomically thin phosphorene sandwiched between two SiO₂ layers, which is placed between SiO₂/TiO₂ distributed Bragg's Reflector (DBR) mirrors. The cavity resonance can be controlled to match well with exciton energy emitting from phosphorene sample. Polariton lasers⁴⁷ can be made using the stimulated scattering from exciton-polaritons that promises more energy efficient generation of coherent light.⁴⁸ The threshold energy for coherent emission from a phosphorene polariton laser will be much smaller as compared to a conventional laser.

Simultaneously, light emitting junctions based on TMD materials have been demonstrated including the lateral *p–n* junctions, vertical heterojunction diodes⁴⁹ and vertical tunneling transistors.⁵⁰ But, their emission wavelength as stated above remains confined in the visible region. Phosphorene based LEDs (Figure 6c) can act as potential sources for NIR and even middle infrared (MIR) region emission for telecommunication applications. Also, as we have demonstrated

earlier excitonic and trionic emissions from phosphorene can be controlled using external back gate tuning.²⁴ Thus, phosphorene can enable tunable wavelength emissions from a single device, by controlling the back-gate voltage as shown in the schematic diagram Figure 6c. A vertically stacked heterojunction with graphene and phosphorene allows for electroluminescence (EL) from the whole device area, unlike Schottky junction or split-gate $p-n$ junction devices providing the benefit of atomically precise interfaces and barrier thickness.

Defect engineering in phosphorene as discussed earlier can lead to potential device applications.⁴² These defects act as efficient trapping centers, which when isolated can act as sources of single-photon emission. 2D materials have several key advantages to host single-photon emitters as they can negate the total internal reflection enabling high light extraction efficiency, enabling integration with photonic waveguides and plasmonic structures. They have been demonstrated recently with h-BN and TMD materials⁴¹ in which quantum defects are ascribed to localized excitons. But, for all single-photon emitters demonstrated in TMDs and h-BN operate in the visible range, limiting their application to quantum communication systems based on NIR fiber transmission. As we have demonstrated in our previous reports,^{39,42} defects can be implanted in phosphorene enabling low energy defect states by either substrate engineering or external oxygen plasma etching. PL emission from phosphorene can be tuned using defect integration with few layer phosphorene. Thus, making phosphorene few layers as an ideal host for single-photon emitters in NIR wavelength (Figure 6d). These defect emissions are in sharp contrast with defect emissions from TMDs, which are only visible at cryogenic temperatures.²¹ The defect emission from these defect/localized states is brighter (higher quantum efficiency) as compared to the free excitonic emission making it more suitable for NIR and MIR single-photon emission-based devices.

7. OTHER ANISOTROPIC MATERIALS

Apart from phosphorene, other anisotropic materials like GeSe/GeS,⁵¹ SnS,⁵² SnSe,⁵³ ReSe₂, ReS₂,⁵⁴ and 2D perovskites⁵⁵ have also shown strong anisotropic optical properties. The theoretically calculated binding energies of the various fundamental quasi-particles are similar to those in phosphorene (Table 1), making them suitable for all the above-mentioned applications. Also, they are made of earth abundant and environmentally friendly elements making them suitable for optoelectronic applications.

8. CONCLUSIONS AND PROSPECTS

The ability to fabricate materials that are atomically thin has led us to explore stronger light-matter interaction that exist at that level. While reflecting on the key reasons for such strong interactions at the 2D limit, we highlighted the role of these interactions in enabling us to study the properties and applications of the quasi-particles such as excitons and trions in this account. Using our recent experimental observations on phosphorene, we highlight the importance of such anisotropic 2D semiconductors that provide a quasi-1D platform in a 2D system enabling even higher binding energies of excitons and trions. First, we calculated exciton and trion binding energies in phosphorene, which is one-order higher as compared to other TMD materials. Higher excitonic/trionic interactions in a quasi-1D anisotropic material enable exciting device applica-

tions, such as exciton-polariton lasers and tunable LEDs. Degradation of phosphorene has been a major deterrent for its broad application. We discussed one of our recently developed technique to precisely thin down the thickness of phosphorene few layers and passivate it using Al₂O₃ simultaneously. Simultaneously, we described the role of defect engineered emissions from phosphorene, which can be used to demonstrate single-photon emitters from phosphorene working in the infrared range. Compared to other 2D materials, defect emissions from anisotropic materials are more stable at room temperature. We envision similar techniques that we have described can be extended to other anisotropic materials, such as ReSe₂, ReS₂, GeS, GeSe₂, and 2D perovskites to explore interesting and even stronger light matter interactions at the 2D limit enabling various optoelectronic and photonics device applications.

AUTHOR INFORMATION

Corresponding Author

*E-mail: yuerui.lu@anu.edu.au.

ORCID

Ankur Sharma: 0000-0002-0863-1857

Yuerui Lu: 0000-0001-6131-3906

Notes

The authors declare no competing financial interest.

Biographies

Ankur Sharma is a Ph.D. student at NEMS lab in Australian National University (ANU). His research interests include 2D materials and device fabrication based on 2D materials.

Han Yan is a third-year undergraduate student at Research School of Engineering, ANU.

Linglong Zhang is a Ph.D. student at Nanjing University, China, and a visiting PhD research student at Australian National University.

Xueqian Sun is a postgraduate student at ANU.

Boqing Liu is a postgraduate student in NEMS lab in ANU.

Dr. Yuerui Lu is an Associate Professor and group leader of Nanoelectro-mechanical System (NEMS) Lab at ANU. His research interests include MEMS/NEMS, nanomanufacturing, renewable energy harvesting, biomedical novel devices, and 2D materials.

REFERENCES

- (1) Chernikov, A.; Berkelbach, T. C.; Hill, H. M.; Rigosi, A.; Li, Y.; Aslan, O. B.; Reichman, D. R.; Hybertsen, M. S.; Heinz, T. F. Exciton binding energy and nonhydrogenic Rydberg series in monolayer WS₂. *Phys. Rev. Lett.* **2014**, *113*, 076802.
- (2) Hill, H. M.; Rigosi, A. F.; Roquelet, C.; Chernikov, A.; Berkelbach, T. C.; Reichman, D. R.; Hybertsen, M. S.; Brus, L. E.; Heinz, T. F. Observation of excitonic Rydberg states in monolayer MoS₂ and WS₂ by photoluminescence excitation spectroscopy. *Nano Lett.* **2015**, *15*, 2992–2997.
- (3) Ling, X.; Wang, H.; Huang, S.; Xia, F.; Dresselhaus, M. S. The renaissance of black phosphorus. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, 4523–4530.
- (4) Mak, K. F.; He, K.; Lee, C.; Lee, G. H.; Hone, J.; Heinz, T. F.; Shan, J. Tightly bound trions in monolayer MoS₂. *Nat. Mater.* **2013**, *12*, 207–211.
- (5) Lin, Y.; Ling, X.; Yu, L.; Huang, S.; Hsu, A. L.; Lee, Y.-H.; Kong, J.; Dresselhaus, M. S.; Palacios, T. Dielectric screening of excitons and trions in single-layer MoS₂. *Nano Lett.* **2014**, *14*, 5569–5576.

- (6) Ye, Z.; Cao, T.; O'Brien, K.; Zhu, H.; Yin, X.; Wang, Y.; Louie, S. G.; Zhang, X. Probing excitonic dark states in single-layer tungsten disulphide. *Nature* **2014**, *513*, 214–218.
- (7) Kheng, K.; Cox, R.; d'Aubigné, M. Y.; Bassani, F.; Saminadayar, K.; Tatarenko, S. Observation of negatively charged excitons X[−] in semiconductor quantum wells. *Phys. Rev. Lett.* **1993**, *71*, 1752.
- (8) Mathieu, H.; Lefebvre, P.; Christol, P. Simple analytical method for calculating exciton binding energies in semiconductor quantum wells. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1992**, *46*, 4092.
- (9) Zhang, S.; Yang, J.; Xu, R.; Wang, F.; Li, W.; Ghufra, M.; Zhang, Y.-W.; Yu, Z.; Zhang, G.; Qin, Q.; Lu, Y. Extraordinary Photoluminescence and Strong Temperature/Angle-Dependent Raman Responses in Few-Layer Phosphorene. *ACS Nano* **2014**, *8*, 9590–9596.
- (10) Brozena, A. H.; Leeds, J. D.; Zhang, Y.; Fourkas, J. T.; Wang, Y. Controlled Defects in Semiconducting Carbon Nanotubes Promote Efficient Generation and Luminescence of Trions. *ACS Nano* **2014**, *8*, 4239–4247.
- (11) Rodin, A.; Carvalho, A.; Castro Neto, A. H. Excitons in anisotropic two-dimensional semiconducting crystals. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2014**, *90*, 075429.
- (12) Thilagam, A. Two-dimensional charged-exciton complexes. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1997**, *55*, 7804.
- (13) Pei, J.; Yang, J.; Wang, X.; Wang, F.; Mokkapati, S.; Lü, T.; Zheng, J.-C.; Qin, Q.; Neshev, D.; Tan, H. H.; Jagadish, C.; Lu, Y. Excited State Biexcitons in Atomically Thin MoSe₂. *ACS Nano* **2017**, *11*, 7468–7475.
- (14) Schulz, S.; O'Reilly, E. P. Excitonic binding energies in non-polar GaN quantum wells. *Phys. Status Solidi C* **2010**, *7*, 1900–1902.
- (15) Berkelbach, T. C.; Hybertsen, M. S.; Reichman, D. R. Theory of neutral and charged excitons in monolayer transition metal dichalcogenides. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2013**, *88*, 045318.
- (16) Rasmussen, F. A.; Thygesen, K. S. Computational 2D materials database: electronic structure of transition-metal dichalcogenides and oxides. *J. Phys. Chem. C* **2015**, *119*, 13169–13183.
- (17) Kammerlander, D.; Prezzi, D.; Goldoni, G.; Molinari, E.; Hohenester, U. Biexciton stability in carbon nanotubes. *Phys. Rev. Lett.* **2007**, *99*, 126806.
- (18) Liang, S.; Ma, Z.; Wei, N.; Liu, H.; Wang, S.; Peng, L. M. Solid state carbon nanotube device for controllable trion electroluminescence emission. *Nanoscale* **2016**, *8*, 6761–9.
- (19) Ma, Y.-Z.; Valkunas, L.; Bachilo, S. M.; Fleming, G. R. Exciton binding energy in semiconducting single-walled carbon nanotubes. *J. Phys. Chem. B* **2005**, *109*, 15671–15674.
- (20) Maultzsch, J.; Pomraenke, R.; Reich, S.; Chang, E.; Prezzi, D.; Ruini, A.; Molinari, E.; Strano, M. S.; Thomsen, C.; Lienau, C. Exciton binding energies in carbon nanotubes from two-photon photoluminescence. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2005**, *72*, 241402.
- (21) Tongay, S.; Suh, J.; Ataca, C.; Fan, W.; Luce, A.; Kang, J. S.; Liu, J.; Ko, C.; Raghunathan, R.; Zhou, J.; Ogletree, F.; Li, J.; Grossman, J. C.; Wu, J. Defects activated photoluminescence in two-dimensional semiconductors: interplay between bound, charged, and free excitons. *Sci. Rep.* **2013**, *3*, 2657.
- (22) Graf, A.; Tropf, L.; Zakharko, Y.; Zaumseil, J.; Gather, M. C. Near-infrared exciton-polaritons in strongly coupled single-walled carbon nanotube microcavities. *Nat. Commun.* **2016**, *7*, 13078.
- (23) Jasti, R.; Bertozzi, C. R. Progress and Challenges for the Bottom-Up Synthesis of Carbon Nanotubes with Discrete Chirality. *Chem. Phys. Lett.* **2010**, *494*, 1–7.
- (24) Xu, R.; Zhang, S.; Wang, F.; Yang, J.; Wang, Z.; Pei, J.; Myint, Y. W.; Xing, B.; Yu, Z.; Fu, L.; Qin, Q.; Lu, Y. Extraordinarily bound quasi-one-dimensional trions in two-dimensional phosphorene atomic semiconductors. *ACS Nano* **2016**, *10*, 2046–2053.
- (25) Yang, J.; Xu, R.; Pei, J.; Myint, Y. W.; Wang, F.; Wang, Z.; Zhang, S.; Yu, Z.; Lu, Y. Optical tuning of exciton and trion emissions in monolayer phosphorene. *Light: Sci. Appl.* **2015**, *4*, e312.
- (26) High, A. A.; Novitskaya, E. E.; Butov, L. V.; Hanson, M.; Gossard, A. C. Control of exciton fluxes in an excitonic integrated circuit. *Science* **2008**, *321*, 229–231.
- (27) Wang, Y.; Zhang, S.; Huang, D.; Cheng, J.; Li, Y.; Wu, S. Screening effect of graphite and bilayer graphene on excitons in MoSe₂ monolayer. *2D Mater.* **2017**, *4*, 015021.
- (28) Thilagam, A. Exciton complexes in low dimensional transition metal dichalcogenides. *J. Appl. Phys.* **2014**, *116*, 053523.
- (29) Ross, J. S.; Wu, S.; Yu, H.; Ghimire, N. J.; Jones, A. M.; Aivazian, G.; Yan, J.; Mandrus, D. G.; Xiao, D.; Yao, W.; Xu, X. Electrical control of neutral and charged excitons in a monolayer semiconductor. *Nat. Commun.* **2013**, *4*, 1474.
- (30) He, K.; Kumar, N.; Zhao, L.; Wang, Z.; Mak, K. F.; Zhao, H.; Shan, J. Tightly bound excitons in monolayer WSe₂. *Phys. Rev. Lett.* **2014**, *113*, 026803.
- (31) Liu, H.; Jiao, L.; Xie, L.; Yang, F.; Chen, J.; Ho, W.; Gao, C.; Jia, J.; Cui, X.; Xie, M. Molecular-beam epitaxy of monolayer and bilayer WSe₂: a scanning tunneling microscopy/spectroscopy study and deduction of exciton binding energy. *2D Mater.* **2015**, *2*, 034004.
- (32) Chaves, A.; Mayers, M. Z.; Peeters, F. M.; Reichman, D. R. Theoretical investigation of electron-hole complexes in anisotropic two-dimensional materials. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2016**, *93*, 115314.
- (33) Yoshida, M.; Popert, A.; Kato, Y. K. Gate-voltage induced trions in suspended carbon nanotubes. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2016**, *93*, 041402.
- (34) Seixas, L.; Rodin, A. S.; Carvalho, A.; Castro Neto, A. H. Exciton binding energies and luminescence of phosphorene under pressure. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2015**, *91*, 115437.
- (35) Favron, A.; Gaufres, E.; Fossard, F.; Phaneuf-L'Heureux, A.-L.; Tang, N. Y. W.; Levesque, P. L.; Loiseau, A.; Leonelli, R.; Francoeur, S.; Martel, R. Photooxidation and quantum confinement effects in exfoliated black phosphorus. *Nat. Mater.* **2015**, *14*, 826–832.
- (36) Wood, J. D.; Wells, S. A.; Jariwala, D.; Chen, K.-S.; Cho, E.; Sangwan, V. K.; Liu, X.; Lauhon, L. J.; Marks, T. J.; Hersam, M. C. Effective passivation of exfoliated black phosphorus transistors against ambient degradation. *Nano Lett.* **2014**, *14*, 6964–6970.
- (37) Kim, J.-S.; Liu, Y.; Zhu, W.; Kim, S.; Wu, D.; Tao, L.; Dodabalapur, A.; Lai, K.; Akinwande, D. Toward air-stable multilayer phosphorene thin-films and transistors. *Sci. Rep.* **2015**, *5*, 8989.
- (38) Chen, X.; Wu, Y.; Wu, Z.; Han, Y.; Xu, S.; Wang, L.; Ye, W.; Han, T.; He, Y.; Cai, Y.; Wang, N. High-quality sandwiched black phosphorus heterostructure and its quantum oscillations. *Nat. Commun.* **2015**, *6*, 7315.
- (39) Pei, J.; Gai, X.; Yang, J.; Wang, X.; Yu, Z.; Choi, D.-Y.; Luther-Davies, B.; Lu, Y. Producing air-stable monolayers of phosphorene and their defect engineering. *Nat. Commun.* **2016**, *7*, 10450.
- (40) Lin, Z.; Carvalho, B. R.; Kahn, E.; Lv, R.; Rao, R.; Terrones, H.; Pimenta, M. A.; Terrones, M. Defect engineering of two-dimensional transition metal dichalcogenides. *2D Mater.* **2016**, *3*, 022002.
- (41) Aharonovich, I.; Englund, D.; Toth, M. Solid-state single-photon emitters. *Nat. Photonics* **2016**, *10*, 631–641.
- (42) Xu, R.; Yang, J.; Myint, Y. W.; Pei, J.; Yan, H.; Wang, F.; Lu, Y. Exciton brightening in monolayer phosphorene via dimensionality modification. *Adv. Mater.* **2016**, *28*, 3493–3498.
- (43) Carvalho, A.; Wang, M.; Zhu, X.; Rodin, A. S.; Su, H.; Castro Neto, A. H. Phosphorene: from theory to applications. *Nature Reviews Materials* **2016**, *1*, 16061.
- (44) Qiao, J.; Kong, X.; Hu, Z.-X.; Yang, F.; Ji, W. High-mobility transport anisotropy and linear dichroism in few-layer black phosphorus. *Nat. Commun.* **2014**, *5*, 4475.
- (45) Liu, X.; Galfsky, T.; Sun, Z.; Xia, F.; Lin, E.-c.; Lee, Y.-H.; Kéna-Cohen, S.; Menon, V. M. Strong light–matter coupling in two-dimensional atomic crystals. *Nat. Photonics* **2015**, *9*, 30–34.
- (46) Bhattacharya, P.; Xiao, B.; Das, A.; Bhowmick, S.; Heo, J. Solid State Electrically Injected Exciton-Polariton Laser. *Phys. Rev. Lett.* **2013**, *110*, 206403.
- (47) Schneider, C.; Rahimi-Iman, A.; Kim, N. Y.; Fischer, J.; Savenko, I. G.; Amthor, M.; Lerner, M.; Wolf, A.; Worschech, L.; Kulakovskii,

V. D.; Shelykh, I. A.; Kamp, M.; Reitzenstein, S.; Forchel, A.; Yamamoto, Y.; Hofling, S. An electrically pumped polariton laser. *Nature* **2013**, *497*, 348–352.

(48) Tsintzos, S. I.; Pelekanos, N. T.; Konstantinidis, G.; Hatzopoulos, Z.; Savvidis, P. G. A GaAs polariton light-emitting diode operating near room temperature. *Nature* **2008**, *453*, 372–375.

(49) Withers, F.; Del Pozo-Zamudio, O.; Mishchenko, A.; Rooney, A. P.; Gholinia, A.; Watanabe, K.; Taniguchi, T.; Haigh, S. J.; Geim, A. K.; Tartakovskii, A. I.; Novoselov, K. S. Light-emitting diodes by band-structure engineering in van der Waals heterostructures. *Nat. Mater.* **2015**, *14*, 301–306.

(50) Ross, J. S.; Klement, P.; Jones, A. M.; Ghimire, N. J.; Yan, J.; Mandrus, D. G.; Taniguchi, T.; Watanabe, K.; Kitamura, K.; Yao, W.; Cobden, D. H.; Xu, X. Electrically tunable excitonic light-emitting diodes based on monolayer WSe₂ p–n junctions. *Nat. Nanotechnol.* **2014**, *9*, 268–272.

(51) Gomes, L. C.; Trevisanutto, P.; Carvalho, A.; Rodin, A.; Castro Neto, A. H. Strongly bound Mott-Wannier excitons in GeS and GeSe monolayers. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2016**, *94*, 155428.

(52) Xia, J.; Li, X.-Z.; Huang, X.; Mao, N.; Zhu, D.-D.; Wang, L.; Xu, H.; Meng, X.-M. Physical vapor deposition synthesis of two-dimensional orthorhombic SnS flakes with strong angle/temperature-dependent Raman responses. *Nanoscale* **2016**, *8*, 2063–2070.

(53) Li, L.; Chen, Z.; Hu, Y.; Wang, X.; Zhang, T.; Chen, W.; Wang, Q. Single-layer single-crystalline SnSe nanosheets. *J. Am. Chem. Soc.* **2013**, *135*, 1213–1216.

(54) Arora, A.; Noky, J.; Druppel, M.; Jariwala, B.; Deilmann, T.; Schneider, R.; Schmidt, R.; Del Pozo-Zamudio, O.; Stiehm, T.; Bhattacharya, A.; Kruger, P.; Michaelis de Vasconcellos, S.; Rohlfing, M.; Bratschkitsch, R. Highly Anisotropic in-Plane Excitons in Atomically Thin and Bulklike 1T'-ReSe₂. *Nano Lett.* **2017**, *17*, 3202–3207.

(55) Stoumpos, C. C.; Malliakas, C. D.; Kanatzidis, M. G. Semiconducting tin and lead iodide perovskites with organic cations: phase transitions, high mobilities, and near-infrared photoluminescent properties. *Inorg. Chem.* **2013**, *52*, 9019–9038.

(56) Zhong, H.-X.; Gao, S.; Shi, J.-J.; Yang, L. Quasiparticle band gaps, excitonic effects, and anisotropic optical properties of the monolayer distorted 1 T diamond-chain structures ReS₂ and ReSe₂. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2015**, *92*, 115438.

(57) Szyniszewski, M.; Mostaani, E.; Drummond, N. D.; Fal'ko, V. I. Binding energies of trions and biexcitons in two-dimensional semiconductors from diffusion quantum Monte Carlo calculations. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2017**, *95*, 081301.

(58) Zhang, D. K.; Kidd, D. W.; Varga, K. The biexciton puzzle. 2015, arXiv1507.07858. aXiv.org e-Print archive. <https://arxiv.org/abs/1507.07858>.

(59) Plechinger, G.; Nagler, P.; Kraus, J.; Paradiso, N.; Strunk, C.; Schüller, C.; Korn, T. Identification of excitons, trions and biexcitons in single-layer WS₂. *Phys. Status Solidi RRL* **2015**, *9*, 457–461.

(60) You, Y.; Zhang, X.-X.; Berkelbach, T. C.; Hybertsen, M. S.; Reichman, D. R.; Heinz, T. F. Observation of biexcitons in monolayer WSe₂. *Nat. Phys.* **2015**, *11*, 477.

CHAPTER 4

Super-transport of Excitons in Atomically Thin Organic Semiconductors at the 2D Quantum Limit

As discussed in Chapter 1, Organic 2D materials in recent times have been shown to exhibit excellent semiconductor properties. Materials like anthracene, tetracene and pentacene show high charge carrier mobilities in crystal phase making them excellent candidates for various future optoelectronic applications. Organic molecular crystals, which are bound by the weak van der Waals cohesive forces between small molecules, are an important class of materials for future electronic, optoelectronic, and photonic devices. This chapter demonstrates the growth and excellent excitonic properties observed from a 2D organic material-pentacene. I chose this

material to experimentally demonstrate excellent molecular orientation dependent excitonic dynamics in organic semiconductors.

The excitonic nature of organic crystals plays an important role in determining their optoelectronic properties. In organic semiconductors, there are typically two types of excitons: Frenkel and charge-transfer (CT) excitons as explained in this chapter. The Frenkel exciton is a neutral excited state in which the electron and hole are placed on the same molecule. Frenkel excitons show the characteristic of large short-range Coulombic interactions and high radiative efficiencies, enabling potential applications in organic light-emitting diode (OLED) and laser devices. Whereas, the CT exciton consists of a pair of charge carriers localized at different molecules. CT excitons exhibit long-range Coulombic interactions and low recombination rates, which makes them suitable for organic solar cells and singlet exciton fission applications. As soon as the energy difference between CT and Frenkel excitons becomes small, both excitons can interact and form new Frenkel–CT mixed states. The mixed states are observed in most bulk and thin film organic semiconductors due to the lack of high crystallinity and the presence of disorders and interfacial states. The strong Frenkel–CT coupling results in the lack of feasibility of organic bulk thin film semiconductors to be potentially used specifically either as highly efficient OLED/lasers or solar cells as mentioned above, which has been a long-standing challenge for bulk thin film organic semiconductors. On the other hand, the characterization of excitons in bulk organic crystals such as polymers is particularly complicated and challenging because of the large amount of disorders and interfacial states in bulk samples.

In order to reduce the Frenkel-CT mixing and study the complex excitonic characters in organic semiconductors, we need to precisely control the crystallinity and molecular aggregation into H- (CT exciton dominated aggregation) and J-type (Frenkel exciton dominated molecular aggregation). However, very limited experimental evidence exists to identify the nature of intrinsic excitons in organic semiconductors because a direct measurement of absorption is challenging due to difficulties in growing high quality ordered optically transparent single crystal samples. Fluorescence spectroscopic results from bulk thin film organic semiconductors are

distorted due to high self-absorption, wave guiding from total internal reflection and depolarization due to crystal birefringence.

In this chapter, the thesis explores the intrinsic excitonic nature of atomically thin single-crystalline 2D pentacene layers that were epitaxially grown on h-BN substrates. The highly clean and sharp crystalline system allowed us to first identify the strongly aggregation-sensitive intrinsic excitonic emissions from the same type of organic materials at the atomic scale. From our temperature-dependent and angle-resolved photoluminescence (PL) measurements, wetting layer (WL) pentacene samples, which had H-type molecular aggregation, showed in-plane isotropic emissions that were dominated by CT excitons. In contrast, monolayer (1L) pentacene samples, which had J-type molecular aggregation, showed one sharp and strongly anisotropic PL emission peak.

Also, in this chapter the thesis reports the coherent excitons at the 2D quantum limit. I firstly observed molecular aggregation enabled ‘super-transport’ of excitons in atomically thin two-dimensional (2D) organic semiconductors between coherent states, with a measured ultra-high effective exciton diffusion coefficient of $\sim 346.9 \text{ cm}^2/\text{sec}$ at room temperature. This value is one to several orders of magnitude higher than the reported values from other organic molecular aggregates and low-dimensional inorganic materials. Without coupling to any optical cavities, the monolayer pentacene sample, an ultraclean 2D quantum system ($\sim 1.2 \text{ nm}$ thick) with high crystallinity (J-type aggregation) and minimal interfacial states, showed superradiant emissions from the Frenkel excitons, which was experimentally confirmed by the temperature-dependent photoluminescence (PL) emission, highly enhanced radiative decay rate, significantly narrowed PL peak width and strongly directional in-plane emission. The coherence in monolayer pentacene samples was observed to be delocalized over ~ 150 molecules, which is significantly larger than the values (a few molecules) observed from other organic thin films. In addition, the super-transport of excitons in monolayer pentacene samples showed highly anisotropic behaviour reported in Chapter 3. These results pave the way for the development of future high-speed excitonic circuits, quantum computing devices, fast OLEDs, and other opto-electronic devices.

Super-transport of Excitons in Atomically Thin Organic Semiconductors at the 2D Quantum Limit

Ankur Sharma,¹ Linglong Zhang,¹ Jonathan O. Tollerud², Miheng Dong,¹ Yi Zhu,¹ Robert Halbich,¹ Tobias Vogl,³ Kun Liang,^{1,3} Hieu T. Nguyen,¹ Fan Wang,⁵ Shilpa Sanwlan², Stuart K. Earl², Daniel Macdonald,¹ Ping Koy Lam,³ Jeff A. Davis² and Yuerui Lu^{1*}

¹Research School of Engineering, College of Engineering and Computer Science, The Australian National University, Canberra, ACT, 2601, Australia

²Centre for Quantum and Optical Science, Swinburne University of Technology, Hawthorn, Victoria, 3122, Australia and ARC Centre of Excellence for Future Low-Energy Electronics Technology, Swinburne University of Technology, Hawthorn, Victoria, 3122, Australia

³Centre for Quantum Computation and Communication Technology, Department of Quantum Science, Research School of Physics and Engineering, The Australian National University, Acton ACT, 2601, Australia

⁴School of Mechatronical Engineering, Beijing Institute of Technology, Beijing 100081, China

⁵Institute for Biomedical Materials and Devices (IBMD), Faculty of Science, University of Technology Sydney, NSW 2007, Australia.

* To whom correspondence should be addressed: Yuerui Lu (yuerui.lu@anu.edu.au)

Abstract:

Long-range and ultrafast transport of coherent excitons is important for development of high-speed excitonic circuits and quantum computing applications. However, most of these coherent excitons have only been observed in some low-dimensional semiconductors when coupled with cavities, as there are large inhomogeneous broadening and dephasing effects on the exciton transport in their native states of the materials. Here, by confining coherent excitons at the 2D quantum limit, we firstly observed molecular aggregation enabled ‘super-transport’ of excitons in atomically thin two-dimensional (2D) organic semiconductors between coherent states, with a measured ultra-high effective exciton diffusion coefficient of $\sim 346.9 \text{ cm}^2/\text{sec}$ at room temperature. This value is one to several orders of magnitude higher than the reported values from other organic molecular aggregates

and low-dimensional inorganic materials. Without coupling to any optical cavities, the monolayer pentacene sample, an ultraclean 2D quantum system (~1.2 nm thick) with high crystallinity (J-type aggregation) and minimal interfacial states, showed superradiant emissions from the Frenkel excitons, which was experimentally confirmed by the temperature-dependent photoluminescence (PL) emission, highly enhanced radiative decay rate, significantly narrowed PL peak width and strongly directional in-plane emission. The coherence in monolayer pentacene samples was observed to be delocalized over ~150 molecules, which is significantly larger than the values (a few molecules) observed from other organic thin films. In addition, the super-transport of excitons in monolayer pentacene samples showed highly anisotropic behaviour. Our results pave the way for the development of future high-speed excitonic circuits, quantum computing devices, fast OLEDs, and other opto-electronic devices.

There has been an increasing interest in recent times to harness the long-range and fast transport of coherent excitons (electron-hole pair quasi-particles) in solid state inorganic semiconductors and molecular systems with confined geometries for enhancing light-matter interactions.^{1, 2, 3} Coherence is critical to engineer quantum electrodynamics (QED)⁴ in low-dimensional systems, such as quantum wells⁵, two-dimensional (2D) materials⁶ and quantum dots⁷, leading to various applications in realizing quantum memories,⁸ single-photon sources,⁹ laser cooling,¹⁰ narrow linewidth lasers,¹¹ high efficiency solar cells,¹² and stable polaritons to achieve Bose Einstein condensates.⁵ Long-range and fast migration of coherent excitons also have tremendous applications in schemes of high-speed excitonic circuits,^{3,13-15} quantum computing,¹⁶⁻¹⁸ and high quantum yield light emitting diodes.¹⁹

A spontaneous coherent emission from a system of several non-interacting dipole active atoms (excitons) was defined as superradiance (SR) by Dicke.²⁰ In this phenomenon interactions between transition dipoles of individual molecules allow coherent delocalization across multiple sites. This leads to a net enhancement in the optical transitional dipole moment (TDM) value and sharp enhancement of the excitonic radiative decay rate of an ensemble of N_c independent emitters as compared to the radiation decay rate of a single emitter.^{2,7} The same principle of coherent delocalized superradiant emission gives rise to an analogous phenomenon called cooperative energy transfer or supertransfer (ST).²¹ The resulting enhanced oscillator strength from delocalization over large molecular assemblies can lead to large scale exciton transport. In a ST process, the molecular assemblies (consisting of N_c molecules) with comparable net TDMs can play the role of acceptors like individual molecules in Förster resonance energy transfer (FRET) mechanism.²² Thus, the excitation (exciton) can transfer to much longer distances in a delocalized molecular assembly before annihilation, resulting in large values of effective exciton diffusion coefficients.

Recently, coherent exciton transport with highly enhanced effective exciton diffusion coefficients ($3\text{--}70\text{ cm}^2/\text{s}$)²³⁻²⁵ was observed in quasi-one-dimensional (quasi-1D) molecular assemblies (cylindrical bundles,²³ nano-tubes²² and wires^{24,25}), which was significantly higher than the migration speeds of incoherent excitons reported in other materials, including conventional organic thin films and their heterostructures ($0.001\text{--}3\text{ cm}^2/\text{s}$)^{26,27}, III–V semiconductor quantum wells ($0.1\text{--}10\text{ cm}^2/\text{s}$)²⁸, atomically thin transition metal dichalcogenides (TMDs) and phosphorene ($0.01\text{--}14.5\text{ cm}^2/\text{s}$)²⁹, *etc.* (Table S1 in Supporting Information). However, the migration speeds of the coherent excitons in these quasi-1D systems²³⁻²⁵ were still hindered by the low overall exciton oscillation strengths (low coherence length with small N_c values), which were mainly

limited by the low quantum confinement of excitons³⁰ (diameter size > 12 nm) and potential disorders and interfacial sites in the systems.³¹ Also, those quasi-1D systems have very small cross-section area for light-matter interactions, limiting their applications for future excitonic devices.^{3,13-15} As predicted by theory, exciton oscillation strength, a key parameter for coherent excitons, is very sensitive to the quantum confinement of the system.³⁰ Therefore, confining the coherent excitons at the 2D quantum limit will be a very promising way to realize the long-range and ultrafast transport of excitons; moreover, the 2D structure can also provide a large cross section area for light-matter interactions, enabling tremendous applications in future excitonic devices.

In this work, from atomically thin organic molecular crystals without any optical cavities, we observed a long-range and ultra-fast migration of Frenkel (FR) excitons between coherent states at the 2D quantum limit. An ultra-high effective exciton diffusion coefficient of $\sim 346.9 \text{ cm}^2/\text{sec}$ at room temperature was reported, which is one to several orders of magnitude higher than the reported values (Table S1 in Supporting Information) from other materials.^{23,25,32} The sharp, strong emission from J-type (monolayer, short as 1L) aggregation in pentacene with its reduced radiative lifetime, peak width and a sharp rise in PL intensity with decreasing temperature, in contrast to the emissions from H-type (wetting layer, short as WL) aggregates, confirms the superradiant emission from the FR excitons. The coherence in 1L pentacene samples was determined to be delocalized over ~ 150 molecules, which is more than one order of magnitude larger than the values (a few molecules) observed from other organic thin films.³³ Our simulation results from time-dependent density functional theory (TDDFT) quantum calculations attribute this to the constructive dipole coupling in J-type aggregation in 1L pentacene to form an enhanced net optical dipole moment, supporting our experimental observations. The super-transport of excitons observed in the macroscopic scale regime will enable the realization

of strongly enhanced light-matter interactions at the quantum limit using such 2D organic materials, which has key applications in developing high-speed quantum computing devices, ultra-fast response time OLEDs, excitonic transistors and other opto-electronic devices.^{8,15,18}

Results

Sample growth and characterization

Single-crystal pentacene (Figure 1) was epitaxially grown layer by layer on a hexagonal boron nitride (h-BN) surface with atomic smoothness and well-defined crystal facets. The first pentacene layer on h-BN was named as the wetting layer (WL; ~0.6 nm thick) and the next layer of pentacene grown on WL was designated as monolayer (1L; ~1.2 nm thick)³⁴ (Figure 1a-c). The layer-dependent arrangement of pentacene molecules over h-BN and their electrical transport properties were described in recent report³⁴. Raman spectroscopy was used to confirm the presence of pentacene on h-BN (Figure S1). PL spectroscopy with a continuous-wave 532 nm excitation laser was used to characterize the excitonic emissions from those atomically thin pentacene layers. The WL region showed much stronger PL emissions than the 1L regions at room temperature (Figure 1d and S2 and associated text). Compared with inorganic TMD 2D semiconductors, the WL showed a much broader PL spectrum at room temperature, which is associated with various band energy levels formed in pentacene due to vibronic couplings between FR and charge-transfer (CT) excitons (Supporting Information note 1 and Figure S3)^{35,36}. On the other hand, 1L region showed a single peak centred around 680 nm that is predominantly FR excitonic emission, which will be explained later. This region is a heterostructure consisting of 1L on top of WL. However, in the PL spectrum from the 1L region, we did not see the higher-energy emission (~550-650 nm) shown in WL sample

(Figure 1d), because the photo-excited charges in WL underneath could be quickly transferred to 1L before radiative emission occurred (Figure S2). Therefore, the PL spectrum measured from 1L region is coming from 1L pentacene sample and reflects its intrinsic nature.

Superradiance and excitonic characteristics

To explore the nature of excitonic transitions, we conducted temperature-dependent PL measurements on the WL and 1L pentacene samples down to 77 K (Figure 2). With decreasing temperature, the PL intensity from WL dropped significantly and the full-width half maximum (FWHM) broadened (Figure 2a); in contrast, 1L pentacene showed the sharp rise of the PL intensity and a significantly reduced FWHM with decreasing temperature (Figures 2b and S4). The opposing temperature dependences were caused by the completely different molecular packings in WL and 1L pentacene, which can be fully understood from the theory of H and J molecular aggregation and their effects on optical emissions^{35,37} (Supporting Information note 2-3; Figures S3). Theoretical values of coupling coefficients (J) and net TDM in each layer were extracted based on its molecular aggregation pattern and coupling (Figure S3a). WL follows a parallel packing of TDMs, and 1L follows a head-to-tail packing of TDMs because of the herringbone packing of pentacene molecules in the unit cell (Figure 1c, and S3)³⁸. J values for 1L and WL pentacene are negative and positive, respectively, which suggest J- and H-type aggregations for 1L and WL, respectively.³⁸ The total TDM and oscillator strength for the lowest excited states (S_1) in WL are both zero, which lead to non-luminescent S_1 states at a temperature of absolute zero. In contrast, the total TDM for S_1 in 1L has a large value (with direction along the b axis of its unit cell), and its corresponding oscillator strength is high (Figure S3a). This resulted in luminescent S_1 states at absolute zero. The large magnitude of net TDM corresponds the phase-locking and constructive coupling of

TDMs in 1L pentacene cooperatively resulting in the sharp rise in PL intensity and reduction in FWHM, which are characteristics of superradiant emission^{33,35,39}.

The phenomenon of superradiance is the combined process of coherent emissions from a cluster of N_c molecular aggregates/chromophores whose oscillator strength is enhanced compared to a single emitter by a factor of N_c owing to the large TDM associated with the molecular assembly^{33,37}. To find which coherent size gives best agreement with experimental temperature-dependence of PL intensity, we considered Boltzmann distribution and introduced a thermal disorder for the on-site energy to mimic the temperature effect for PL emission (Supporting Information note 2). With the derived thermal disorder parameter, we simulated the PL intensities for various clusters with different sizes. We found that a superlattice with $N_c \sim 150$ at absolute zero is in best agreement with the T-dependence of the PL intensity in 1L pentacene from experiments (Figure S5). This indicates that the exciton for measured PL emission in 1L is highly possible to delocalize over ~ 150 molecules within a cluster of limited size. The N_c value can also be estimated by the sharp reduction in FWHM of the PL emission as the temperature decreases.³⁹ Based on this technique and our measurements in Figure 2c and S4, we estimated this value to be over 100 molecules, which is in close agreement with the above extracted value. The extracted N_c value from our 1L pentacene sample is more than one order of magnitude larger than that observed from tetracene thin film ($N_c \sim$ a few molecules).³³ The N_c value signifies the extent of FR exciton delocalization over 100 consecutive dipoles in 1L pentacene. The enhanced oscillator strength is distributed over these consecutive dipoles and results in a large net TDM as shown in Figure S3.

Excitonic superradiance also leads to shortening of excitation radiative decay lifetime for the emission^{2,4,7,11,33,39} by a factor of N_c . To confirm this coherent superradiance from 1L, we measured the temperature-dependent lifetimes of two excitonic emissions from WL

and 1L pentacene samples using time resolved photoluminescence (TRPL) measurements with a resolution of 2.1 ps after deconvolution (Figure S6). The lifetime observed from 1L pentacene sample significantly dropped from $\sim 12.7 \pm 0.8$ ps at room temperature down to $\sim 4.1 \pm 0.7$ ps at 77 K (Figure 2c). To further confirm the measurement accuracy of the lifetime, we performed time and spectrally resolved differential transient reflectance (TR) measurements on WL and 1L pentacene samples at 77 K using a pump-probe technique with a time resolution of 200 fs. 1L pentacene sample showed a clear dip in the differential TR mapping centred at 677 nm; in contrast, the dip from WL sample was not clear (Figure 2d-e). The relaxation of this feature in 1L sample follows a fast decay (lifetime of $\sim 4.2 \pm 0.53$ ps) (Figure 2f). The fitting of the decay curve was done using a single exponential decay and a 95% confidence interval, giving an estimated lifetime range of 3.6-4.7 ps (Figure S7). Further details about the measurements and the fitting are explained in supporting information Figure S7 and associated text. The consistency between the two complementary techniques confirms the accuracy of our lifetime values measured from our TRPL system. With the decrease of temperature, the significant reduction of emission lifetime was consistent with the observed sharp rise of the PL intensity in 1L pentacene sample (Figure 2b), confirming the fast and radiative nature the decay as expected for superradiance.

Further, the radiative lifetime of singlet FR excitonic emissions in bulk pentacene thin films (which are the non-coherent monomer states) was experimentally established to be ~ 1200 ps.⁴⁰ We also confirmed the lifetime from our bulk thin film pentacene grown on the same h-BN substrate, which was measured to be 1241.1 ps at room temperature (Figure S8 and associated text). The significantly reduced lifetime (~ 12.7 ps) in our 1L pentacene sample as compared to the value (~ 1200 ps) from the non-coherent states in thin film pentacene, coupled with the consistent temperature-dependent PL emission and

lifetime, further substantiates superradiant emission from 1L pentacene. The value of N_c , as extracted from this sharp reduction in lifetime is ~ 100 at room temperature, which is again in close agreement with the aforementioned extracted values based the highly-enhanced PL intensity and reduced FWHM with the decrease of temperature. In contrast, the lifetimes from WL pentacene sample were measured to be 2.89 ns using TRPL at room temperature and 2.64 ns at 77 K (Figure 2c), much larger than the values from 1L pentacene samples, confirming the non-coherent nature of the CT excitons in WL samples.

We further performed PL measurements with angle-resolved excitation and emission polarizations (Figure 2g and S9) to confirm the anisotropic nature of superradiant FR excitonic emissions from 1L. PL intensity from 1L strongly depended on the emission polarization angle θ and showed a period of 180 degrees; on the contrary, the emission from WL was isotropic (Figure 2g). The strongly directional total TDM in 1L pentacene theoretically predicted (Figure S3a) is expected to lead to an in-plane anisotropic emission of those FR excitons. Henceforth, the zero-degree reference in the polar plots (Figure 2f) and subsequent figures can be identified as the b axis of the unit cell in 1L pentacene (Figure 1c and S3a). The directional emission in 1L pentacene sample was independent of the excitation polarization angle of incident laser (Figure S9). Similar anisotropy for PL emission from 1L pentacene was observed from 1L samples at room temperature (Figure S10). Normally, the dichroic ratio (DR) is a term used to characterize the in-plane anisotropy of optical transitions⁴¹. Here, it is defined as $DR = I_{\parallel} / I_{\perp}$, where $I_{\parallel}$ and $I_{\perp}$ are the PL peak intensities measured at polarization angles of 0° and 90° , respectively. The measured DR values of PL emission from 1L for emission (Figure 2g-blue curve) polarizations at 77 K were high up at 10.3, which indicates the strongly anisotropic nature of PL emission from 1L. At room temperature the DR value observed

was close to 5.9 from 1L samples. In sharp contrast, the measured DR values from PL emission in WL pentacene were isotropic both at room temperature and 77 K (Figure 2g-red curve), which suggests that these peaks are dominated by the contribution of CT excitons.⁴² Supporting Information Note 4 showed a further detailed discussion on the different nature of excitonic states in WL and 1L.

Long-range and superfast exciton transport

The same principle of coherent delocalized superradiant emission gives rise to an analogous phenomenon called cooperative energy transfer or supertransfer.²¹ The resulting enhanced oscillator strength from delocalization over large molecular assemblies can lead to large scale exciton transport. The near-field direct imaging technique with a charge-coupled device (CCD) camera^{24,25,43} was used to detect the diffusion length of bright excitons from WL and 1L pentacene samples (Figure 3). Figure 3a (3b) shows the measured contour plots of PL intensity as a function of emission wavelength and space of exciton diffusion from 1L (WL) pentacene sample at 77 K, respectively. The spatial distribution of PL intensity can be extracted at the specific energies (shown by dotted lines in Figure 3a and 3b). Figure 3c shows the extent of spatial diffusion in a steady 1D diffusion model. A gaussian fitting routine^{24,43} was used to quantitatively compare the reflected excitation beam to the emission profile emerging from pentacene. Both emission and laser profiles were fitted using a bivariate normal distribution and their FWHMs were extracted. The spatial extent of exciton diffusion (diffusion length L_D) was extracted by taking the square root of the difference between the variances of the emission image and of the passive laser spot. The exciton diffusion lengths (L_D) in 1L and WL pentacene samples were measured to be $0.55 \pm 0.06 \mu\text{m}$ and $1.36 \pm 0.16 \mu\text{m}$, respectively (Figure 3d). All the measurements were taken at low excitation power of around 6 μW . We also did measurements with different power

ranging from 6-215 μW and similar diffusion lengths and lifetimes were observed, which shows the minimized and ignorable effect of exciton-exciton annihilation in our measurements (Figure S11).^{22,44} Using the measured lifetimes of excitonic emissions (τ), the effective exciton diffusion coefficient (D_{eff}) could be extracted using the equation^{25,44} $L_D = \sqrt{2D_{\text{eff}}\tau}$. Using the lifetimes (Figure 2e), the extracted diffusion coefficients from 1L and WL pentacene samples at 77 K were 354.5 ± 50.1 cm^2/sec and 3.5 ± 0.2 cm^2/sec , respectively (Figure 3d). The D_{eff} value obtained from 1L is almost one to two orders of magnitude higher than the reported values from other organic/inorganic systems with coherent and delocalized excitonic emissions (3-70 cm^2/sec , Table 1 in Supporting Information).²³⁻²⁵ At the same time this value is around 3 orders of magnitude higher than value of diffusion constant reported for non-coherent singlet excitons in bulk thin film pentacene by Marciniak *et al.*⁴⁰

We attribute this ultra-high value of exciton diffusion coefficient in 1L to as the *supertransport* phenomenon. The reason we were able to achieve these large effective exciton diffusion coefficients is three-fold. Firstly, in our 1L pentacene samples, the strong intermolecular coupling (J-type aggregation) results in a strong net exciton oscillator strength, and thus the delocalized and superradiant excitonic emissions. Within each delocalized segment, the excitation energy propagates ballistically²¹, compared to the diffusive hopping described FRET. Delocalized excitons in principle accelerate energy transfer as compared to incoherent molecular hopping transfer because delocalization can define an effective hopping length that can be much larger than nearest inter-molecular spacings (Supporting Information note 5).⁴⁵⁻⁴⁷ Secondly, because of the high-quality epitaxial 2D growth, our pentacene samples have highly-ordered crystallinity and minimized defects/disorders, resulting in long delocalization lengths and large coherence lengths ($N_c \sim 150$ as shown in Figure S5 and extracted from temperature

dependent PL and FWHM measurements), which significantly benefited the transport speed of coherent excitons. The exciton delocalization length is defined by competition between intermolecular coupling and disorders²², which can be clearly seen from the comparison between PL spectra from high-quality and low-quality samples. In some 1L samples with low-quality growths, the FR exciton peak at ~680 nm was weak; instead, the high energy CT peaks would show up in the PL spectra (Figure S12; Supporting Information note 6). Compared with the high-quality 1L pentacene samples as shown in Figure 2, those low-quality 1L samples showed broader peak and lower PL peak intensity at 680 nm, and longer radiative lifetimes of the FR excitons (Figure S13), which is caused by the reduced coherence length in the low-quality 1L samples. In experiment, we also found that the disorders and interfacial states would increase as sample thickness increases, which leads to the de-coherence and reduced exciton delocalization length in thick samples, like 2L and bulk samples (both have J-aggregation). The 2L pentacene sample also showed the sharp emission peak at 680 nm, but the peak has slightly wider width and much lower PL intensity as compared to 1L (Figure S14). Whereas, bulk pentacene showed a broad PL emission and the 680 nm emission peak is almost negligible (Figure S8), due to the significantly reduced coherence length caused by the disorders and interfacial states in the sample, similar to other bulk organic thin films.³³ Of course, our 1L samples are still not perfect. There is still lots of room to improve the sample quality, which might give us higher coherence length and longer exciton diffusion length. Thirdly, the quantum confinement of the system will be beneficial to the speed of exciton transport, since the confinement can increase the exciton oscillation strength³⁰ (Supporting Information Note 7). Our 1L pentacene samples (~1.2 nm thick) have the intrinsic high confinement at the 2D quantum limit. Moreover, the excitons in 1L are highly anisotropic and can be aligned in a quasi-1D space along the *b* axis, which further

increases the confinement of exciton transport in 1L pentacene. In summary, structural uniformity with defect free interface, highly confined excitons and excellent intermolecular coupling (large oscillator strengths) results in the supertransport of excitons in 1L pentacene. On the other hand, the diffusion coefficient ($3.5 \text{ cm}^2/\text{sec}$; Figure 3d) of the CT excitons in WL sample is also much larger than that of other similar CT excitons reported recently²⁷. Even though there is no coherence observed in WL, the strong spatial confinement of the excitons ($\sim 0.6 \text{ nm}$ thick) and the almost defect-free interfaces in WL samples, lead to the long and fast propagation of long-lived CT excitons.²⁴ In addition, the waveguiding effects can be excluded, as the thickness of the thickness of 1L and WL pentacene samples were $< 1.5 \text{ nm}$ and the h-BN layer underneath was only around 4 nm (measured by AFM), thus making it insufficient for any light trapping and waveguiding, similar to previous reports.²⁵

It is important to remark here that the observed diffusion was from bright singlet excitons in our 1L and WL pentacene samples and the long-lived triplet excitons *via* the singlet fission in pentacene would not affect the diffusion measurements (Figure 3). The reasons are two folds. Firstly, the triplet states are non-radiative dark states^{48,49} and cannot be detected by the confocal photoluminescence setup we employed for our measurements.³² Secondly, the regeneration of emissive singlets *via* subsequent triplet fusion is not allowed in pentacene and singlet fission in pentacene is expected to be exothermic and unidirectional^{50,51} because the relaxed triplet in pentacene has significantly less than half the energy of the singlet. This is in contrast to the situation in tetracene, where the near-degenerate singlet and triplet-pair energy levels permit both the singlet fission and the triplet fusion to occur.

It is also important to remark here that the observed supertransport of excitons in 1L pentacene should be related to the unique properties of single fission in pentacene. Firstly,

singlet fission in pentacene, an ultrafast non-radiative decay, occurs within a time scale of ~ 80 fs.⁵¹ On the picosecond time scale, the singlet fission in pentacene thin films has a very small total yield of approximately 2%.⁴⁰ In our 1L pentacene sample, both our pump-probe (Figure 2d) and TRPL (Figure 2c inset) measurements showed a mono-exponential radiative decay of ~ 4 ps, which indicates the minimal contribution of non-radiative singlet fission mechanisms in the 1-10 ps regime, consistent with previous report.⁴⁰ Secondly, our 1L pentacene sample at 77 K showed much stronger PL intensity than our 2L and bulk pentacene samples (Figure 2b, Figure S15 and S8), which suggests a highly reduced singlet fission rate in our 1L sample. This could be attributed to the minimized disorders in our 1L samples and the impact of the molecule packing on singlet fission in organic molecules.⁵²⁻⁵⁵ Of course, it would be a very interesting future topic to further explore the aggregation and layer-dependent singlet fission in 2D pentacene samples.

Superfast and angle-dependent transport of coherent excitons at room temperature

Semiconductors with the long-range and ultra-fast transport of excitons at room temperature are critical for future high-speed excitonic circuits and quantum computing devices¹⁶⁻¹⁸ that can operate at room temperature. Here, we also observed the superfast and angle-dependent transport of excitons from 1L pentacene samples at room temperature (Figure 4). In our measurement system, the polarization angle of incident laser was fixed to be parallel to the diffusion mapping direction. The exciton diffusion lengths and effective diffusion coefficients along two axes (b and a , labelled as 0° and 90° , respectively) of pentacene unit cell were measured, by rotating the sample with respect to the polarization of incident laser. The measured exciton diffusion length from 1L pentacene sample showed a maximum value of $0.93 \pm 0.09 \mu\text{m}$ along the b axis (0°), and a minimum value of $0.37 \pm 0.02 \mu\text{m}$ along a axis (90°) (Figure 4a and 4c). In contrast,

the measured exciton diffusion length from WL sample was not angle-dependent, showing a constant value of $\sim 1.31 \pm 0.2 \mu\text{m}$ (Figure 4b and 4d). The exciton emission lifetime measured from 1L pentacene sample changed from $\sim 12.7 \text{ ps}$ at polarization angle of 0° to $\sim 5.6 \text{ ps}$ at polarization angle of 90° (Figure 4e). Whereas, the measured lifetime from WL pentacene sample remained largely unchanged ($\sim 2.8 \text{ ns}$) with changing the incident polarization angle (Figure 4e). The effective exciton diffusion coefficients were thus extracted and shown in Figure 4f. 1L pentacene sample showed a clear anisotropic exciton transport, with an ultra-high effective diffusion coefficient of $346.9 \pm 24.1 \text{ cm}^2/\text{sec}$ along b axis and $95.3 \pm 10.2 \text{ cm}^2/\text{sec}$ along a axis (Figure 4f). Whereas, the WL shows a consistent effective diffusion coefficient of $\sim 2.4 \pm 0.1 \text{ cm}^2/\text{sec}$ along different axes of the sample, due to its isotropic excitonic emission behaviour.

Conclusion

In conclusion, from high-quality atomically thin organic 2D semiconductors, we observed the supertransport of excitons between coherent excitonic states with an ultra-high effective diffusion coefficient of $346.9 \text{ cm}^2/\text{sec}$ at room temperature, which is around one to several orders of magnitude higher than the reported values from other organic quasi-1D and thin film molecular aggregates²²⁻²⁴. We successfully identified molecular aggregation-sensitive PL emissions in atomically thin single-crystal organic semiconductors with different types of aggregation (H- and J-type) at the 2D quantum limit. The 1L pentacene samples with J-type aggregation (FR exciton dominated) showed superradiant emission, which was experimentally confirmed by the temperature-dependent PL emission, highly enhanced radiative decay rate, significantly narrowed PL peak width and strongly directional in-plane emission. The excitons in 1L pentacene samples were extracted to be delocalized over ~ 150 molecules. In addition, the super-transport of excitons in monolayer pentacene samples showed highly anisotropic

behaviour. On the other hand, the WL pentacene samples with H-type aggregation (CT exciton dominated) showed a fast migration of isotropic CT excitons with a measured diffusion coefficient of $\sim 2.4 \text{ cm}^2/\text{sec}$ at room temperature, a few times larger than that of other similar CT excitons reported²⁷. Even though there is no coherence observed in WL, the strong spatial confinement of the excitons ($\sim 0.6 \text{ nm}$ thick) and the almost defect-free interfaces in WL samples, lead to the long and fast propagation of long-lived CT excitons at the 2D quantum limit.²⁴ Our results provided the important experimental demonstration of the long-range and superfast transport of excitons between coherent states at the 2D quantum limit, paving the way for promising applications for future high-speed excitonic circuits, quantum computing devices, fast OLEDs, and other opto-electronic devices.

Methods

Material growth: h-BN flakes were mechanically exfoliated onto a thermally grown 285 nm thick SiO_2 layer deposited over silicon substrate. Before physical vapour deposition (PVD), optical microscope was used to characterize the topological information. The pentacene (purchased from Chem Supply: P0030-1G) was then deposited over the h-BN flakes, kept centred in a vacuum tube in the furnace. h-BN sheet on SiO_2/Si substrate was placed around 15 cm downstream and a molecular pump was used to evacuate the quartz tube to $\sim 10^{-4}$ mbar. The furnace was heated up to $130\sim 150^\circ\text{C}$ for 15~30 mins to grow pentacene. Then, the whole system was naturally cooled down to room temperature under vacuum. The number of layers were optimized by controlling source temperature, growth time and substrate position. All the samples were characterized, and layer thickness were identified using the standard AFM measurements, which were collected in ambient atmosphere at room temperature with a Bruker Multi-Mode III AFM.

Optical Characterization: PL measurements at room temperature and 77 K were conducted using a Horiba LabRAM system equipped with a confocal microscope, a

charge-coupled device (CCD) Si detector, and a 532 nm diode-pumped solid-state (DPSS) laser as the excitation source. For temperature-dependent (above 77 K) measurements, the sample was placed into a microscope-compatible chamber with a low temperature controller (using liquid nitrogen as the coolant). In the experiment, the incident polarization angle was controlled by an angle-variable half-wave plate and was fixed, and the polarization angle of the emission (θ) was determined by using an angle-variable polarizer located in front of the detector. Time resolved PL measurements were conducted in a setup which incorporates μ -PL spectroscopy and a time-correlated single photon counting (TCSPC) system. A linearly polarized pulse laser (frequency doubled to 522 nm, with 300 fs pulse width and 20.8 MHz repetition rate) was directed to a high numerical aperture (NA= 0.7) objective (Nikon S Plan 603). PL signal was collected by a grating spectrometer, thereby either recording the PL spectrum through a charge coupled device (CCD; Princeton Instruments, PIXIS) or detecting the PL intensity decay by a Si single-photon avalanche diode (SPAD) and the TCSPC (PicoHarp 300) system.

Measurements of exciton diffusion lengths: Exciton diffusion measurements were carried out using the same PIXIS CCD detector coupled with a X100 (NA= 1.49, oil suspended) objective lens. The pulsed 522 nm laser was used for excitation with a beam diameter $\sim$ 500 nm (confirmed by CCD imaging) with collection time of 1s per measurement. The diffusion mapping direction was well aligned with the polarization of the excitation laser. The collected light was spectrally filtered to remove the pump laser wavelength. Spectral measurements were made using a grating spectrometer (Acton, SpectraPro 2750). The focal plane of the sample was imaged using the zeroth order of the grating and the spectrometer CCD, giving a spatial resolution of about 200 x 200 nm in space, corresponding to a pixel (20 μ m x 20 μ m) on the CCD. The PL intensity at a particular excitonic emission energy was plotted as a function of the distance from the excitation

centre ($x = 0$ in Figures 3-4). The spatial extent of exciton diffusion (diffusion length L_D) was found by taking the square root of the difference between the variances of the emission image and of the passive laser spot.

Pump-probe transient reflectivity measurements: Transient reflectivity measurements were performed with a home-built pump-probe setup. Degenerate, linearly polarized pump and probe pulses were produced by splitting ~ 200 fs pulses from a non-collinear optical parametric amplifier (Light Conversion Orpheus-2N) tuned to 680 nm. A half-wave plate in the probe line rotated the polarization to be orthogonal to that of the pump. The pump was delayed using a motorized delay stage to control the pump-probe timing. Pump and probe pulses were recombined to be nearly spatially overlapped and focussed onto the sample with a 25.4 mm focal length lens. Telescopes in the pump and probe lines were used to tune the divergence/waist size of the pump and probe beams. The focal spot size and fluence of the pump and probe were $30\text{ }\mu\text{m}$, $90\text{ }\mu\text{J}/\text{cm}^2$ and $15\text{ }\mu\text{m}$, $12\text{ }\mu\text{J}/\text{cm}^2$ respectively.

The probe pulses were spectrally resolved across a fast CMOS array detector (Andor Zyla) by an imaging spectrometer (Andor Kymera). The detector recorded spectra at 5.21 kHz, synced to the laser repetition rate of 20.83 kHz. A data analysis technique based on lock-in detection was used to isolate only the component of the probe modulated at the same frequency as the chopper in the pump beam, which was also synced to the laser output. A polarizer was used to filter out the pump signal coupled with an iris. The residual pump still appears minimally both as a background signal and as interference fringes between the pump and the probe. The interferometric pump contributions were removed using a Fourier filter with a width of 400 fs, and the static background was removed by subtracting the signal observed at negative pump-probe delays (i.e. probe arriving before the pump). The data presented in Figure 2 is the result of 11 and 5 repeats

of a 15 ps scan of the pump probe delay for 1L and WL respectively, with a step size of 100 fs and a 1 second dwell at each step.

Author Contributions

Y. L. conceived and supervised the project; M. D, L. Z, K. L. prepared pentacene samples; A. S. carried out all the optical measurements; A. S, Y. L. and R. H. analysed the data; A. S. took the AFM imaging; J.T., S.S., S.E., and J.D. helped with setup and measurements from TR pump-probe; H. T. N., D. M., T. V., P. K. L., Y. Z. and F. W. contributed to the set up for optical measurements; A. S. and Y. L. drafted the manuscript and all authors contributed to the manuscript.

Supporting Information

All additional data and supporting information and methods are presented in the supporting information file.

Acknowledgements

We would like to acknowledge the financial support from ANU PhD student scholarship, China Scholarship Council, Australian Research Council, ANU Major Equipment Committee fund, National Natural Science Foundation of China and Australian Centre for Advanced Photovoltaics. We would also like to thank Professor Chennupati Jagadish and Professor Barry Luther-Davies from the Australian National University for their facility support. We acknowledge the helpful discussions with Professor Haibo Ma from Nanjing University, China.

Competing financial interests

The authors declare that they have no competing financial interests.

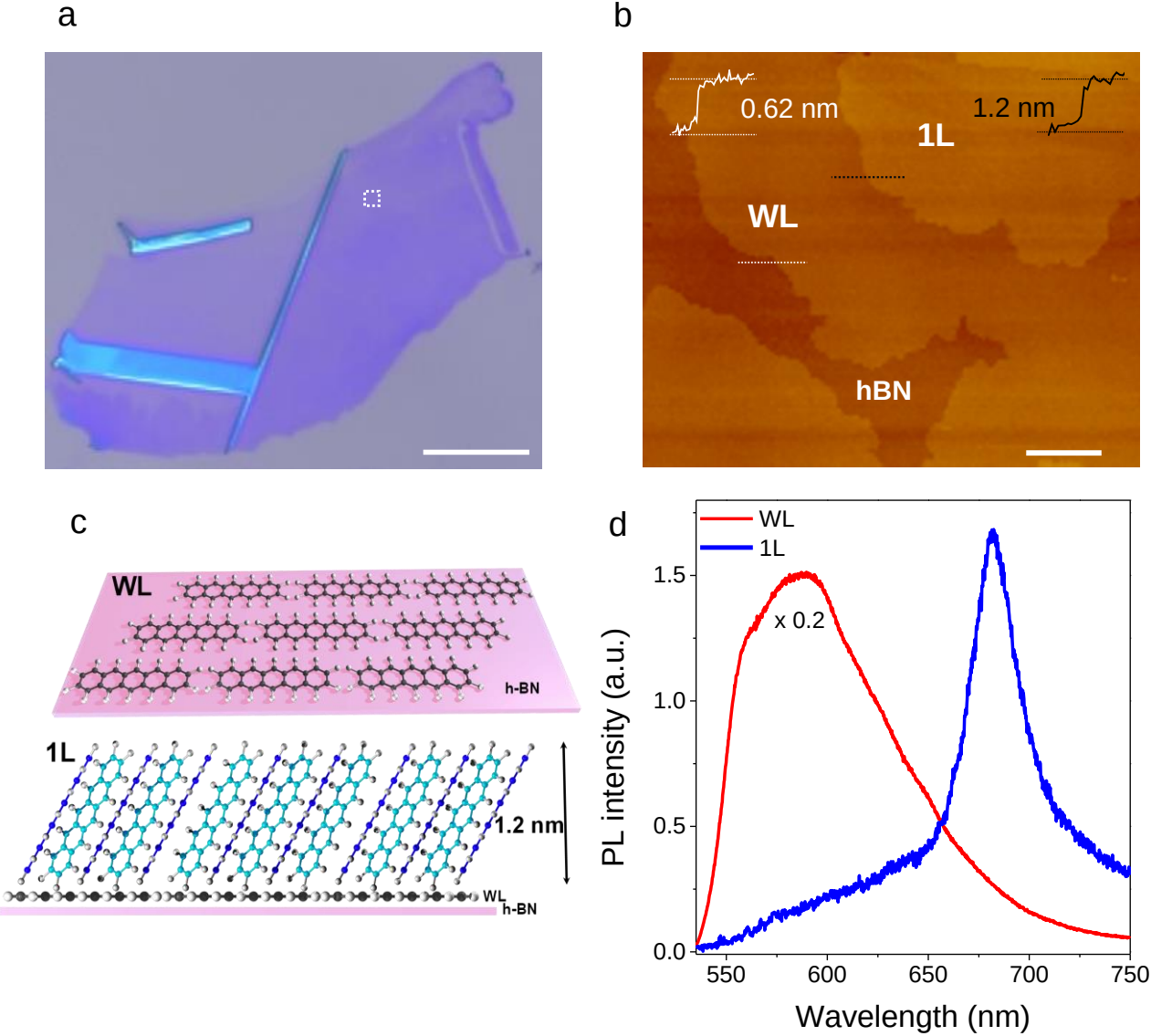


Figure 1

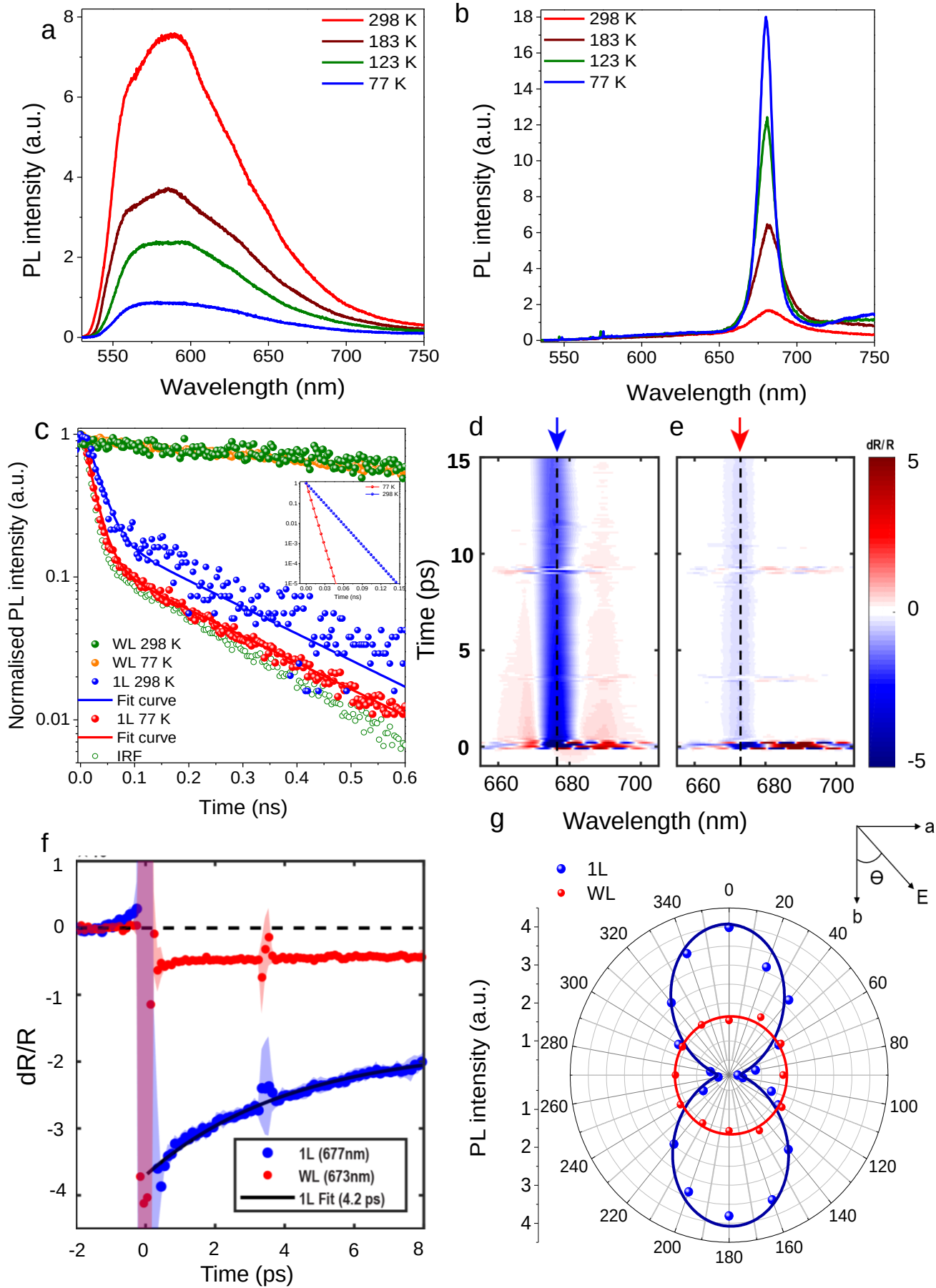


Figure 2

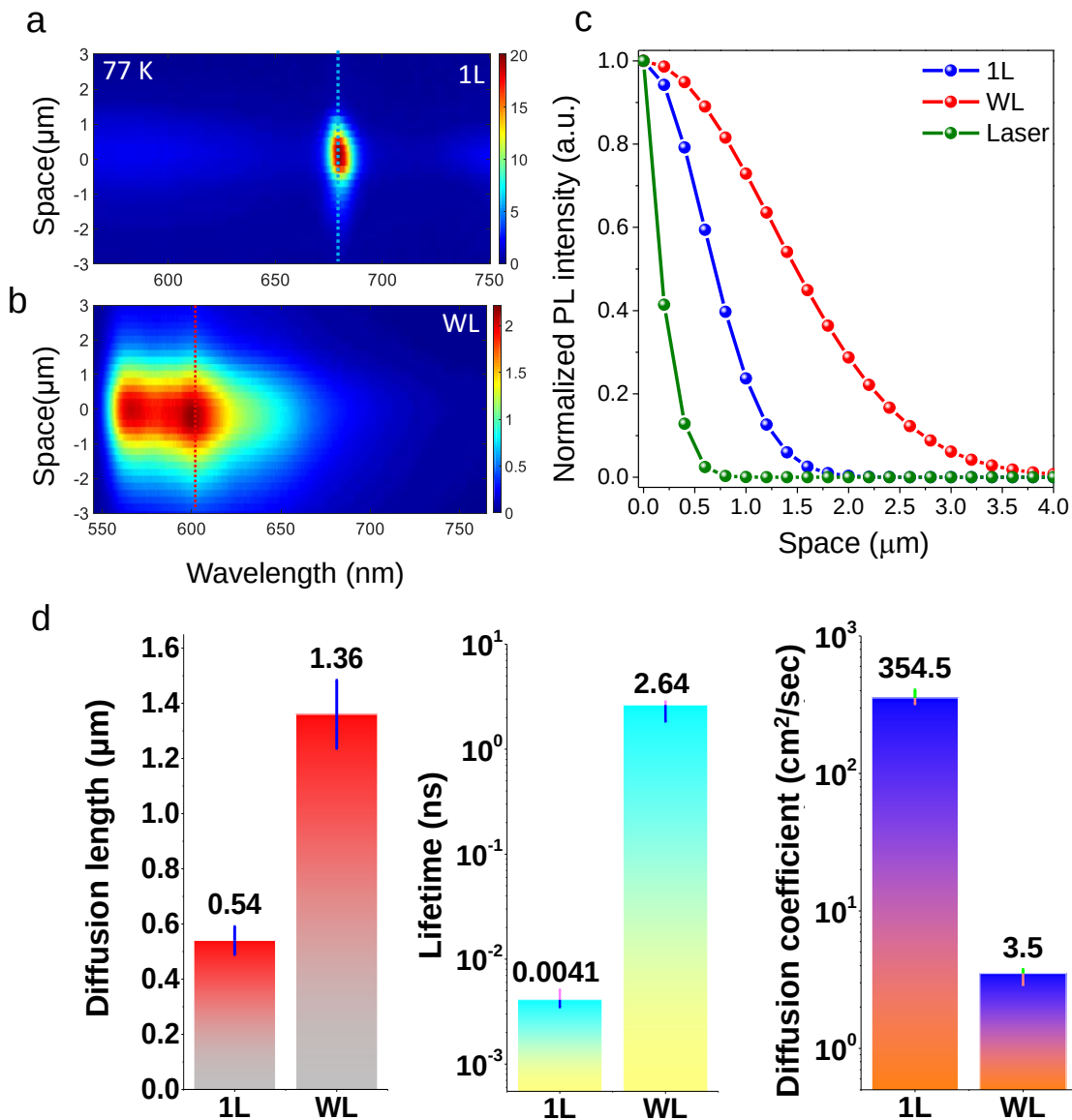


Figure 3

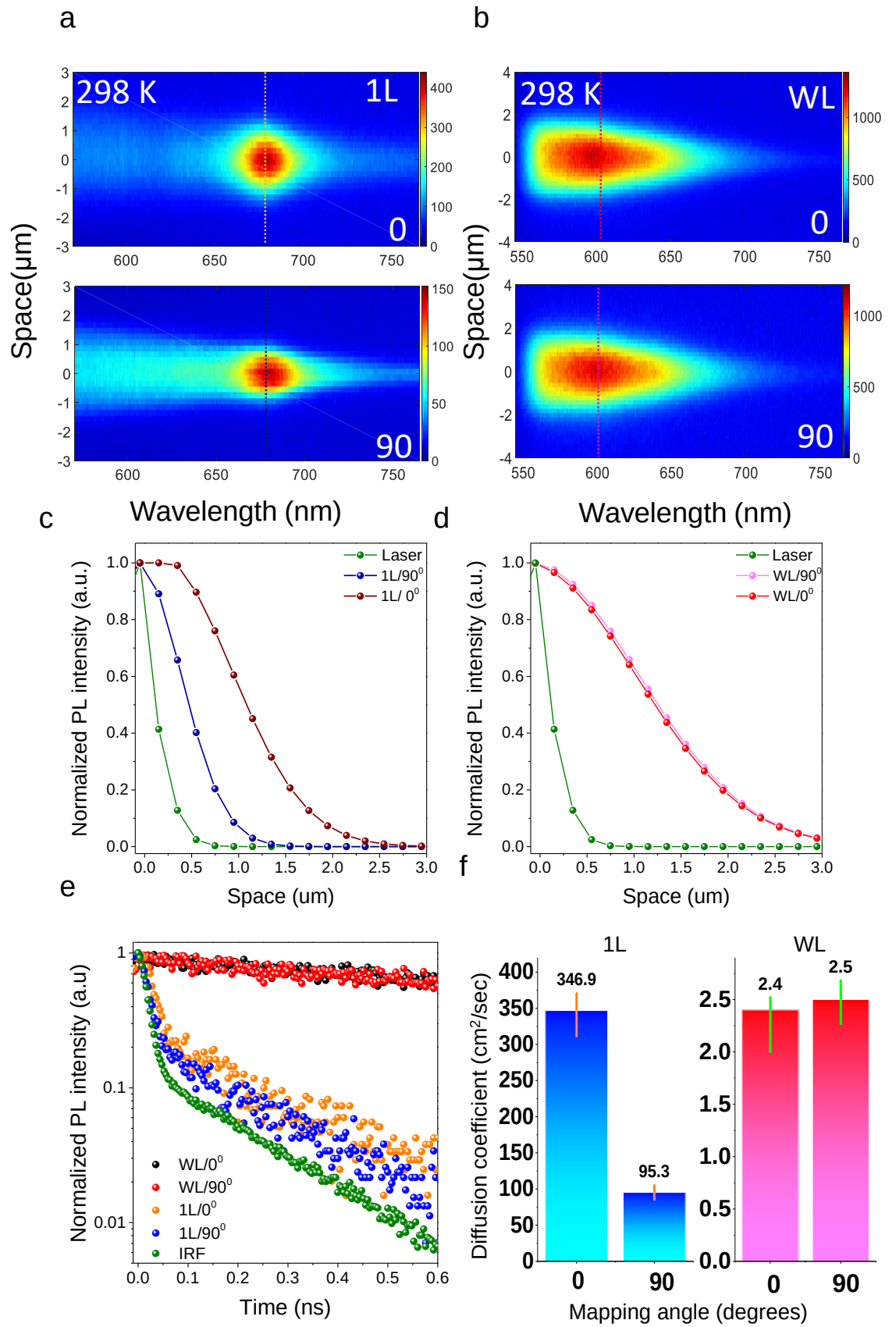


Figure 4

FIGURE CAPTIONS

Figure 1 | Characterization of atomically thin 2D layered pentacene samples. **a**, Optical microscope image of the sample used for measurements. The scale is 80 μm . **b**, Zoomed in Atomic force microscope (AFM) image of the dashed square region in (a), showing the actual measured thickness of WL and 1L pentacene. The scale is 2 μm . **c**, Schematic diagram showing the orientation and alignment of pentacene molecules in WL and 1L over h-BN and a SiO_2/Si substrate. **d**, Measured PL spectra from WL and 1L samples at room temperature.

Figure 2 | Temperature-dependent optical measurements. **a-b**, Measured PL spectra at various temperatures for WL (a) and 1L (b), respectively. For 1L, a sharp peak at ~ 680 nm (designated as FR excitonic emission) rises sharply as temperature decreases. **c**, Time-resolved PL emission (normalized) from WL and 1L pentacene samples at 77 and 298 K. The orange/green balls represent the measured decay curve from WL, which is from CT exciton emission. An effective long lifetime of 2.64 ns (2.89 ns) was extracted from the orange (green) decay curve at 77 K (298 K), by a fitting with deconvolution using the instrument response function (IRF) (green dots). The red/blue balls represent decay curve from 1L, which is from FR exciton emission. The red (blue) decay curve was fitted (solid line) with deconvolution using IRF, giving an effective short lifetime value of 4.1 ps (12.7 ps) for 1L at 77 K (298 K). The inset shows the deconvoluted curves obtained from 1L. **d-e**, Time and spectrally resolved transient differential reflectance of 1L (c) and WL (d) recorded using ~ 200 fs degenerate pump and probe with spectra centered at 680 nm. **f**, Slices of the TR for the 1L (blue) and WL (red) at 677nm and 673nm, respectively. A lifetime of 4.2 ps was extracted from the 1L decay, while the WL response was effectively constant across this range. The feature at 3.5 ps is due to interference between the pump pulse and a weak reflection of the probe pulse. **g**, Measured polar plot of PL intensity as a function of emission polarization angle θ from 1L (blue) and WL (red) pentacene samples at 77 K, revealing the anisotropic (isotropic) excitonic nature of emission from the 1L (WL) pentacene. In experiment, the excitation polarization angle was fixed and the polarization angle of the emission θ was determined by using an angle-variable polarizer located in front of the detector. The solid lines are fitted curves using a $\cos^2\theta$ function.

Figure 3 | Exciton transport mapping using near-field imaging. a-b, Measured contour plots of PL intensity as a function of emission wavelength and space of exciton diffusion from 1L (a) and WL (b) pentacene samples at 77 K. The middle of laser excitation spot is at $x = 0$. **c,** Spatial profile plotted along the dotted lines in a-b for different types of excitonic peaks, showing the diffusion lengths of excitons in WL and 1L. **d,** Comparison plots of diffusion lengths (left; from Figure 3a-c), lifetime (middle; from Figure 2e) and extracted diffusion coefficients, measured from WL and 1L samples, at 77 K. The error bars represent the experimental variation observed from measurements in multiple samples.

Figure 4 | Superfast and angle-dependent exciton transport at room temperature. a-b, Measured contour plots of PL intensity as a function of emission wavelength and space from 1L (a) and WL (b) pentacene samples at room temperature, with spatial mapping direction parallel (top panel; marked as 0°) and perpendicular (bottom panel; marked as 90°) to the b axis of molecular lattices as shown in Figure S3a. In our measurement system, the mapping direction is parallel to the polarization angle of incident laser. The polarization angles 0° and 90° have been marked according to the references set in Figure 2f inset. **c-d,** Spatial profile plots along the dotted lines in a-b at two perpendicular mapping directions (0° and 90°), showing the angle-dependent exciton transport in 1L (c) and WL (d) pentacene samples. **e,** Time-resolved PL emission (normalized) from WL and 1L pentacene samples at room temperature. The black and red balls represent the measured decay curve from WL pentacene samples with incident polarization angle of 0° and 90° , respectively. Effective lifetimes of 2.8 and 2.8 ns were extracted from the black and red decay curves, respectively, by fittings with deconvolution using the instrument response function (IRF) (green dots). The orange and blue balls represent the measured decay curve from 1L pentacene samples with incident polarization angle of 0° and 90° , respectively. The orange and blue decay curves were fitted with deconvolution using IRF, giving an effective short lifetime value of 12.7 and 5.6 ps, respectively. **f,** Comparison plots of extracted diffusion coefficients measured from 1L (left panel) and WL (right panel) samples under the designated mapping angles at room temperature.

References

- 1 Shen, J.-t. & Fan, S. Coherent photon transport from spontaneous emission in one-dimensional waveguides. *Optics Letters* **30**, 2001-2003 (2005).
- 2 Bradac, C. *et al.* Room-temperature spontaneous superradiance from single diamond nanocrystals. *Nature Communications* **8**, 1205 (2017).
- 3 Boulais, É. *et al.* Programmed coherent coupling in a synthetic DNA-based excitonic circuit. *Nature Materials* **17**, 159 (2018).
- 4 Goban, A. *et al.* Superradiance for atoms trapped along a photonic crystal waveguide. *Physical Review Letters* **115**, 063601 (2015).
- 5 Goldberg, D. *et al.* Exciton-lattice polaritons in multiple-quantum-well-based photonic crystals. *Nature Photonics* **3**, 662 (2009).
- 6 Lopez-Sanchez, O., Lembke, D., Kayci, M., Radenovic, A. & Kis, A. Ultrasensitive photodetectors based on monolayer MoS₂. *Nature Nanotechnology* **8**, 497-501(2013).
- 7 Scheibner, M. *et al.* Superradiance of quantum dots. *Nature Physics* **3**, 106 (2007).
- 8 Reimann, R. *et al.* Cavity-modified collective Rayleigh scattering of two atoms. *Physical Review Letters* **114**, 023601 (2015).
- 9 Chou, C., Polyakov, S., Kuzmich, A. & Kimble, H. Single-photon generation from stored excitation in an atomic ensemble. *Physical Review Letters* **92**, 213601 (2004).
- 10 Wolke, M., Klinner, J., Keßler, H. & Hemmerich, A. Cavity cooling below the recoil limit. *Science* **337**, 75-78 (2012).
- 11 Bohnet, J. G. *et al.* A steady-state superradiant laser with less than one intracavity photon. *Nature* **484**, 78 (2012).
- 12 Lunt, R. R., Giebink, N. C., Belak, A. A., Benziger, J. B. & Forrest, S. R. Exciton diffusion lengths of organic semiconductor thin films measured by spectrally resolved photoluminescence quenching. *Journal of Applied Physics* **105**, 053711 (2009).
- 13 High, A. A., Novitskaya, E. E., Butov, L. V., Hanson, M. & Gossard, A. C. Control of exciton fluxes in an excitonic integrated circuit. *Science* **321**, 229-231 (2008).
- 14 Grosso, G. *et al.* Excitonic switches operating at around 100 K. *Nature Photonics* **3**, 577 (2009).
- 15 Baldo, M. & Stojanović, V. Optical switching: Excitonic interconnects. *Nature Photonics* **3**, 558 (2009).
- 16 Imamog, A. *et al.* Quantum information processing using quantum dot spins and cavity QED. *Physical Review Letters* **83**, 4204 (1999).
- 17 Biolatti, E., Iotti, R. C., Zanardi, P. & Rossi, F. Quantum information processing with semiconductor macroatoms. *Physical Review Letters* **85**, 5647 (2000).
- 18 Solinas, P., Zanardi, P., Zanghì, N. & Rossi, F. Holonomic quantum gates: a semiconductor-based implementation. *Physical Review A* **67**, 062315 (2003).
- 19 Singh-Rachford, T. N. & Castellano, F. N. Photon upconversion based on sensitized triplet-triplet annihilation. *Coordination Chemistry Reviews* **254**, 2560-2573 (2010).
- 20 Dicke, R. H. Coherence in spontaneous radiation processes. *Physical Review* **93**, 99 (1954).
- 21 Abasto, D. F., Mohseni, M., Lloyd, S. & Zanardi, P. Exciton diffusion length in complex quantum systems: the effects of disorder and environmental fluctuations on symmetry-enhanced supertransfer. *Phil. Trans. R. Soc. A* **370**, 3750-3770 (2012).

- 22 Wan, Y., Stradomska, A., Knoester, J. & Huang, L. Direct Imaging of Exciton Transport in Tubular Porphyrin Aggregates by Ultrafast Microscopy. *Journal of the American Chemical Society* **139**, 7287-7293 (2017).
- 23 Caram, J. R. *et al.* Room-Temperature Micron-Scale Exciton Migration in a Stabilized Emissive Molecular Aggregate. *Nano Letters* **16**, 6808-6815 (2016).
- 24 Clark, K. A., Krueger, E. L. & Vanden Bout, D. A. Direct measurement of energy migration in supramolecular carbocyanine dye nanotubes. *The Journal of Physical Chemistry Letters* **5**, 2274-2282 (2014).
- 25 Haedler, A. T. *et al.* Long-range energy transport in single supramolecular nanofibres at room temperature. *Nature* **523**, 196 (2015).
- 26 Shaw, P. E., Ruseckas, A. & Samuel, I. D. Exciton diffusion measurements in poly (3-hexylthiophene). *Advanced Materials* **20**, 3516-3520 (2008).
- 27 Zhu, T. *et al.* Highly mobile charge-transfer excitons in two-dimensional WS₂/tetracene heterostructures. *Science Advances* **4**, eaao3104 (2018).
- 28 Vörös, Z., Balili, R., Snoke, D., Pfeiffer, L. & West, K. Long-distance diffusion of excitons in double quantum well structures. *Physical Review Letters* **94**, 226401 (2005).
- 29 Sun, D. *et al.* Observation of rapid exciton–exciton annihilation in monolayer molybdenum disulfide. *Nano Letters* **14**, 5625-5629 (2014).
- 30 Wu, S., Cheng, L. & Wang, Q. Excitonic effects and related properties in semiconductor nanostructures: roles of size and dimensionality. *Materials Research Express* **4**, 085017 (2017).
- 31 Lunt, R. R., Benziger, J. B. & Forrest, S. R. Relationship between crystalline order and exciton diffusion length in molecular organic semiconductors. *Advanced Materials* **22**, 1233-1236 (2010).
- 32 Wan, Y. *et al.* Cooperative singlet and triplet exciton transport in tetracene crystals visualized by ultrafast microscopy. *Nature Chemistry* **7**, 785 (2015).
- 33 Lim, S.-H., Bjorklund, T. G., Spano, F. C. & Bardeen, C. J. Exciton Delocalization and Superradiance in Tetracene Thin Films and Nanoaggregates. *Physical Review Letters* **92**, 107402 (2004).
- 34 Zhang, Y. *et al.* Probing Carrier Transport and Structure-Property Relationship of Highly Ordered Organic Semiconductors at the Two-Dimensional Limit. *Physical Review Letters* **116**, 016602, doi:10.1103/PhysRevLett.116.016602 (2016).
- 35 Bardeen, C. J. Excitonic processes in molecular crystalline materials. *MRS Bulletin* **38**, 65-71 (2013).
- 36 Spano, F. C. & Yamagata, H. Vibronic Coupling in J-Aggregates and Beyond: A Direct Means of Determining the Exciton Coherence Length from the Photoluminescence Spectrum. *The Journal of Physical Chemistry B* **115**, 5133-5143, doi:10.1021/jp104752k (2011).
- 37 Spano, F. C. The Spectral Signatures of Frenkel Polarons in H- and J-Aggregates. *Accounts of Chemical Research* **43**, 429-439, doi:10.1021/ar900233v (2010).
- 38 Würthner, F., Kaiser, T. E. & Saha-Möller, C. R. J-Aggregates: From Serendipitous Discovery to Supramolecular Engineering of Functional Dye Materials. *Angewandte Chemie International Edition* **50**, 3376-3410, doi:10.1002/anie.201002307 (2011).
- 39 Cong, K. *et al.* Dicke superradiance in solids. *JOSA B* **33**, C80-C101 (2016).
- 40 Marciniak, H., Pugliesi, I., Nickel, B. & Lochbrunner, S. Ultrafast singlet and triplet dynamics in microcrystalline pentacene films. *Physical Review B* **79**, 235318 (2009).

- 41 Montali, A., Bastiaansen, C., Smith, P. & Weder, C. Polarizing energy transfer in
42 photoluminescent materials for display applications. *Nature* **392**, 261-264 (1998).
43 Hestand, N. *et al.* Polarized Absorption in Crystalline Pentacene: Theory vs
44 Experiment. *The Journal of Physical Chemistry C* **119**, 22137-22147 (2015).
45 Kato, T. & Kaneko, T. Transport Dynamics of Neutral Excitons and Trions in
46 Monolayer WS₂. *ACS Nano* **10**, 9687-9694 (2016).
47 Mouri, S. *et al.* Nonlinear photoluminescence in atomically thin layered WSe₂
48 arising from diffusion-assisted exciton-exciton annihilation. *Physical Review B*
49 **90**, 155449 (2014).
50 Saikin, S. K., Eisfeld, A., Valleau, S. & Aspuru-Guzik, A. Photonics meets
51 excitonics: natural and artificial molecular aggregates. *Nanophotonics* **2**, 21-38
52 (2013).
53 Lloyd, S. & Mohseni, M. Symmetry-enhanced supertransfer of delocalized
54 quantum states. *New Journal of Physics* **12**, 075020 (2010).
55 Chuang, C., Lee, C. K., Moix, J. M., Knoester, J. & Cao, J. Quantum diffusion on
molecular tubes: Universal scaling of the 1D to 2D transition. *Physical Review
Letters* **116**, 196803 (2016).
Smith, M. B. & Michl, J. Singlet fission. *Chemical Reviews* **110**, 6891-6936
(2010).
Piland, G. B., Burdett, J. J., Dillon, R. J. & Bardeen, C. J. Singlet fission: From
coherences to kinetics. *The Journal of Physical Chemistry Letters* **5**, 2312-2319
(2014).
Jundt, C. *et al.* Exciton dynamics in pentacene thin films studied by pump-probe
spectroscopy. *Chemical Physics Letters* **241**, 84-88 (1995).
Wilson, M. W., Rao, A., Ehrler, B. & Friend, R. H. Singlet exciton fission in
polycrystalline pentacene: from photophysics toward devices. *Accounts of
Chemical Research* **46**, 1330-1338 (2013).
Lukman, S. *et al.* Tuning the role of charge-transfer states in intramolecular
singlet exciton fission through side-group engineering. *Nature Communications*
7, 13622 (2016).
Lukman, S. *et al.* Tuneable singlet exciton fission and triplet-triplet annihilation
in an orthogonal pentacene dimer. *Advanced Functional Materials* **25**, 5452-5461
(2015).
Roberts, S. T. *et al.* Efficient singlet fission discovered in a disordered acene film.
Journal of the American Chemical Society **134**, 6388-6400 (2012).
Yost, S. R. *et al.* A transferable model for singlet-fission kinetics. *Nature
Chemistry* **6**, 492 (2014).

Supporting Information

Super-transport of Excitons in Atomically Thin Organic Semiconductors at the 2D Quantum Limit

Ankur Sharma,¹ Linglong Zhang,¹ Jonathan O. Tollerud², Miheng Dong,¹ Yi Zhu,¹ Robert Halbich,¹ Tobias Vogl,³ Kun Liang,^{1,3}, Hieu T. Nguyen,¹ Fan Wang,⁵ Shilpa Sanwlani², Stuart K. Earl², Daniel Macdonald,¹ Ping Koy Lam,³ Jeff A. Davis² and Yuerui Lu^{1*}

¹Research School of Engineering, College of Engineering and Computer Science, The Australian National University, Canberra, ACT, 2601, Australia

²Centre for Quantum and Optical Science, Swinburne University of Technology, Hawthorn, Victoria, 3122, Australia and ARC Centre of Excellence for Future Low-Energy Electronics Technology, Swinburne University of Technology, Hawthorn, Victoria, 3122, Australia

³Centre for Quantum Computation and Communication Technology, Department of Quantum Science, Research School of Physics and Engineering, The Australian National University, Acton ACT, 2601, Australia

⁴School of Mechatronic Engineering, Beijing Institute of Technology, Beijing 100081, China

⁵Institute for Biomedical Materials and Devices (IBMD), Faculty of Science, University of Technology Sydney, NSW 2007, Australia.

* To whom correspondence should be addressed: Yuerui Lu (yuerui.lu@anu.edu.au)

Supporting Information Note 1: Exciton types and theory

Excitons are defined as the quasi bound state of electron and hole pair, which are attracted to each other by coulombic electrostatic forces. Based on the degree of charge separation which in turn is determined by material dielectric, the excitons can be broadly classified into the following categories¹:

Wannier-Mott (W-MT) excitons are generally found in materials with large dielectrics, thus electric field screening reduces the Coulomb interaction between e^- and h^+ . This results in much larger size for this kind of excitons, which is sometimes larger than space lattice. In W-MT excitons, smaller effective mass of e^- also favours the large radii of excitons. Typical binding energies reported here are around 0.01 eV. They are found mostly in inorganic semiconductors have been recently shown to exist in monolayer TMDs as well.

Frenkel (FR) excitons, whereas are found in materials with low dielectric constants, the Coulomb interaction between e^- and h^+ is much stronger, thus have smaller radii. They are observed mostly in organic materials such as anthracene, pentacene and other materials with low dielectric constants, thus enhancing the Coulomb interaction between e^- and h^+ resulting in much smaller radii. The size is of the same order as a unit cell and often reside on the same molecule. Binding energies range from 0.5-1.0 eV.

Charge transfer (CT) excitons are the intermediates between FR and W-MT excitons. They occur when e^- and h^+ occupy adjacent molecules. They are considered as a localized, structured version of W-MT exciton, where a higher dielectric constant permits the radius to expand over many sites. Their excitonic wave function resembles that of a hydrogen atom. Both CT and FR excitons can have localized wave functions.

Supporting Information Note 2: Role of molecular packing and temperature on optical properties

The effect of molecular packing on excitonic states was firstly reported by Kasha *et al.*², who extended the geometry-related FR exciton treatment by Davydov.³ In our model, we define J to be excitonic coupling between different local FR exciton states located at nearest-neighbour molecules. The oscillator strength of an optical transition is a function of the total TDMs in an aggregate of molecules as shown below theoretically. If the Coulombic repulsion is stronger than the Coulombic attraction, their competition will favour a positive J value ($J > 0$) and vanishingly small total TDM, which will lead to an optically forbidden lowest excited state (S_1) (Figure S3b)⁴. In contrast, if the Coulombic attraction is stronger than the Coulombic repulsion, their competition will favour a negative J value ($J < 0$) and large total TDM, which will result in an optically allowed S_1 (Figure S3c). The result of this competition mainly depends on the orientation rather than the distance between molecules.⁵ Molecular aggregates are usually considered to be H-type when $J > 0$ and J-type when $J < 0$.⁵ Generally, side-by-side molecular orientations lead to $J > 0$, whereas head-to-tail orientations lead to $J < 0$.

For a transition from state $|\Psi_a\rangle$ to another state $|\Psi_b\rangle$, its transition dipole moment (TDM) is⁶

$$\text{TDM}(a \rightarrow b) = \langle \Psi_a | \hat{\mu} | \Psi_b \rangle = \langle \Psi_a | q\mathbf{r} | \Psi_b \rangle = \int \Psi_a^*(\mathbf{r}) q(\mathbf{r}) \mathbf{r} \Psi_b(\mathbf{r}) d\mathbf{r} \quad (1)$$

where $q(r)$ is the charge on the particle at an arbitrary position ' r '. TDM is not the oscillator strength (f), but it is the most crucial parameter for determining f .⁷

$$f(a \rightarrow b) = \frac{2m_e(E_b - E_a)}{3\hbar^2} \text{TDM}(a \rightarrow b)^2 \quad (2)$$

where, E_b and E_a are the energy levels associated with states ‘b’ and ‘a’ respectively.

In short, the magnitude of TDM determines the strength of the optical transition to a large extent. Additionally, its α ($= x, y, z$ or a, b, c) component determines the incident light polarized absorption (or transition) along α direction.

Temperature dependence of PL intensity of 1L pentacene

In order to find which coherent size gives best agreement with experimental temperature-dependence of PL intensity, we consider Boltzmann distribution and introduce a thermal disorder for the on-site energy to mimic the temperature effect for PL emission. The thermal disorder is modelled by a Gaussian distribution function with the standard deviation $\sigma = \sqrt{akT}$, where k is the Boltzmann constant, a is a system dependent parameter, and in this work is derived through a linear fitting of σ over $\sqrt{T}$ with computational statics of on-site energy fluctuation of $T = 100, 200$ and 300 K. For this, we perform 1 ns molecular dynamics (MD) simulation for pentacene crystals at each temperature ($T=100, 200$ and 300 K) with COMPASS (Version 2.8) force field by using Material Studio 8.0. With this simulated trajectory of 1 ns, we extract 1000 snapshots to calculate on-site energy fluctuation by statistics on single molecule time-dependent density functional theory (TDDFT) calculations.

However, thermal disorder will cause fluctuations for both onsite energies and excitonic couplings and accordingly break the symmetry in the aggregation model. This will lead to thermal deactivation and activation for PL emissions in *J*- and *H*-type aggregations in 1L and WL pentacene, respectively. The DFT calculations further support the fact that the sharp PL observed in 1L pentacene at low temperature can mainly be caused by the super-radiance of FR excitons in their J-type aggregates.^{4, 8, 9, 10} With the derived thermal disorder parameter, we simulate the PL intensities for various monolayer clusters with different sizes. We find a lattice with $N_c \sim 150$ gives the best fitting for the T-dependence of PL intensity in 1L pentacene with experiments (Figure 2d). This indicates that the exciton for experimentally measured PL emission in 1L is highly possible to delocalize over ~ 150 molecules within a cluster of limited size.

Supporting Information Note 3: Electronic Hamiltonian and its basis set

In order to simulate the PL spectrum in molecular aggregates, in this work we adopt the widely used electronic model for molecular excitonic systems,

$$H = H_{FE} + H_{CT} + H_{FE-CT} \quad (3)$$

The total Hamiltonian includes three parts and $\hbar = 1$ was taken. The first part represents FR exciton Hamiltonian.

$$H_{FE} = \sum_n (\omega_{0-0} + \Delta_{0-0}) |n\rangle \langle n| + \sum_{\{m,n\}} J_{m,n} |m\rangle \langle n| \quad (4)$$

The first summation in equation 4 is the energy of excitons, where ω_{0-0} is the molecular excitation energy ($S_0 \rightarrow S_1$) of an individual molecule in gas phase and Δ_{0-0} is the gas-to-crystal shift. State $|n\rangle$ is a pure electronic state in which the n th site is excited, whereas all other molecules remain in their ground state. The second term, $J_{m,n}$, represents excitonic coupling between nearest neighbor sites m and n .

$$\begin{aligned} H_{CT} = & \sum_{n_+, n_-} \omega_{CT} |n_+; n_- \rangle \langle n_+; n_-| + \sum_{n_+, n_-} 't_e \{|n_+; n_- \rangle \langle n_+; n_- + 1| + h.c. \\ & + \sum_{n_+, n_-} 't_h \{|n_+; n_- \rangle \langle n_+ + 1; n_-| + h.c. \} \end{aligned} \quad (5)$$

The second part in equation 3 for the CT Hamiltonian can be described by equation 5. The first term accounts for the energy of all CT pairs, $|n_+; n_- \rangle$ (with $n_+ \neq n_-$) with a cation on site n_+ and an anion on site n_- , whereas all other chromophores in the stack are in their electronic ground states. The last two terms represent electron and hole hopping with transfer integral t_e and t_h .

$$\begin{aligned} H_{FE-CT} = & \sum_n D_e \{|n\rangle \langle n; n+1| + |n\rangle \langle n; n-1| + h.c. \} \\ & + \sum_n D_h \{|n\rangle \langle n+1; n| + |n\rangle \langle n-1; n| + h.c. \} \end{aligned} \quad (6)$$

The last part in equation 3 for the coupling of FR exciton states and CT states is described by equation 6. Here D_e and D_h are exciton dissociation integrals. For simplicity, one can take $t_e = D_e$ and $t_h = D_h$.

The parameters in the above model are derived from DFT and TDDFT calculations of molecular monomers or dimers at M06-2X/6-31G level by using *GAUSSIAN 09* program. J , t_e and t_h represent the nearest-neighbour excitonic coupling, electron hopping and hole hopping integrals respectively.

In our calculation, we consider one-particle FR exciton states and two-particle CT states as the basis set for the Hamiltonian. Thus, the wave function can be written as a linear combination of these FR and CT states.

$$|\Psi\rangle = \sum_n c_n |n\rangle + \sum_{n_+, n_-} c_{n_+, n_-} |n_+; n_-\rangle \quad (7)$$

We extracted the number of coherent molecules N_c by calculating participation ration (PR) for the α^{th} eigenstate

$$PR(\alpha) = \frac{\sum_n c_n(\alpha)^2}{\sum_n c_n(\alpha)^4} \quad (8)$$

Supporting Information Note 4: Excitonic character in WL and 1L governed by molecular packing

The excitonic nature of organic crystals plays an important role in determining their optoelectronic properties.^{4, 9, 10} In organic semiconductors FR and CT excitons are most commonly observed.^{8, 11} (See Supporting Information Note 1). As soon as the energy difference between CT and FR excitons becomes small, both excitons can interact and form new FR–CT mixed states.¹¹ Intermolecular coupling also influences the complex excitonic character in organic molecules. The mixed states are observed in most bulk and thin film organic semiconductors due to the lack of high crystallinity, scattering and the presence of disorders and interfacial states.^{12, 13, 14} Precise and controlled growth of organic molecular crystals in atomically thin 2D states provides an ideal platform for isolating the smaller and tightly bound FR¹⁵ excitons as they have closer packing of molecules within a unit cell.^{15, 16, 17} In order to reduce the FR-CT mixing and to observe the aggregation-controlled coherence phase locking and subsequent superradiant emission, the crystallinity and molecular aggregation into H- (CT exciton dominated aggregation) and J-type (FR exciton dominated molecular aggregation) has to be controlled, as theoretically predicted by Spano et al.¹⁰

In our case, the highly clean and sharp crystalline system allowed us to observe long-range coherent super-transport from FR excitons which are de-localized over hundreds of pentacene molecules, due to of the minimized defect, disorders and interfacial states in the monolayer regime. WL pentacene samples, which had H-type molecular aggregation, showed in-plane isotropic emissions that were dominated by CT excitons. In contrast, 1L pentacene samples, which had J-type molecular aggregation, showed one sharp and strongly anisotropic PL emission peak (See Supporting Information Note 2 for theoretical simulation details). The WL region showed much stronger PL emissions than the 1L regions at room temperature (Figure 1d). Compared with inorganic TMD 2D semiconductors, the WL shows a much broader PL spectra at room temperature, which is due to the strong couplings between FR and CT excitons in organic materials.^{15, 18} The broad PL spectrum is associated with various band energy levels formed in pentacene due to vibronic coupling between FR and CT states¹⁰. 1L on the other hand shows a single peak centred around 680 nm which is predominantly FR excitonic emission as explained by our polarization dependent measurements in Figure

2g and also explained below. We grew several samples of pentacene in various growth conditions, giving us different optical properties from 1L depending on growth conditions (Figure S3). The poorly grown 1L samples also gave us broad high energy CT excitonic peaks in addition to the narrow FR excitonic peak at 680 nm overlapping with the emission energies from WL in certain samples, showing the mixed FR and CT emissions from 1L. Whereas, some 1L samples gave us only the CT emission with little FR emission. This clearly highlights the role of well-defined molecular arrangements in de-coupling the intermixing of FR and CT excitons. We have chosen the 1L sample which gave us only FR emission for further analysis to independently study the behaviour of CT and FR excitons in WL and 1L viz.

We also performed PL measurements with an angle-resolved emission polarization (Figure 2f) to confirm the anisotropic nature of superradiant FR excitonic emissions from 1L. In the experiment, the incident polarization angle was controlled by an angle-variable half-wave plate and was fixed, and the polarization angle of the emission (θ) was determined by using an angle-variable polarizer located in front of the detector. In polarization-dependent PL measurement at 77 K, we found that intensity of PL emission from 1L strongly depended on the emission polarization angle θ and shows a period of 90 degrees. On the contrary the emission from WL was completely anisotropic (Figure 2f). The strongly directional total TDM in 1L pentacene predicted by our simulation (Figure S3a) was expected to lead to an in-plane anisotropic emission of those FR excitons. The observed strong anisotropy of PL emission from 1L pentacene further confirms the strong optical alignment of molecules in a specific orientation and agrees very well with the prediction from our simulations, which confirms that the superradiant emission from 1L pentacene observed in 1L and 2L pentacene at low temperature is dominated by FR excitons.

Supporting Information Note 5: Coherent exciton transport and supertransport

The diffusion of FR excitons that are commonly found in organic semiconductors migrate much slower as compared to their Wannier counterparts in inorganic materials. This is because of lower dielectric constant in organic materials and results in lower diffusion lengths in organic materials.^{19, 20} The energy transfer is dominated by incoherent Förster resonant energy transfer mechanism (FRET)²¹, which involved hopping of charges from one chromophore to the other *via* dipole moment interactions. This mechanism is based on dipole-dipole electromagnetic interaction and occurs when emission spectrum of donor molecule has significant overlap with absorption of the acceptor molecule. It is a non-radiative transfer and relies on long-range Columbic coupling between the nearby molecules.²⁰ Due to this incoherent hopping, the diffusion of FR excitons is limited. Incoherent energy transfer is generally determined by inter-molecular spacing, defect states, excitonic lifetime and range of columbic coupling also referred to as Förster radius.^{19, 22} All these factors lead to smaller diffusion of FR excitons inorganic molecules and molecular assemblies.

However, in organic molecules the inter-molecular coupling can become very strong if the crystallinity is strong.^{23, 24} If the coupling between organic molecules is strong, the FR excitons can be delocalized over multiple molecules forming a delocalized coherent state for the exciton, which eventually leads to superradiant emissions.²⁵ In this phenomenon interactions between transition dipoles of individual molecules allow coherent delocalization across multiple sites. The correlated states lead to a macroscopic optical polarization proportional to the number of atoms or molecules comprising the coherent domain.^{26, 27} This leads to a net enhancement in the optical transitional dipole moment (TDM) value and sharp enhancement of the excitonic radiative decay rate of an ensemble of N_c independent emitters as compared to the radiation decay rate of a single emitter.^{28, 29} The same principle of coherent delocalized superradiant emission gives rise to an analogous phenomenon called cooperative energy transfer or supertransfer (ST).³⁰ The resulting enhanced oscillator strength from delocalization over large molecular assemblies can lead to large scale exciton transport. Here, the molecular assemblies

(consisting of N_c molecules) with comparable net TDMs can play the role of acceptors like individual molecules in FRET mechanism.²¹ Thus, the excitation (exciton) can transfer to much longer distances in a coherent delocalized molecular assembly before annihilation, resulting in large values of diffusion coefficients. This strong intermolecular coupling plays an important role in developing coherent effects and determines long-range coherent exciton transport, which has been demonstrated in some quasi 1D systems recently. Delocalized excitons principally accelerate energy transfer as compared to incoherent hopping transfer because delocalization allows for a hopping length that is much larger as compared to intermolecular spacing.²²

Supporting Information Note 6: Relationship between crystalline order and diffusion length

As discussed above the charge or energy transfer mechanism in organic molecules requires hopping of excitation from one molecule to other (incoherent) or from one delocalized state to other (coherent). In either case, the distance between interacting molecules or states is critical. This intermolecular distance is a function of degree of crystallinity in the molecule.³¹ Hence, the diffusion of excitons in organic system is a direct function of crystallinity. Lunt *et al.*³² and Sim *et al.*³¹ recently experimentally demonstrated that exciton transport diffusion length is a monotonic function of the extent of crystalline order. The reduction in diffusion lengths with decreasing crystallinity is due to increase in non-radiative losses in highly disorders systems, as determined by fluorescence quantum yield measurements as a function of grain size in Perylenetetracarboxylic dianhydride (PTCDA).³³

We observed a similar trend during the growth optimization process of our pentacene samples. The samples which used h-BN surfaces that were exposed to air for a long time or had uneven morphology (detected optically) gave us low crystalline growth, as characterized by AFM measurements. In contrast the samples grown on homogenous and unexposed h-BN substrates gave a much stronger crystallinity and smooth pentacene growth, confirmed by surface roughness measurements. All the samples were characterized by AFM right after their growth. During the growth of pentacene samples in our case, we observed that the optical performance was also critically affected by the order of crystallinity in our growth as shown in Figure S5. The samples that had lower crystallinity showed a PL spectrum similar to earlier reports.³⁴ The broad PL spectrum obtained even from 1L samples is due to vibronic mixing of CT and FR states (Samples 2-4 in Figure S5). After several rounds of optimization, we could precisely control the growth conditions and orientation of molecules in 1L (Sample 1 in Figure S5). There were no CT peaks reported from highly crystalline samples, demonstrating only a sharp FR excitonic emission at 680 nm. Due to reduced defects, lack of interfacial sites and high crystallinity in our samples we could observe higher diffusion coefficients even for short-lived FR excitonic emissions from 1L pentacene samples.

Supporting Information Note 7: Dimensionality and oscillator strength

Apart from coherent delocalization and high order crystallinity, the exciton diffusion process in organic molecules is also a function of the oscillator strength of the excitons.^{20, 23, 24, 36} The oscillator strength in return is strongly influenced by the effective dimensionality of the solid-state system as theoretically demonstrated by Wu *et al.*³⁷ The oscillator strength can be highly enhanced by reducing the effective dimensionality of the system. Thus, it is critical for us to develop a true 2D system that can confine the excitons in 2D quantum limit to further enhance the diffusion of the FR excitons.

The quantum confinement effect plays a key role in determining the spatial diffusion of excitons.²⁴ For the same reason, several recent attempts to achieve higher diffusion coefficients with molecular aggregates have used quasi-1D structures like tubes²² or wires²⁴ to enhance the diffusion using J-type aggregation. In our pentacene WL and 1L system, the excitons were spatially confined in a 2D space, which increases the possibility of directed excitonic energy transfer within the 2D plane with limited out of plane losses and hopping. Further, in 1L as we have established the excitons were found to be anisotropic and aligned along the ‘*b*’ axis of the unit cell of pentacene (Figure 2f in main text and associated text). This led to further confinement and transport if excitons are in a quasi-1D system, which eventually led to observation of ultra-high exciton diffusion coefficients in our samples.

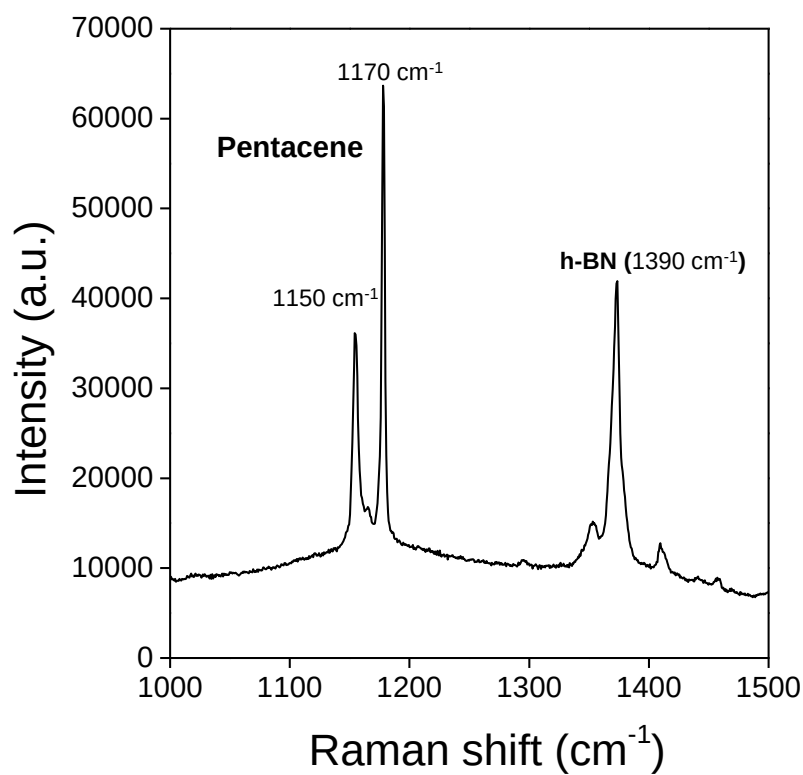


Figure S1 | Measured Raman spectrum from a 2D pentacene sample grown on a h-BN flake. Peaks at 1150 cm⁻¹ and 1170 cm⁻¹ are for pentacene and peak at 1390 cm⁻¹ is for h-BN.

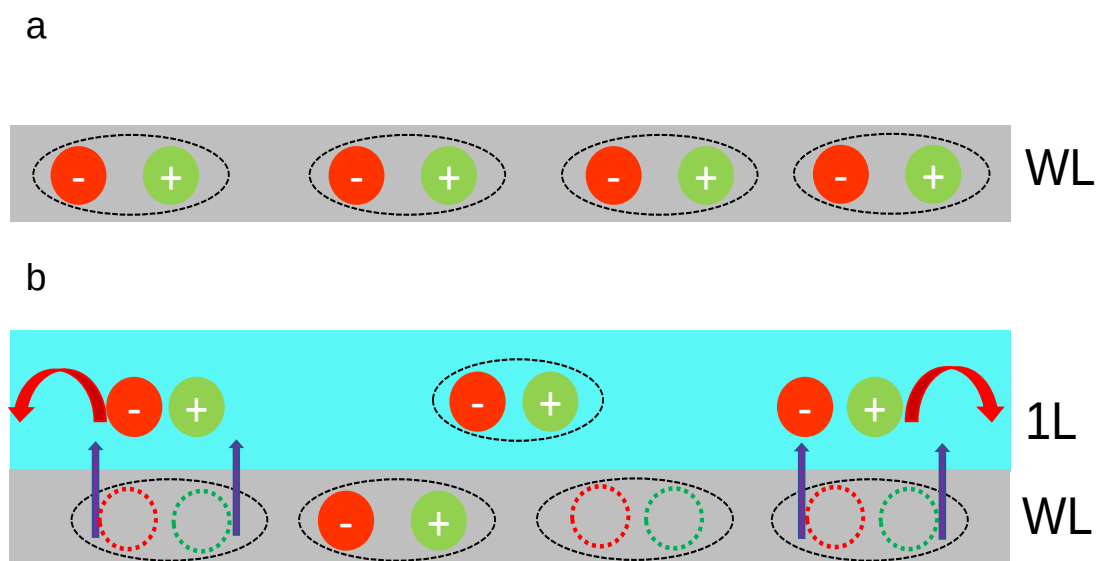


Figure S2 | Schematic diagram showing the interlayer charge transfer and different intra-layer charge transport mechanism in WL (a) and 1L+WL (b). As shown in a previous report³⁴, WL pentacene is not conducting due to the absence of intralayer π - π stacking. The charges interact by long range coulombic coupling in WL; in contrast 1L shows 2D hopping transport. The purple arrows represent interlayer charge transfer. The red curved arrows represent the hopping of charges in 1L. Here, we only show the photo-excited charges generated in WL, not in 1L.

The charges interacted by long-range Coulombic coupling in WL (Figure S2a); in contrast, 1L showed 2D hopping transport. The photo-excited charges in the 1L layers had much higher in-plane diffusion than those in WL, which led to lower PL efficiencies in 1L pentacene. For the 1L+WL hetero-structure (1L region), the photo-excited charges in WL underneath could be quickly transferred to 1L and diffused laterally in 1L before radiative emission occurred (Figure S2b). This led to quenching of the PL intensity. This type of ultrafast interlayer charge transfer phenomena has been observed for both inorganic 2D hetero-structures³⁸ and organic–inorganic interfaces.³⁹

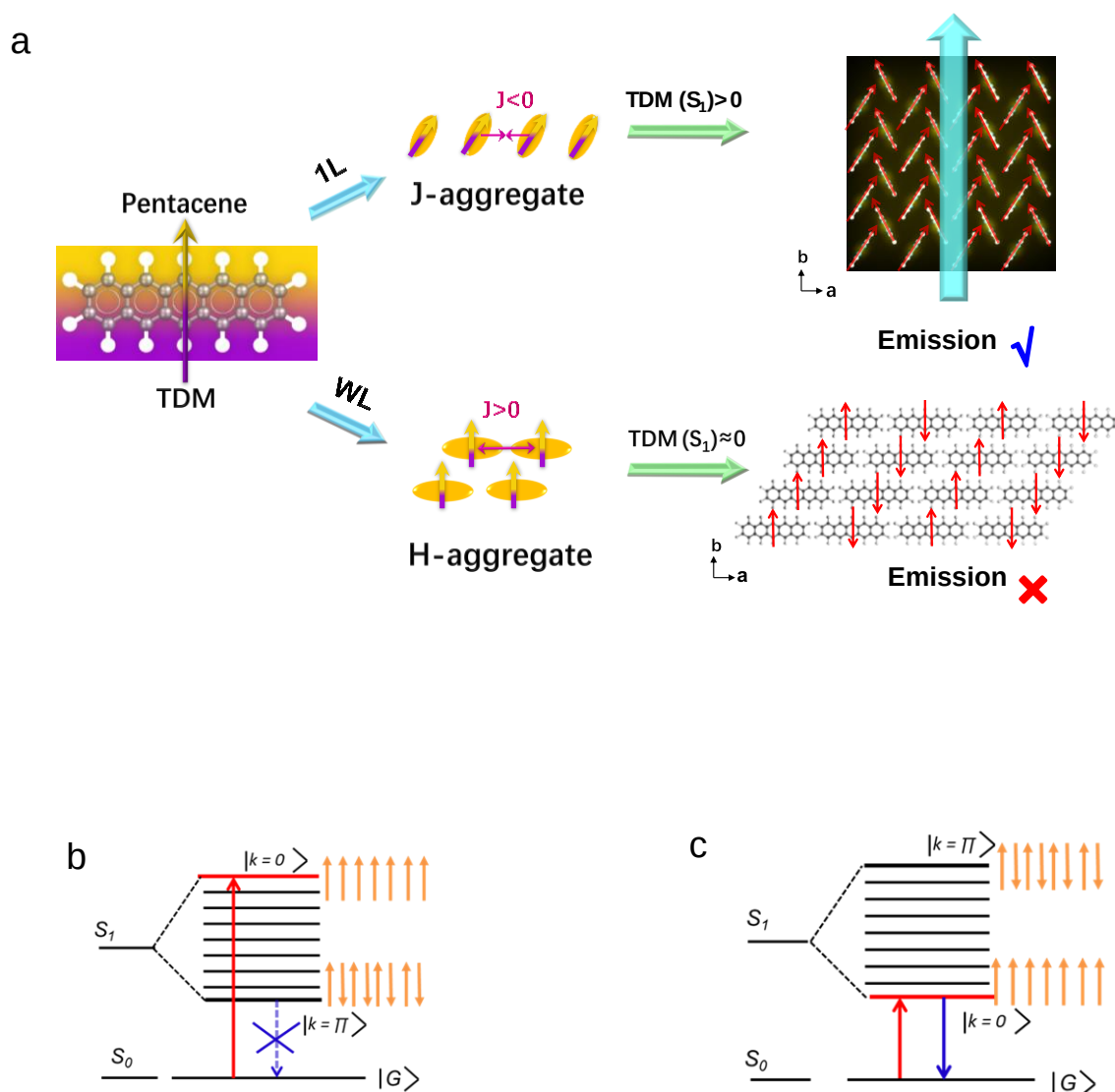


Figure S3 | Molecular packing and the FR exciton model. **a**, The TDMs at each molecule (red arrows) follow a head-to-tail packing in 1L as shown, while in WL TDMs are packed side-by-side to each other. The pink arrows represent the Coulombic interaction force between neighboring molecules. J is the excitonic coupling between different local FR exciton states located at nearest-neighbor molecules. Based on our simulation, J is negative in 1L (corresponding to J-type aggregation) and hence there is a net positive total TDM value along the “ b ” axis (as shown by purple arrow) allowing for emission from 1L, while J is positive in WL (corresponding to H-type aggregation) and hence a close to null total TDM, resulting in very little emission from WL. **b**, **c** Schematics showing the excited states in an ideal H- (a) and J-type (b) monomer.

Optical transitions from and to ground state are only allowed for excited state band with $k = 0$, where k is the quantum number of the wave vector, representing the excitonic states. Orange arrows indicate the spin of electrons in each state. In J-type the 0-0 transition results in enhanced coherent emission due to coupling of TDMs, eventually causing super radiant emissions.

Reason for blue-shifted WL PL spectra: The WL is blue-shifted because it is an H-aggregate as compared with the spectra from 1L/2L. This can be understood by looking at the schematic in Figure S3b (See below), where the optically allowed bands are always at much higher energies as compared to the J-type aggregates. This blue-shift from H-aggregates was also predicted by Kasha et al.² and Spano et al.⁹

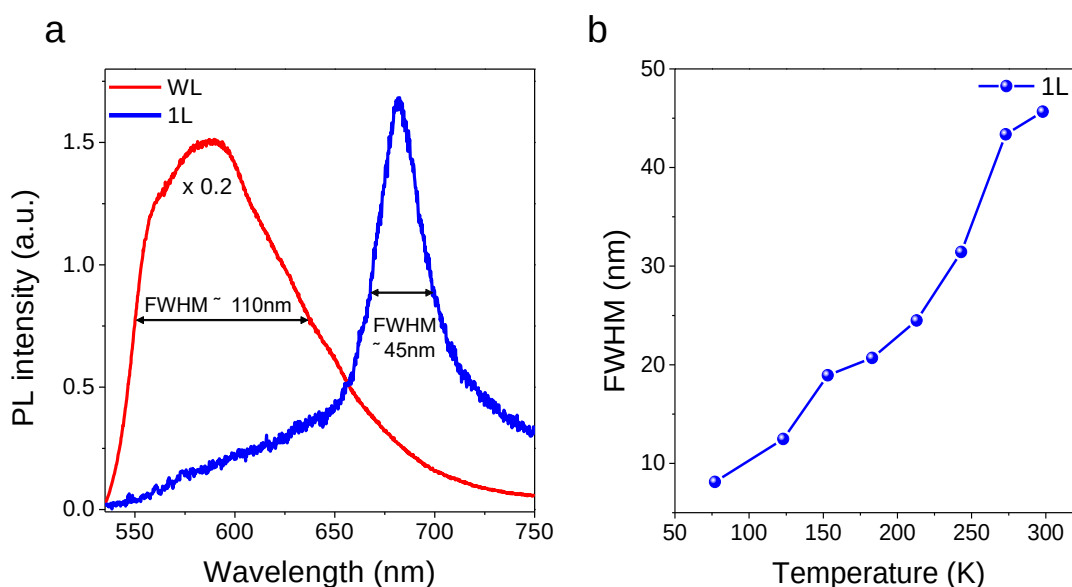


Figure S4 | Measured FWHM with decreasing temperature. a, PL spectra and respective FWHM at 298 K from WL and 1L. **b,** Measured Full-width half maximum (FWHM) as a function of temperature from 1L PEN.

The FWHM from WL overall is much higher at 298 K as compared with narrow linewidth from 1L, suggesting a dominant coherent component in the emission. As shown in the figure above the WL spectra is very broad with FWHM ~110 nm, which

arises due to CT and FR mixing in the WL. The FWHM from 1L has been plotted as a comparison show the extent of reduction in 1L as compared to broad WL PL spectra.

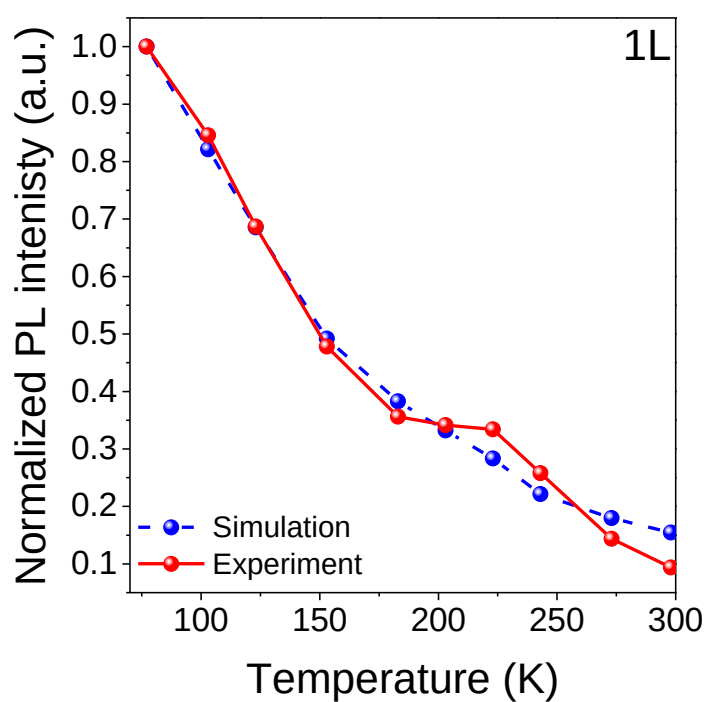


Figure S5 | PL intensity as a function of temperature from 1L as simulated by solving the Boltzmann distribution, in comparison with experimental data from Figure 2b.

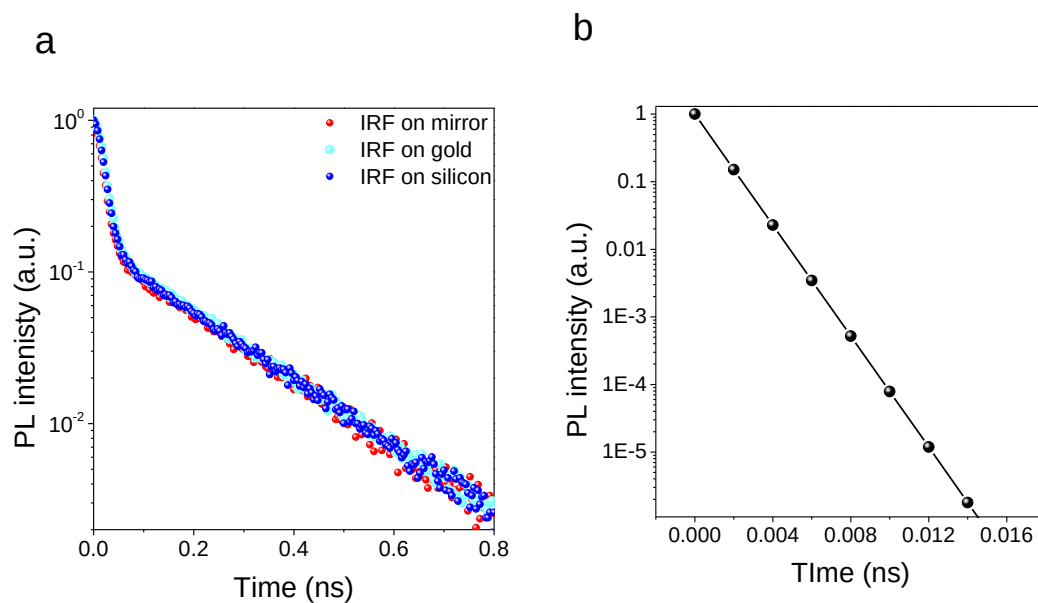


Figure S6 | Instrument response functions. **a**, as measured from different reflective surfaces. The IRF is very stable from different surfaces. **B**, Deconvoluting of one IRF over other gives a system resolution of 2.1 ps as shown by the deconvoluted graph.

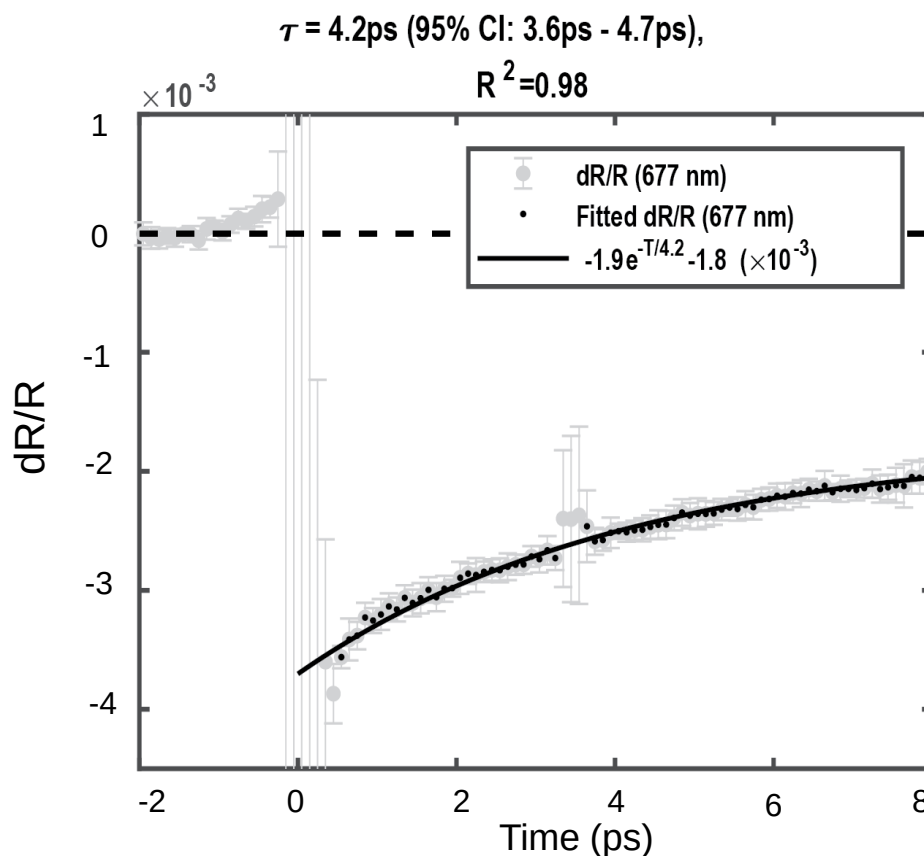


Figure S7 | Fitting and error analysis. The figure shows the fitting of the decay curve from pump-probe measurements with a 95% confidence interval giving a lifetime range of 3.55-4.6 ps and the best fit with a value of 4.2 ps.

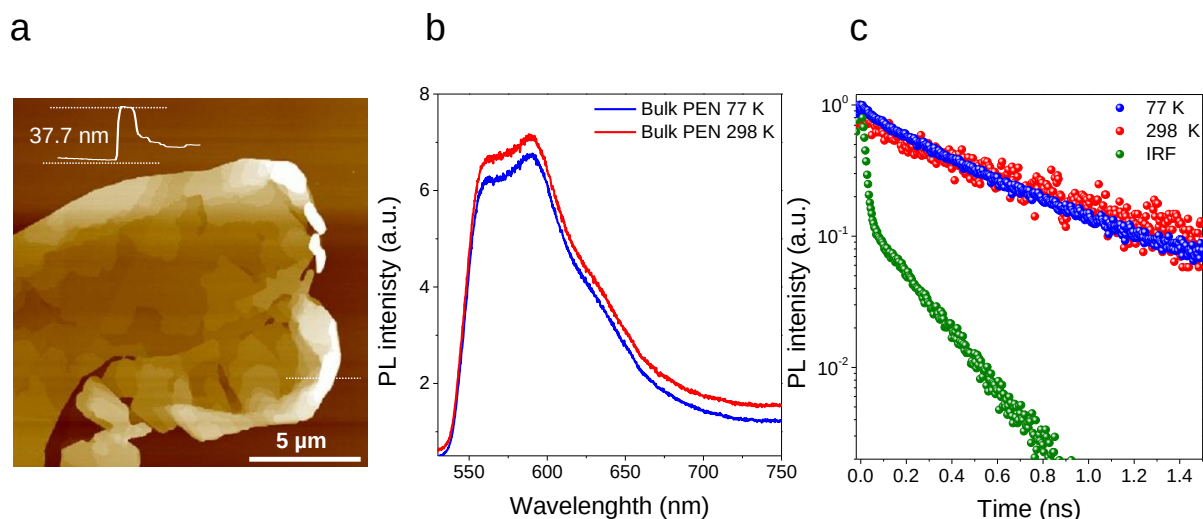


Figure S8 | PL emission from bulk thin-film pentacene, a, AFM image of the bulk thin film pentacene grown over h-BN with a thickness of around 37.7 nm. **b**, PL emission at 77 K from the bulk pentacene, which is dark as compared to WL. **c**, the decay curve from bulk pentacene at 298/77 K, giving an effective lifetime of 1.241/1.014 ns.

The emission from bulk pentacene layers is a broad PL spectrum, which changes negligibly with lowering of the temperature. The sharp peak emission at 680 nm is missing from the bulk pentacene. The broad PL spectra can be attributed to the coupling of CT and FR states, arising from the disorders and interfacial states, which has been reported in literature previously as well.^{9, 10} The lifetime from the bulk pentacene peak at 600 nm emission is 1.241 ns at 298 K, which changes to 1.014 ns at 77 K. The linewidth of the spectra is one order of magnitude higher (>100 nm as compared to 8 nm from 1L pentacene) from bulk pentacene, suggesting a non-coherent emission.

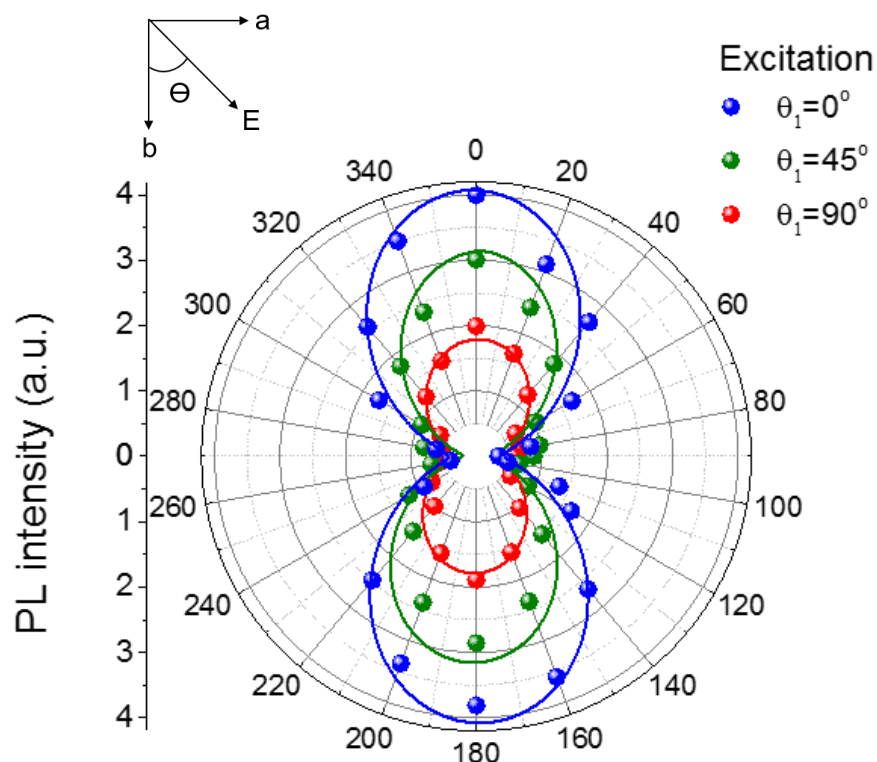


Figure S9 | Emission polarization measurements from 1L PEN at different laser polarizations. The polarization dependent PL measurements from 1L at 77 K. In experiment, the excitation polarization angle θ_1 was fixed at 0° and the polarization angle of the emission (θ_2) was determined by using an angle-variable polarizer located in front of the detector. We also changed θ_1 and repeated the measurements. We observed that PL emission from 1L always shows the maximum PL intensity at $\theta_2 = 0^\circ$ and the minimum PL intensity at $\theta_2 = 90^\circ$, regardless of the excitation polarization angle θ_1 used 0° (grey), 45° (magenta) and 90° (blue).

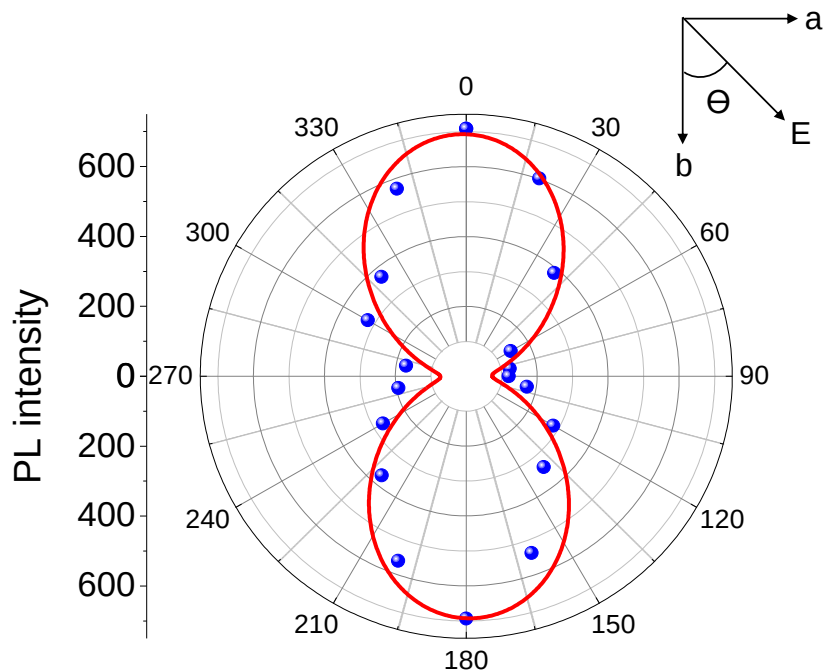


Figure S10 | Measured angle-resolved PL for excitation polarization from the 1L at room temperature. a, Measured angle-resolved PL spectra for emission polarization from 1L pentacene. The LDR is around 5.9 at room temperature. The incident polarization angle (θ) was controlled by an angle-variable polarizer. The excitation laser power remained constant. The solid balls represent the measured experimental values and solid lines are fitted curves using a $\cos^2\theta$ function.

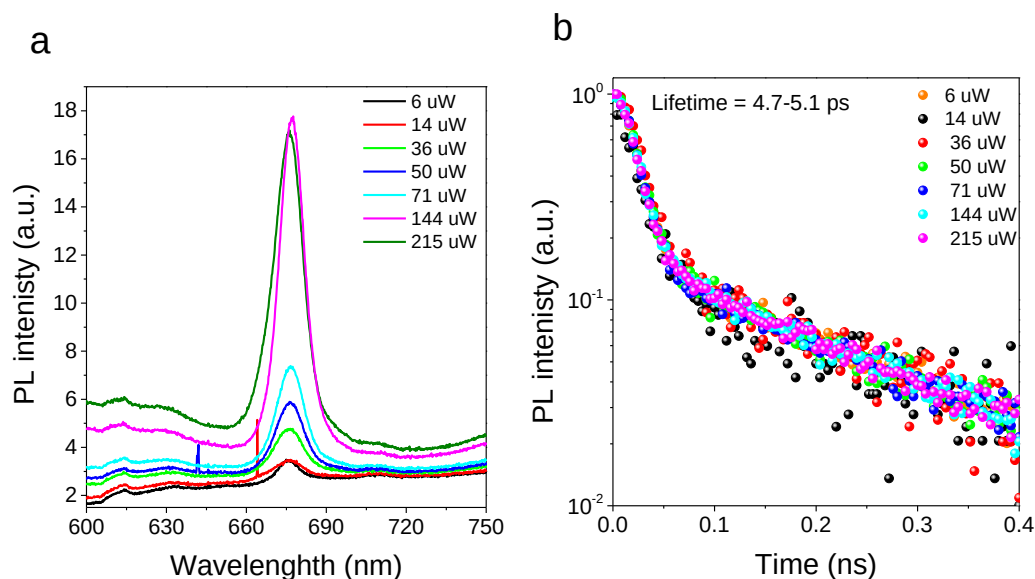


Figure S11 | Power dependent time-resolved PL at 77 K. Power dependent measurements at 77 K were carried out on 1L pentacene samples, to confirm the exciton-exciton annihilation effects. We observed an almost constant lifetime (4.7 -5.1 ps) ranging from a very low laser power to a high laser power ranging from 6 μW to 215 μW . The consistent lifetime suggest that the EEA does not play a key role in defining the exciton diffusion characteristics in our sample as shown in the figure below.

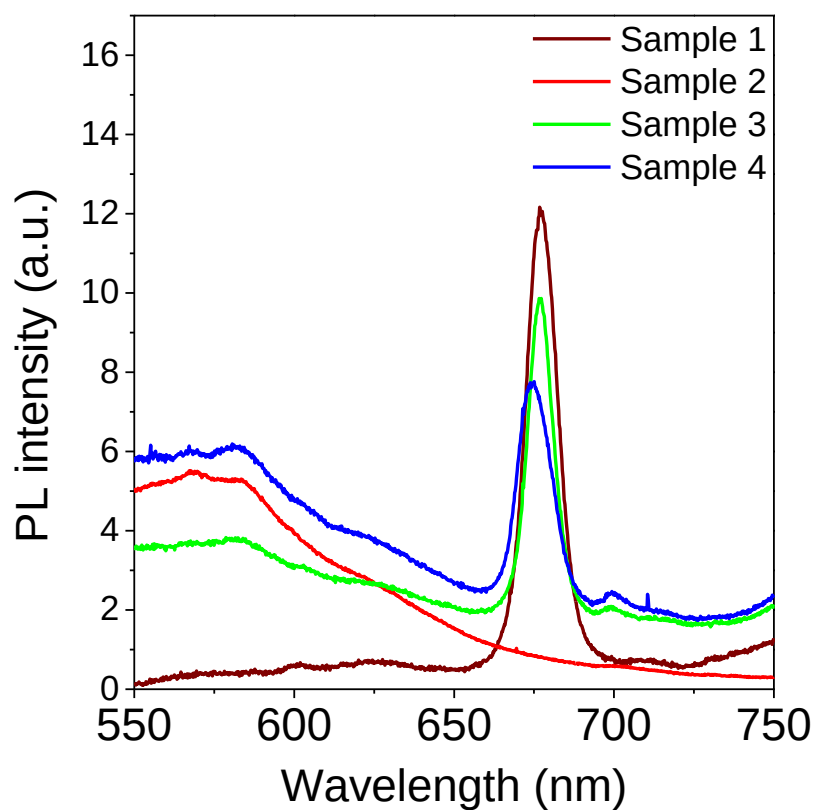


Figure S12 | Measured PL spectra from various quality of 1L pentacene samples at 77 K, fabricated under different growth conditions by CVD method.

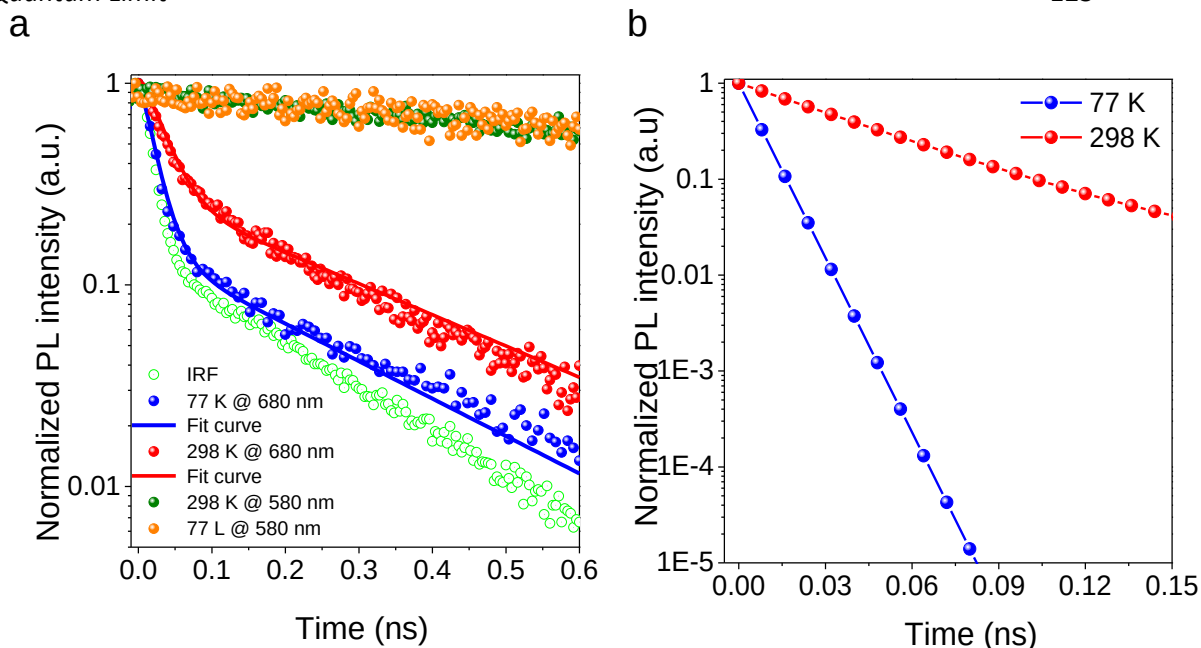


Figure S13 | Temperature dependent time-resolved PL for low-quality 1L

pentacene (sample 3). **a**, Time-resolved PL emission (normalized) from 1L pentacene (680 nm, superradiant peak) sample 3 (See Figure S4) at 77 K (blue balls) and 298 K (orange balls). The solid lines represent the fitting curves for both the temperatures. An effective long lifetime of 51.2 ps was extracted from the orange decay curve (298 K) by a fitting with deconvolution using the instrument response function (IRF) (green dots). The lifetime extracted from blue curve (77 K) was 7.6 ps. The drastic reduction in lifetime with decreasing temperature, further supports the superradiance emission from 1L. The effective lifetime at 77 K is slightly higher than what we have reported in Figure 4 (4.1 ps), which may be due to the low crystallinity of the sample 3 as compared to sample 1. **b**, Time-resolved PL emission from the CT excitonic emission at ~580 nm from 1L pentacene sample. The lifetime extracted from the CT peaks is ~2.1 ns and 2.3 ns at 77 K and 298 K respectively. The lifetime is significantly higher as compared to the coherent FR emission peak at 680 nm, due to non-coherent emission from CT excitonic states, which do not show superradiant emission, further supporting the coherent emission visible at 680 nm even from low crystalline samples. **c**, Deconvoluted lifetime curves showing a drastic reduction in lifetime with decreasing temperature.

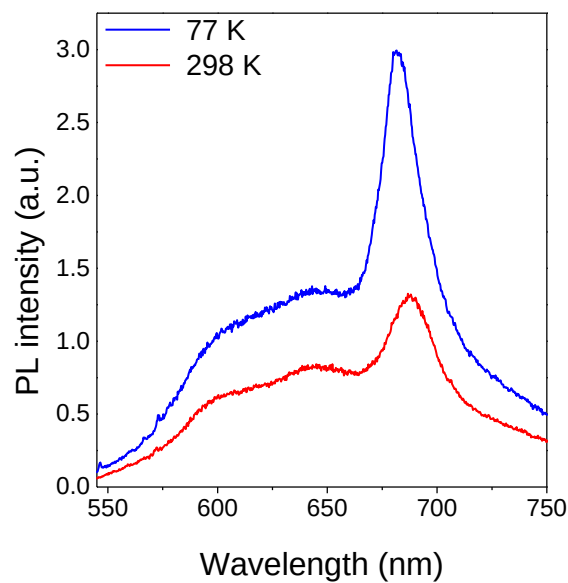


Figure S14 | Temperature dependent PL measurements from 2L PEN. PL spectra from 2L regime of PEN samples. The sharp PL emission at 680 nm is visible from 2L but coupled with high-energy CT emissions. The FWHM at 298 K from 2L is ~49 nm and at 77 K is ~30 nm, which is much broader as compared to 1L.

Table S1: Diffusion coefficients from various organic/in-organic materials: experimental values

Material Type	Material Name	Diffusion Coefficient (cm^2/sec)	Temperature (K)
Inorganic systems	GaAs Quantum wells ⁴¹	0.1-10	4.2
	1L MoS ₂ ⁴²	0.05-0.1	298
	1L WSe ₂ ⁴³	14.5	298
	1L WS ₂ ⁴⁴	0.41	298
	1L MoTe ₂ ⁴⁵	0.1	70
	Phosphorene ⁴⁶	5 E-3	4
	WS ₂ -tetracene heterostructure ⁴⁷	1	298
	Wse ₂ -thin film/bulk ⁴⁸	15/9	298
Organic systems	C8S3-J aggregates ²⁴	70	298
	Light harvesting nanotubes (LHNs-amphiphilic cyanine dyes) ²³	55	298
	Carbon Nanotubes ⁴⁹	44	298
	Meso-tetra(4-sulfonatophenyl) porphyrin ²²	3-6	298
	Tetracene thin film ⁵⁰	2.8	298
	Poly-3 hexylthiophene ⁵¹	1.8 E-3	298
	C ₇₀ thin film ⁵²	3.5 E-3	77
	Pentacene thin films ⁵³	2.5 E-2	298
This work	2D Pentacene-WL	2.4	298
		3.5	77
	2D Pentacene-1L	346.9	298
		354.5	77

References

1. Pope M, Swenberg CE. Electronic processes in organic solids. *Annual Review of Physical Chemistry* 1984, **35**(1): 613-655.
2. Kasha M. Energy Transfer Mechanisms and the Molecular Exciton Model for Molecular Aggregates. *Radiation Research* 1963, **20**(1): 55-70.
3. Davydov A. Theory of molecular excitations. *Plenum Press, New York* 1971, **7**: 387-394.
4. Spano FC, Silva C. H-and J-aggregate behavior in polymeric semiconductors. *Annual Review of Physical Chemistry* 2014, **65**: 477-500.
5. Grégoire P, Vella E, Dyson M, Bazán CM, Leonelli R, Stingelin N, *et al.* Excitonic coupling dominates the homogeneous photoluminescence excitation linewidth in semicrystalline polymeric semiconductors. *arXiv preprint arXiv:170203378* 2017.
6. Braslavsky SE. Glossary of terms used in photochemistry, (IUPAC Recommendations 2006). *Pure and Applied Chemistry* 2007, **79**(3): 293-465.
7. Robinson JW. *Atomic spectroscopy*. CRC Press, 1996.
8. Hestand N, Yamagata H, Xu B, Sun D, Zhong Y, Harutyunyan AR, *et al.* Polarized Absorption in Crystalline Pentacene: Theory vs Experiment. *The Journal of Physical Chemistry C* 2015, **119**(38): 22137-22147.
9. Spano FC. The Spectral Signatures of Frenkel Polarons in H- and J-Aggregates. *Accounts of Chemical Research* 2010, **43**(3): 429-439.
10. Spano FC, Yamagata H. Vibronic Coupling in J-Aggregates and Beyond: A Direct Means of Determining the Exciton Coherence Length from the Photoluminescence Spectrum. *The Journal of Physical Chemistry B* 2011, **115**(18): 5133-5143.
11. Hoffmann M, Schmidt K, Fritz T, Hasche T, Agranovich VM, Leo K. The lowest energy Frenkel and charge-transfer excitons in quasi-one-dimensional structures: application to MePTCDI and PTCDA crystals. *Chemical Physics* 2000, **258**(1): 73-96.
12. Chua L-L, Zaumseil J, Chang J-F, Ou EC-W, Ho PK-H, Sirringhaus H, *et al.* General observation of n-type field-effect behaviour in organic semiconductors. *Nature* 2005, **434**(7030): 194.
13. Lee K, Oh MS, Mun Sj, Lee KH, Ha TW, Kim JH, *et al.* Interfacial Trap Density-of-States in Pentacene-and ZnO-Based Thin-Film Transistors Measured via Novel Photo-excited Charge-Collection Spectroscopy. *Advanced Materials* 2010, **22**(30): 3260-3265.
14. Podzorov V, Menard E, Borissov A, Kiryukhin V, Rogers J, Gershenson M. Intrinsic charge transport on the surface of organic semiconductors. *Physical review letters* 2004, **93**(8): 086602.

15. Bardeen CJ. Excitonic processes in molecular crystalline materials. *MRS Bulletin* 2013, **38**(01): 65-71.
16. Rogers JA. Toward paperlike displays. *Science* 2001, **291**(5508): 1502-1503.
17. Sirringhaus H, Tessler N, Friend RH. Integrated optoelectronic devices based on conjugated polymers. *Science* 1998, **280**(5370): 1741-1744.
18. Hoffmann M, Schmidt K, Fritz T, Hasche T, Agranovich V, Leo K. The lowest energy Frenkel and charge-transfer excitons in quasi-one-dimensional structures: application to MePTCDI and PTCDA crystals. *Chemical Physics* 2000, **258**(1): 73-96.
19. Zhu T, Wan Y, Huang L. Direct Imaging of Frenkel Exciton Transport by Ultrafast Microscopy. *Accounts of Chemical Research* 2017, **50**(7): 1725-1733.
20. Mikhnenko OV, Blom PW, Nguyen T-Q. Exciton diffusion in organic semiconductors. *Energy & Environmental Science* 2015, **8**(7): 1867-1888.
21. Jang S, Newton MD, Silbey RJ. Multichromophoric Förster resonance energy transfer. *Physical Review Letters* 2004, **92**(21): 218301.
22. Wan Y, Stradomska A, Knoester J, Huang L. Direct Imaging of Exciton Transport in Tubular Porphyrin Aggregates by Ultrafast Microscopy. *Journal of the American Chemical Society* 2017, **139**(21): 7287-7293.
23. Caram JR, Doria S, Eisele DrM, Freyria FS, Sinclair TS, Rebentrost P, *et al.* Room-Temperature Micron-Scale Exciton Migration in a Stabilized Emissive Molecular Aggregate. *Nano Letters* 2016, **16**(11): 6808-6815.
24. Clark KA, Krueger EL, Vanden Bout DA. Direct measurement of energy migration in supramolecular carbocyanine dye nanotubes. *The journal of physical chemistry letters* 2014, **5**(13): 2274-2282.
25. Dicke RH. Coherence in spontaneous radiation processes. *Physical Review* 1954, **93**(1): 99.
26. Cong K, Zhang Q, Wang Y, Noe GT, Belyanin A, Kono J. Dicke superradiance in solids. *JOSA B* 2016, **33**(7): C80-C101.
27. Gross M, Haroche S. Superradiance: An essay on the theory of collective spontaneous emission. *Physics Reports* 1982, **93**(5): 301-396.
28. Bradac C, Johnsson MT, van Breugel M, Baragiola BQ, Martin R, Juan ML, *et al.* Room-temperature spontaneous superradiance from single diamond nanocrystals. *Nature Communications* 2017, **8**(1): 1205.
29. Scheibner M, Schmidt T, Worschech L, Forchel A, Bacher G, Passow T, *et al.* Superradiance of quantum dots. *Nature Physics* 2007, **3**(2): 106.
30. Abasto DF, Mohseni M, Lloyd S, Zanardi P. Exciton diffusion length in complex quantum systems: the effects of disorder and environmental fluctuations on symmetry-enhanced supertransfer. *Phil Trans R Soc A* 2012, **370**(1972): 3750-3770.

31. Sim M, Shin J, Shim C, Kim M, Jo SB, Kim J-H, *et al.* Dependence of Exciton Diffusion Length on Crystalline Order in Conjugated Polymers. *The Journal of Physical Chemistry C* 2014, **118**(2): 760-766.
32. Lunt RR, Benziger JB, Forrest SR. Relationship between crystalline order and exciton diffusion length in molecular organic semiconductors. *Advanced Materials* 2010, **22**(11): 1233-1236.
33. Lunt RR, Giebink NC, Belak AA, Benziger JB, Forrest SR. Exciton diffusion lengths of organic semiconductor thin films measured by spectrally resolved photoluminescence quenching. *Journal of Applied Physics* 2009, **105**(5): 053711.
34. Zhang Y, Qiao J, Gao S, Hu F, He D, Wu B, *et al.* Probing Carrier Transport and Structure-Property Relationship of Highly Ordered Organic Semiconductors at the Two-Dimensional Limit. *Physical Review Letters* 2016, **116**(1): 016602.
35. Xu W, Akins DL. Absorption and exciton emission by an aggregated cyanine dye occluded within mesoporous SBA-15. *The Journal of Physical Chemistry B* 2002, **106**(8): 1991-1994.
36. Haedler AT, Kreger K, Issac A, Wittmann B, Kivala M, Hammer N, *et al.* Long-range energy transport in single supramolecular nanofibres at room temperature. *Nature* 2015, **523**(7559): 196.
37. Wu S, Cheng L, Wang Q. Excitonic effects and related properties in semiconductor nanostructures: roles of size and dimensionality. *Materials Research Express* 2017, **4**(8): 085017.
38. Hong X, Kim J, Shi S-F, Zhang Y, Jin C, Sun Y, *et al.* Ultrafast charge transfer in atomically thin MoS₂/WS₂ heterostructures. *Nature Nanotechnology* 2014, **9**(9): 682-686.
39. Jariwala D, Howell SL, Chen K-S, Kang J, Sangwan VK, Filippone SA, *et al.* Hybrid, Gate-Tunable, van der Waals p–n Heterojunctions from Pentacene and MoS₂. *Nano Letters* 2016, **16**(1): 497-503.
40. Akselrod GM, Deotare PB, Thompson NJ, Lee J, Tisdale WA, Baldo MA, *et al.* Visualization of exciton transport in ordered and disordered molecular solids. *Nature Communications* 2014, **5**: 3646.
41. Vörös Z, Balili R, Snoke D, Pfeiffer L, West K. Long-distance diffusion of excitons in double quantum well structures. *Physical Review Letters* 2005, **94**(22): 226401.
42. Sun D, Rao Y, Reider GA, Chen G, You Y, Brézin L, *et al.* Observation of rapid exciton–exciton annihilation in monolayer molybdenum disulfide. *Nano Letters* 2014, **14**(10): 5625-5629.
43. Cadiz F, Robert C, Courtade E, Manca M, Martinelli L, Taniguchi T, *et al.* Exciton diffusion in WSe₂ monolayers embedded in a van der Waals heterostructure. *Applied Physics Letters* 2018, **112**(15): 152106.
44. Yuan L, Huang L. Exciton dynamics and annihilation in WS₂ 2D semiconductors. *Nanoscale* 2015, **7**(16): 7402-7408.

45. Froehlicher G, Lorchat E, Berciaud S. Direct versus indirect band gap emission and exciton-exciton annihilation in atomically thin molybdenum ditelluride (MoTe₂). *Physical Review B* 2016, **94**(8): 085429.
46. Surrente A, Mitiglu A, Galkowski K, Klopotoski L, Tabis W, Vignolle B, *et al.* Onset of exciton-exciton annihilation in single-layer black phosphorus. *Physical Review B* 2016, **94**(7): 075425.
47. Zhu T, Yuan L, Zhao Y, Zhou M, Wan Y, Mei J, *et al.* Highly mobile charge-transfer excitons in two-dimensional WS₂/tetracene heterostructures. *Science Advances* 2018, **4**(1): eaao3104.
48. Cui Q, Ceballos F, Kumar N, Zhao H. Transient absorption microscopy of monolayer and bulk WSe₂. *ACS nano* 2014, **8**(3): 2970-2976.
49. Moritsubo S, Murai T, Shimada T, Murakami Y, Chiashi S, Maruyama S, *et al.* Exciton diffusion in air-suspended single-walled carbon nanotubes. *Physical Review Letters* 2010, **104**(24): 247402.
50. Wan Y, Guo Z, Zhu T, Yan S, Johnson J, Huang L. Cooperative singlet and triplet exciton transport in tetracene crystals visualized by ultrafast microscopy. *Nature Chemistry* 2015, **7**(10): 785.
51. Shaw PE, Ruseckas A, Samuel ID. Exciton diffusion measurements in poly (3-hexylthiophene). *Advanced Materials* 2008, **20**(18): 3516-3520.
52. Kozlov OV, de Haan F, Kerner RA, Rand BP, Cheyns D, Pshenichnikov MS. Real-time tracking of singlet exciton diffusion in organic semiconductors. *Physical Review Letters* 2016, **116**(5): 057402.
53. Marciniak H, Pugliesi I, Nickel B, Lochbrunner S. Ultrafast singlet and triplet dynamics in microcrystalline pentacene films. *Physical Review B* 2009, **79**(23): 235318.

CHAPTER 5

Quasi-line spectral emissions from high crystalline 1D Organic Nanowires

The advantages of low dimensional materials for various optoelectronic applications have been described in detail in Chapter 1. Apart from 2D materials, there have been attempts to make one dimensional (1D) nanomaterials such as nanowires, nanobelts and nanoribbons for various electronic applications. The most common examples are the carbon nanotubes (CNTs) as described in chapter 3. But, most of these attempts to make 1D systems have been with inorganic materials and polymers. There is extensive research literature available on various inorganic nanowires. But, very few of them talk about 1D organic nanowires. As discussed in Chapter 1 and 4, the organic materials especially light molecular weight molecules like pentacene can prove to be effective candidates for 1D systems that can generate and propagate light effectively for optoelectronic device applications. The organic nanowires that have been reported in literature

have mostly been grown in liquid phase or through liquid exfoliation processes. Thus, their suitability for applications in solid state electronic applications was very limited. In solid state it is always difficult to achieve right dimensionality and proper molecular adsorption of the substrate as reported in literature. The growth of 1D organic nanowires on substrates has been hindered by lack of dimensionality control, defect states and low crystalline growth resulting in their limited applications.

This chapter demonstrate a high crystalline and ordered 1D organic nanowire of pentacene (PEN) grown by physical vapor deposition on hBN using the same CVD technique as in Chapter 4. We observe a well resolved vibronic photoluminescence (PL) spectra from the wires at room temperature. Attributed to specific molecular configuration and higher degree of orientation of molecules as compared to bulk thin film of pentacene. At low temperature, this chapter reports the first experimental demonstration of Shpol' skii effect in an organic solid-state system. I observed a quasi-line spectrum with width $\sim 2\text{-}3$ nm and a very high value of Debye-Waller factor from our 1D wires. The results in this chapter pave the way for organic 1D wires (with quasi-line spectra) for applications in lasing, nanosensors and interconnects/functional units in next generation miniaturized optoelectronics.

This chapter focusses on a new 1D system grown using same organic material-pentacene as in chapter 4. 1D nanomaterials are especially critical for their applications in light emitting displays, lasing applications and serve as functional or connecting units of various devices. While working with organic nanomaterials for 2D growth, I encountered some 1D growth during some of my growth iterations which got my interest. The optical properties which I observed from these 1D organic nanowires were exciting and some of which have never been reported before from solid state systems before. This chapter aims to utilize the excitonic expertise reported in chapter 4 and use it to explain the intriguing optical emissions from the 1D organic nanowire. The observation of quasi-line spectra (referred to as Shpol' skii effect) is critical for applications of these organic nanowires in tunable wavelength emission displays, optically driven lasers, bio-chemical sensors and high quantum yield LEDs.

Quasi-line spectral emissions from high crystalline 1D Organic Nanowires

Ankur Sharma¹, Ahmed Khan¹, Yi Zhu¹, Robert Halbich¹, Wendi Ma¹ and Yuerui Lu^{1*}

¹Research School of Electrical, Energy and Materials Engineering, College of Engineering and Computer Science, the Australian National University, Canberra, ACT, 2601, Australia.

* To whom correspondence should be addressed: Yuerui Lu (yuerui.lu@anu.edu.au)

ABSTRACT: Zero phonon line (ZPL) emissions have key applications in single photon emission sources, quantum information processing and single molecule spectroscopy. All recent attempts to realize ZPL emissions are based on the techniques of confining and doping molecules in matrices or solutions at low temperature-Shpol'skii systems. The requirement of two-component systems reduces the light emission efficiency from the molecules and limits their applications in solid state electronic applications and quantum computing devices. Here, we report the first experimental demonstration of Shpol'skii effect in a one-component organic solid-state system at low temperature. We observe a ZPL emission with width of ~1-2 nm and a high value of Debye-Waller factor (0.72) from our epitaxial grown high-crystalline and ordered 1D organic nanowire, which is attributed to specific molecular configuration and higher degree of orientation of molecules as compared to bulk thin film counterpart. Our results pave the way for organic 1D wires (with quasi-line spectra) for applications in lasing, nanosensors and interconnects/functional units in next generation miniaturized optoelectronics.

Keywords: Shpol'skii effect, organic nanowires, quasi-line spectra, crystallinity.

Introduction

Zero phonon lines (ZPL)(1) are narrow sharp peak emission at low temperature which are purely electronic in nature. They have characteristic vibrational structure and hence can be used for determining photophysical, photochemical and physicochemical properties of complex compounds.(2) Hence, there has been a tremendous revival of interest in narrow line-width emissions due to their fundamental applications in single photon emission sources, which have key applications in linear optics quantum information processing.(3) ZPLs have also been established to be applied for nano lasers,(4, 5) optical waveguides,(4, 6) flexible/cost-effective optical devices(7, 8) and tunable-wavelength emission displays.(9, 10), optical data storage(11) and processing in the space-frequency domain and single impurity molecule spectroscopy.(12) Zero-phonon or quasi-line spectral emissions were reported by Shpol'skii(13) in 1962 at low temperature by inducing the molecules in a matrix or solution at low temperatures, thus confirming the phonon less nature of these emissions.

There have been several attempts to generate similar quasi-line or Shpol'skii spectra emissions. Recently, self-assembled InAs quantum dots(3) and trapped atoms have been demonstrated as such sources for highly indistinguishable single photons and quasi-line emissions. Several complex polyatomic organic molecules embedded in molecular crystals or solutions have been demonstrated in the past to obtain ZPL emissions (See Table S1). But, all of them have been two-component systems which require the desired chromophore to be in a frozen solution or matrices in order to reduce the phonon sideband emissions. This dilutes the light emitting molecule concentration in the matrix and hence the light generation efficiency is considerably reduced.(2, 6, 7) There have been no reports so far which show a single component and single-crystal molecule solid-state system generating Shpol'skii spectra. Broad phonon sideband emission arises due to

different energy level of molecules in a system(14) and that is why they need to be put in matrices or solutions as discussed above, to confine their degree of freedom and achieve narrow quasi-line spectral emissions. In a single-crystal molecule system, high crystallinity is the key to observe Shpol'skii effect but until now it has been a challenge to grow highly crystalline solid states systems that generate ZPL emissions. One-dimensional (1D) nanostructures such as nanowires, nanoribbons/belts and nanotubes have gathered significant attention due to their two dimensional quantum confinement.(7, 15) This makes them promising candidates for achieving quasi-line spectral emissions. But most those nanomaterials have been mostly externally doped conjugated polymers(16-18) or large two dimensional non-linear extended aromatic systems like hexabenzocoronene.(15, 19) That makes it difficult to achieve large scale high order crystalline and defect free growth of 1D structures, especially with molecules that show π - π face stacking necessary to make 1D structures.(19, 20) Most of the reported 1D organic structures have been demonstrated in liquid phase(21, 22) grown by using self-assembly in liquid phase solutions, restricting their applications in solid state electronic devices.(23) Low molecular weight organic materials on the other hand offer a distinct advantage as compared to their inorganic counterparts in terms of their good processability,(24) large-scale/low-cost synthesis,(7, 19) high photoluminescence (PL) efficiency(25) and molecular tunability of electronic properties.(26, 27)

But, in solid state growth of organic molecules over a substrate, it is difficult to achieve dimensionality control and effectively control the width and length of the 1D nanostructure.(7, 19) Moreover, it is well known that in organic crystalline structures the opto-electronic and electronic properties are a direct function of the molecular orientation, degree of crystallinity and defect states in the lattice.(28, 29) For ensemble organic molecular systems in solution, the local arrangement of the molecules in the solution affects their ability to absorb light and hence affects their optoelectronic

properties.(30) There have been recent reports on using physical vapor deposition (PVD)(9, 10, 14, 31) techniques to grow solid states 1D crystalline organic structures. However, they still have not been able to control monodispersity of the organic molecules, especially with low-molecular weight organic molecules as deposition sources.(7, 19)

Here, we present a single component, high crystalline organic 1D nanowire made from single-crystal low molecular weight oligoacene- pentacene (PEN) molecule deposited on hexagonal boron nitride (hBN) using a low temperature PVD process. We report interesting optical properties from the 1D nanowires at room and low temperature. The PL spectra from the nanowires is clearly resolvable into three vibronic peaks at room temperature as compared to the broad sideband emission from bulk thin film pentacene. We attribute this PL spectra to a high degree of crystallinity and reduced degrees of translational and rotational freedom(32) of molecules in 1D PEN wire. Hence, resulting in clearly resolvable vibronic energy levels and reduced charge-phonon coupling in the lattice. At cryogenic temperatures, due to further freezing of molecular degrees of freedom and reduction of thermal phononic coupling results in quasi-line spectra(33) from PEN wires- the Shpol'skii effect.(2, 13) The reported quasi-line spectra have a linewidth of ~1-2 nm and are a resultant of the reduced phononic coupling with the excitons in the lattice(2). The linewidth reported in our case is much lower as compared to the linewidth reported from similar organic 1D nanostructures(14) grown using similar PVD methods. These quasi line spectra arising at low temperatures are ZPLs(2) attributed to zero-phonon transitions between the electronic energy levels of the organic molecules, confirmed by a high value of the Debye-Waller factor (DW).(2, 33) We further establish the high crystallinity and higher degree of molecular orientation of the PEN molecules in the 1D nanowire structure using polarization-resolved PL emission spectra and time-resolved PL emission. We also demonstrate a metal oxide semiconductor (MOS) device incorporating the 1D PEN wire to effectively demonstrate an external electric control of

the quasi line spectral emission at low temperatures. Our results effectively demonstrate the use of PEN 1D organic nanowires for future optoelectronic devices such as nanolasers(34), OFETs(35), multi-colored light emitting diodes (LEDs)(10), optically driven lasers(36), photodetectors, logic gates and construction of interconnects and functional units of next generation miniaturized optoelectronics.(7)

Results and Discussion

Among light-weight oligoacenes, pentacene and its derivatives have shown best performances in thin-film devices(37). Thus, we chose pentacene for our 1D growth. Figure 1a shows the optical image of the PEN wires grown on hBN substrate. hBN provides a defect free and dangling bond free flat area for molecular deposition with high degree of molecular orientation(38). Mechanically exfoliated few-layer hBN sheets were transferred onto a 285 nm SiO₂/Si substrate. The PEN was then deposited using a thermal vapor deposition process using a tube furnace (Figure S1). (See Methods and Supplementary information Note 1). The grown PEN wires were characterized using Raman spectroscopy (Figure S2). The growth of the PEN wires was optimized at various growth temperatures (Figure S3a) and time durations (Figure S3b) to achieve long length and high crystalline 1D nanowires. High resolution AFM imaging was used to characterize the physical thickness and diameter of the PEN wires (Figure 1b). Most of the PEN wires had a circular cross-section with an average width of ~300-400 nm and an average thickness of ~250-300 nm. The average length of the wires was ~14 μ m, which is much higher than previously reported PVD grown 1D nanowires on substrates(7, 10, 14). Figure 1c shows the schematic growth mechanism of 1D PEN nanowires on hBN substrates. First, the smaller PEN molecules are connected linearly by H-bonds forming long chains and depositing over hBN surface utilizing σ - π interaction with the substrate(38). The vertical deposition then is a result of van der Waals interaction between

pentacene molecules. At this juncture, as the deposition rate increases, π - π interactions between PEN molecules cause the molecules to bend inwards facing each other(7) leading to the formation of wire like 1D structures. We confirmed the same using high resolution SEM imaging (Figure 1d).

The prepared samples were then excited using a 532 nm CW laser. The resultant PL emission spectra is shown in Figure 1e. The PL spectra from the 1D PEN wire is clearly resolved in to three peaks at 600 nm, 660 nm and 730 nm. The origin of the peaks is explained later. The spectrum from 1D PEN wires is in sharp contrast to the broad and much weaker PL emission from thin film pentacene grown on the same substrate and bulk pentacene samples. The optical absorption and emission from organic molecular assemblies is a direct function of the molecular crystallinity and degree of orientation(29). Hence, well resolved and high-intensity PL emission from 1D wires is a resultant of the highly crystalline an ordered growth of PEN wires on a clean defect free flat hBN adsorption surface. To further confirm the role of hBN in achieving ordered growth, we re-ran the growth of PEN wires using the same methods and conditions on a SiO₂/Si substrate. We observed tiny needle like 1D structures protruding out of micelle like nucleation sites (Figure S4). The growth of those 1D PEN structures on SiO₂ was highly disordered and the PL emission (Figure S4c) were much weaker and less resolved as compared to the wires grown on hBN. Thus, establishing the role of hBN as a template or adsorbent surface for the ordered high crystalline and dimensionality controlled growth of 1D PEN wires.

Shpol' skii effect and quasi-line spectra

To further understand the optical properties of crystalline 1D PEN wires and substantiate their role for various optoelectronic applications, we performed temperature dependent PL spectroscopy down to 77 K. Figure 2a shows the PL spectra from 1D PEN wires at

various temperatures. The spectra start to resolve into various sharp and narrow linewidth peaks as the temperature decreases. The first emergence of narrow peaks is spotted at 213 K (Figure S5). At 77 K, the spectrum is clearly resolved into sharp quasi-line emission peaks with an average line width of 2-3 nm (See Table S2 for fitted peak positions). In some optimal growth cases, we observed the line-width to be ~ 1 nm (Figure S6). Whereas, we did not observe such narrow linewidth PL peaks from 1D needles grown on SiO₂ (Figure 2b). The emergence of quasi-line spectra from 1D PEN wires is very different from the broad sideband PL emission from thin film PEN grown on similar hBN substrate (Figure S7).

The origin of quasi-line spectra from 1D PEN wires and the difference with thin film PEN be explained using the energy level band diagram in Figure 2c. In bulk thin films of organic molecules such as pentacene, the emission band broadening/dispersion results mainly from the fact that various molecules have different energy levels(39). As a result, multiple vibronic band are formed (also called Davydov splitting(40)). The energy levels (in both ground and excited states) are roughly divided in vibronic sub-bands, defined by the number of quanta v ($=1,2,\dots$). Each vibronic band has further vibrational sub-bands induced due phononic coupling of charges (indicated by $\dot{v}=1,2,\dots$) The width of each vibronic band incorporating molecular interaction and vibrational frequency of molecules has been theoretically calculated by Spano et al.(41) Due to low crystallinity, the charges couple with phonons (vibrations) in the crystal lattice plane to form diffused vibronic/vibrational bands (as shown Figure 2c). Each vibrational band is spread due to this strong phononic coupling of rotational translational states of charges(2). The interaction of molecules with lattice phonons is represented by spread of vibrational sublevels. Multiplicity of characteristic vibrational and vibronic bands of these molecules results in further diffusiveness of electronic-vibrational bands and causes a quasi-continuum spectrum as obtained from bulk thin films. The inhomogeneous spectral

broadening arises from electronic transitions involving lattice phonons, giving rise to a comparatively broad phonon sideband emission (PSB)(2, 32).

In our single crystalline, 1D PEN wires due to flat h-BN substrate, the molecules are confined distinctly in the lattice with a specific geometric configuration and higher degree of orientation(4, 6, 7, 14) as compared to bulk organic thin films, with less defect and interfacial states. This limits the large rotational and translational degrees of freedom of molecules and this ordered environment drastically reduces the phonon coupling resulting in narrower optical transitions(2). Even at room temperature (Figure 2c), narrowing of vibrational level occurs, simplifying the optical spectra into discrete narrower emissions (Figure 1e). The emergence and enhancement of vibrational structures can be attributed the increases of long-range order and higher degree of molecular orientation in PEN wires.

At low temperature all vibronic transitions can be further resolved (with FWHM $\sim$ 2-3 nm), resulting in an almost quasi-line spectrum. This emergence of these atomic-like quasi-line spectra is called Shpol'skii effect(13, 42) and was reported in frozen organic solutions at low temperatures by Shpol'skii in 1952. At low temperatures, the degrees of freedom for the molecules are further frozen resulting in further reduced electron-phonon coupling. This causes the PL spectra to be resolved into quasi-line peaks or the narrow zero-phonon lines(43) (ZPL) emissions from the vibronic/vibrational sub bands to ground state (as shown in Figure 1c). Such line-spectra only appears upon specific transitions in the band structure, which do not involve lattice phononic vibrations (analogous of Mössbauer(44) lines). The reduction in spread of vibronic/vibrational sub bands occurs due to high ordered growth of PEN molecules over hBN and further reduction in phonon-electron coupling at low temperature. It has been shown in the literature that Shpol'skii effect is affected by guest-host molecular interactions(31, 32). Hence, the emergence of Shpol'skii spectrum can be attributed to these two factors: highly ordered molecular

orientation (high crystallinity) and low temperature. The non-visibility of these ZPLs from PEN needles on SiO₂ (Figure 2b) further substantiates this.

It has been shown theoretically that the electron-phonon coupling and change of temperature influences the FWHM and integrated PL emission from organic matrices(33, 37). To further confirm the Shpol'skii effect and the role of ZPLs in the spectra obtained from 1D PEN wire, we performed temperature dependent FWHM and Integrated PL intensity analysis. The relation between the integrated intensity of the ZPL and total intensity of the (ZPL+PSB) band is determined by linear-electron phonon coupling and is called Debye-Waller factor (DW)(2, 45) and is defined by the following equation (1).

$$DW = \frac{I_{ZPL}}{I_{ZPL} + I_{PSB}}$$

where, I_{ZPL} is the integrated PL intensity from the sharp zero-phonon line peak and I_{PSB} is the total integrated area of the remaining broad sideband emissions.

The variation of extracted DW factor from 1D PEN wire as a function of temperature is shown in Figure 2d. The high value of DW factor (0.72) at 77 K confirms the limited phonon coupling with the charges resulting in quasi-line spectra. As a comparison we have also shown calculated DW factor for an excitonic emission from 1L WSe₂ monolayer. The linewidth of PL emission peak is also a direct function of phonon coupling. Figure 2e (Figure S8) shows the variation in full-width half maximum (FWHM) from peak 1 (peak 2,3) emissions from 1D PEN wire and 1L WSe₂ monolayer. The FWHM from 1D PEN wire is much lower as compared to the excitonic peak width at 77 K from 1L WSe₂. The sharp reduction in FWHM ($\sim 2-3$ nm at 77 K) from the PEN wire PL peak 1, confirms the reduced phonon coupling in the PEN crystal lattice(46) resulting in quasi-line spectral emissions, which is consistent with previously reported ZPL emissions from low dimensional organic materials(2) and other Shpol'skii matrices (See table S1). We further performed pumping power dependent PL measurements at 77 K

(Figure S9), which confirmed the mission to be below lasing threshold.

High order crystallinity and molecular orientation

To further understand the crystalline structure and orientation of pentacene molecule unit cells inside the 1D PEN wire, we performed polarization angle resolved PL emission spectroscopy at both room temperature and 77 K. Figure 3a shows the PL spectra at various emission polarization angles at room temperature. PL intensity from 1D PEN wires strongly depended on the emission polarization angle θ and showed a period of 180 degrees. Peak 1 (600 nm) showed opposite polarization dependence as compared to peaks 2 (660 nm) and 3 (730 nm). Based on the polarization data and theoretically predicted π - π (47) molecular packing in pentacene(37), we can identify the crystal faces in PEN wire as shown in Figure 3b. The wires grow along the 100 face(19, 31) (see inset SEM image in Figure 3b). Figure 3c shows the polar plot of PL intensities as a function of polarization angles. Peak 1 is clearly polarized along the short 'b' axis of PEN unit cell, while peak 2 and 3 are aligned along the 'a' axis(31). This clearly highlights anisotropy in 1D PEN wires originating due to high crystalline and ordered growth in the 1D wires. We performed similar polarization resolved measurements at 77 K (Figure 3d) to understand the anisotropic behaviour of the Shpol'skii spectra observed at 77 K. We observed the same trend as at room temperature. The quasi-line spectra peaks 1 and 2 (See Table S2) are aligned along the 'b' axis (Figure 3e). The remaining quasi-linear peaks were aligned along the 'a' axis of PEN unit cell as shown in Figure 3f and Figure S10. Increased crystallinity and order can also lead to enhanced lifetime of PL emission peaks in crystalline materials(48, 49). To substantiate the high crystallinity in our 1D nanowires, we also performed time-resolved PL (TRPL) measurements at room temperature and 77 K. Figure 4a shows the decay curve obtained from peaks 1,2 and 3 from PEN 1D wire at room temperature and the bulk thin film. The decay trace curves were deconvoluted with

respect to the instrument response function (IRF) and then were fitted using the equation:

$$I = A \exp\left(-\frac{t}{\tau_1}\right) + C$$

, where I is the PL intensity, A and C are constants, ' t ' is time, and

τ_1 is decay rate indicating emission lifetime. The long single exponential lifetime represents radiative recombination time at room temperature.⁽⁵⁰⁾ An effective lifetime of $\tau_1 = 3.36 \pm 0.6$ ns, 3.07 ± 0.3 ns and 2.74 ± 0.4 ns (Figure 4c) was extracted for peaks 1, 2 and 3 respectively at room temperature, which is about three times higher than the extracted radiative lifetime from thin film pentacene of 1.24 ns. Similarly, at 77 K, effective radiative lifetime for 5 major peaks was extracted as shown in Figures 4b, d. The effective lifetime from 1D PEN wire increased to an average ~ 4.5 ns (Figure 4d) while the thin film lifetime was reported to be around 1.01 ns. Thus, establishing the high order crystallinity and high degree of molecular orientation in our 1D PEN nanowires.

MOS device based on 1D PEN nanowires

We further incorporated the 1D PEN nanowire into a metal-oxide semiconductor (MOS) device to use external static back gate voltage to manipulate the quasi-line spectra for various optoelectronic device applications. Figure 5a shows the schematic diagram of the MOS device used for back gate voltage dependent PL modulation. During the measurements, the gold electrode was grounded, and the p⁺ doped Si substrate was used as a back gate providing a uniform electrostatic doping for the 1D PEN in this MOS device. The measured PL spectrum was very sensitive to the electrostatic doping and can be significantly modulated by the gate voltage. The PL intensity decreases when we inject negative charge into the samples, indicating that the 1D PEN has an initial n-type doping, Figure 5b(c) shows the variation in PL spectra at different back gate voltages at 298 K (77 K). The variation in PL intensities with back gate voltage is evident even for quasi-line spectra peaks at low temperature. The variation in PL intensity of peaks 1, 4 and 12 (See Table S2) as a function of back gate voltage is shown in Figure 5d. Electrostatic

control of the quasi-line spectra is further demonstrated through change in DW factor as a function of back gate voltage (Figure S11). Thus, establishing the applications of 1D PEN nanowires in future optoelectronic device applications.

Conclusion

In conclusion, we have demonstrated a quasi-line spectrum from a single component, solid state system of low-molecular weight single crystalline molecule organic material. We experimentally observed zero-phonon lines in the PL emission spectra from 1D PEN nanowires originating due to Shpol'skii effect at cryogenic temperatures, which have not been reported before from single molecular crystalline solid-state systems. This was achieved due to a highly crystalline and ordered growth of PEN molecules in a 1D nanowire grown over an adsorbent defect free and flat hBN surface. Control of dimensionality and order in PVD process has been a challenge to grow similar 1D organic nanostructures for various optoelectronic applications. We demonstrated an optimized 1D nanowire which has high crystallinity and subsequently exciting optical properties for future optoelectronics. The restriction in degrees of freedom and reduced electron-phonon coupling in 1D nanowires lead to vibronically well-resolved PL spectra. At low temperatures, further thermal phonon coupling is reduced, and the PL spectra is resolved into quasi zero-phonon lines- the Shpol'skii spectra, as evident through extracted FWHM and DW factors from temperature dependent measurements. We further establish the high crystallinity through angle and time-resolved PL measurements. We finally demonstrate a MOS device based on 1D PEN nanowires, which shows an external control of quasi-line spectra using back gate voltage. Our results pave the way for use of organic 1D nanowires in nanolasers, OFETs, optical waveguides, chemical sensors, photodetectors and functional/interconnecting units of future nano optoelectronic and photonic devices.

Methods

Material growth: h-BN flakes were mechanically exfoliated onto a thermally grown 285 nm thick SiO₂ layer deposited over silicon substrate. Before physical vapor deposition (PVD), optical microscope was used to characterize the topological information. The pentacene (purchased from Chem Supply: P0030-1G) was then deposited over the h-BN flakes, kept centered in a vacuum tube in the furnace. h-BN sheet on SiO₂/Si substrate was placed around 15 cm downstream and a molecular pump was used to evacuate the quartz tube to $\sim 10^{-4}$ mbar. The furnace was heated up to 135-185°C for various time intervals to grow PEN wires. (See S.I. Note 1). Then, the whole system was naturally cooled down to room temperature under vacuum. All the samples were characterized, and layer thickness were identified using the standard AFM measurements, which were collected in ambient atmosphere at room temperature with a Bruker Multi-Mode III AFM. For the MOS structure, used for back gate-dependent PL measurements, we transferred the 100 nm thick gold electrode to contact part of the 1D PEN nanowire as the probing pad. The voltage was supplied using a Kiethly 4200 semiconductor analyzer.

Optical Characterization: PL measurements at room temperature and 77 K were conducted using a Horiba LabRAM system equipped with a confocal microscope, a charge-coupled device (CCD) Si detector, and a 532 nm diode-pumped solid-state (DPSS) laser as the excitation source. For temperature-dependent (above 77 K) measurements, the sample was placed into a microscope-compatible chamber with a low temperature controller (using liquid nitrogen as the coolant). In the experiment, the incident polarization angle was controlled by an angle-variable half-wave plate and was fixed, and the polarization angle of the emission (θ) was determined by using an angle-variable polarizer located in front of the detector. Time resolved PL measurements were conducted in a setup which incorporates μ -PL spectroscopy and a time-correlated single

photon counting (TCSPC) system. A linearly polarized pulse laser (frequency doubled to 522 nm, with 300 fs pulse width and 20.8 MHz repetition rate) was directed to a high numerical aperture (NA= 0.7) objective (Nikon S Plan 603). PL signal was collected by a grating spectrometer, thereby either recording the PL spectrum through a charge coupled device (CCD; Princeton Instruments, PIXIS) or detecting the PL intensity decay by a Si single-photon avalanche diode (SPAD) and the TCSPC (PicoHarp 300) system.

Author Contributions

Y. L. conceived and supervised the project; A.K. and Y. Z. prepared pentacene samples; A. S. carried out all the optical measurements; A. S, Y. L. and A. K. analyzed the data; A. S. took the AFM imaging; R. H., W. M., Y. Z. helped with the schematic preparation and sample optimization. A. S. and Y. L. drafted the manuscript and all authors contributed to the manuscript.

Supplementary Information

All additional data and supporting information and methods are presented in the supplementary information file.

Acknowledgements

We would like to acknowledge the financial support from ANU PhD student scholarship, China Scholarship Council, Australian Research Council, ANU Major Equipment Committee fund, National Natural Science Foundation of China. We would also like to thank Professor Chennupati Jagadish and Professor Barry Luther-Davies from the Australian National University for their facility support.

Competing financial interests

The authors declare that they have no competing financial interests.

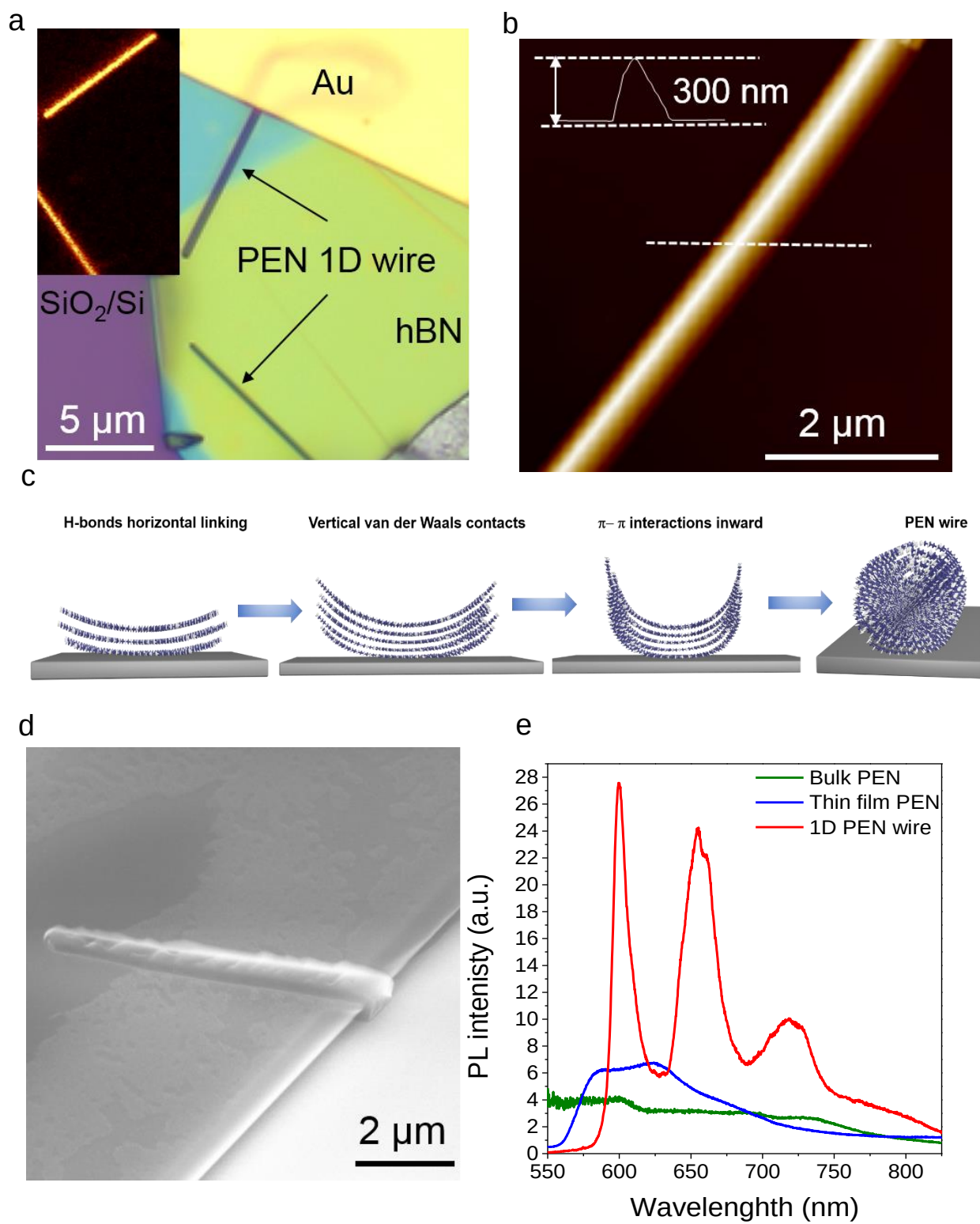


Figure 1

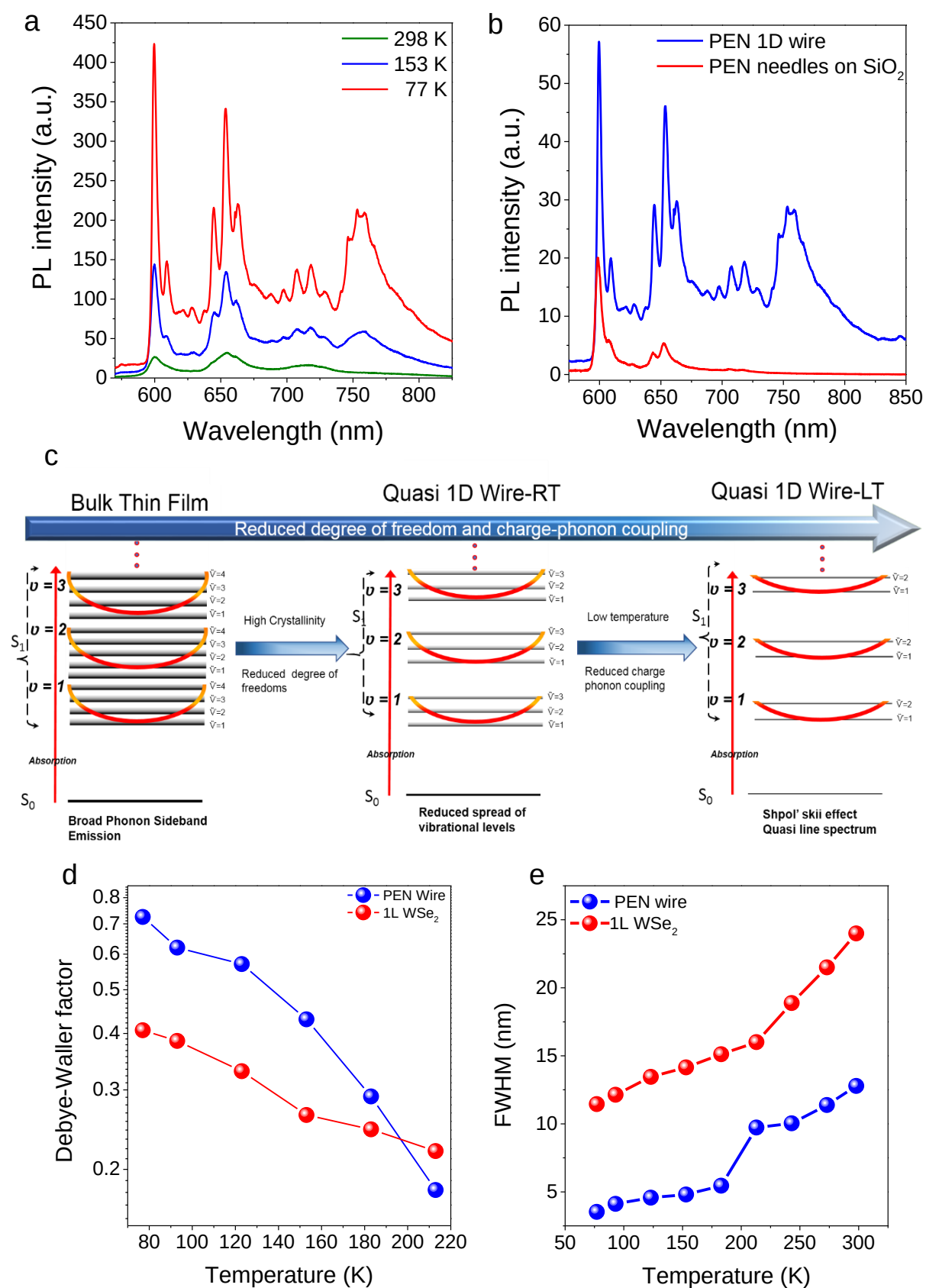


Figure 2

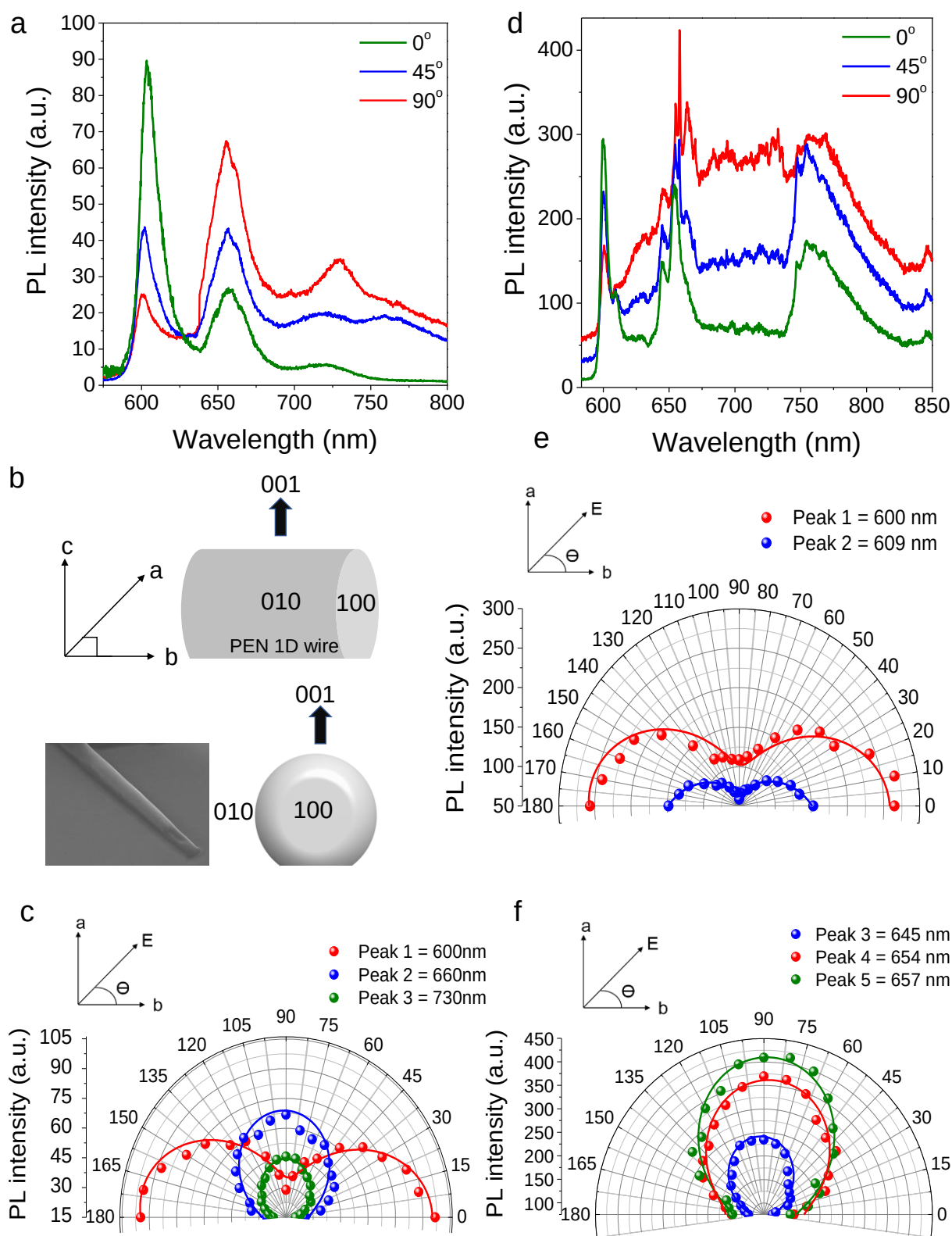


Figure 3

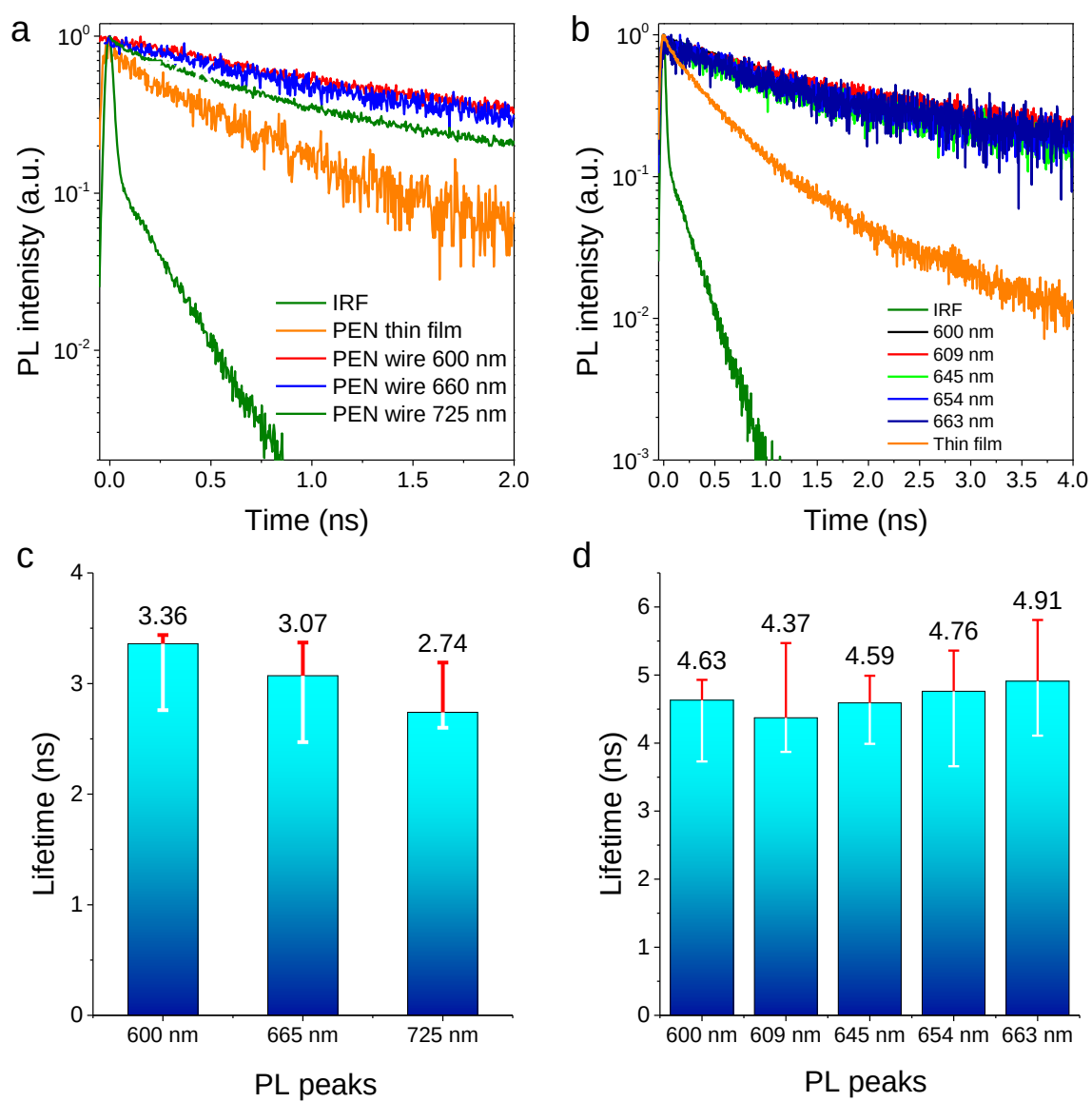


Figure 4

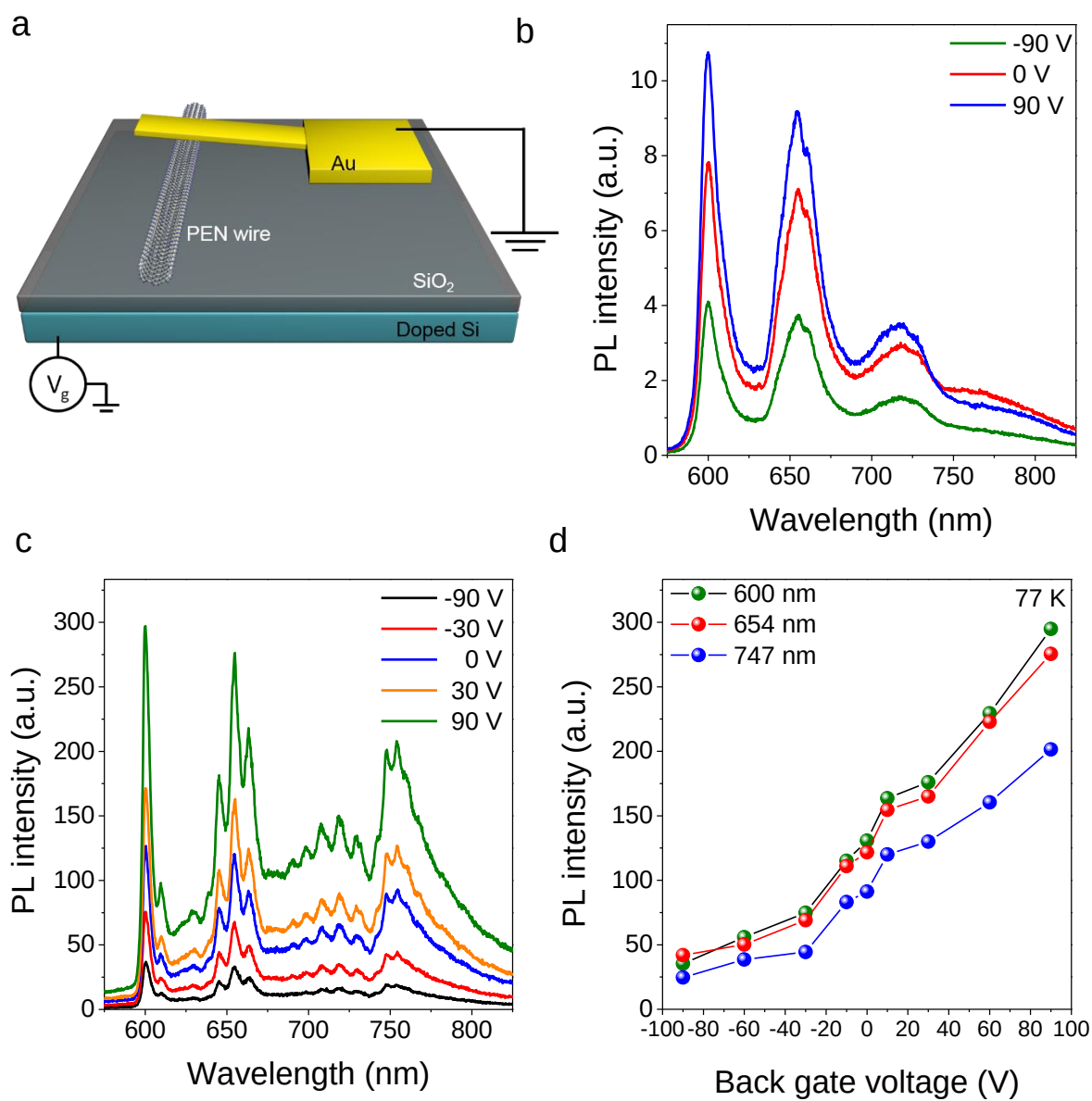


Figure 5

Figure Captions

Figure 1 | Characterization of PEN wires **a**, Optical microscope image of the quasi 1D PEN wires used for measurements. The scale bar is 5 μm . Inset: PL mapping image of the PEN wires showing the strong emission from wires. **b**, Zoomed Atomic force microscope (AFM) image of the PEN wires confirming the diameter to be ~ 300 nm. **c**, Schematic representation of the growth mechanism of the PEN wires during the vapor deposition mechanism. See text for details. **d**, SEM image of the PVD grown PEN wires on hBN substrate, showing the morphology of the wire. **e**, PL emission spectra (red curve) from PEN wires at room temperature, showing three clear peaks at 600 nm, 660 nm and 730 nm. Broad sideband PL emission from bulk (green) and thin film crystalline pentacene grown on hBN (blue) is also shown for comparison.

Figure 2 | Temperature dependent PL emission and Shpol'skii effect. **a**, Measured PL spectra at various temperatures from PEN wires. The vibronic levels are well resolvable at cryogenic temperatures as evident from quasi-line spectral emissions. **b**, PL emission spectra comparison between PEN wires grown on hBN with PEN needles grown in SiO_2 at 77 K. The PEN needles on SiO_2 do not show the clearly resolvable vibronic levels as shown from PEN wires grown on hBN. **c**, Schematic showing the energy level diagram in pentacene. The exciton bands with vibrational coupling for pentacene thin film (left) are shown. Only first three vibronic bands are shown. The vibronic bands (red) are demonstrated by $v = 1, 2, 3, \dots$ and the vibrational bands (grey) formed due to strong coupling between the exciton and phonons are shown by $\tilde{v} = 1, 2, 3, \dots$. The spread or thickness of vibrational levels accounts for the level of phononic coupling and degree of freedom in all cases. The molecules in bulk thin film case are at various energy levels leading to an emission band broadening and the PL emission is a broad sideband phononic emission as shown in Figure 1d. The vibronic levels in PEN wires at RT are further resolved due to confinement of molecules distinctly in the lattice with specific geometric configuration and high degree of orientation. In this case more neighboring molecules have similar energy levels, leading to a degenerate PL emission spectrum as shown in Figure 1d. At low temperature (right), the charge-phonon coupling, or vibrational coupling is further reduced leading to even further reduced thickness of vibrational levels at low temperature. As result the vibronic levels are well defined due to reduced degree of freedom of molecules and minimal charge-phonon coupling. This effect of observing

quasi-line spectra at low temperature is called Shpol'skii effect as shown in Figure 2a. **d**, Debye-Waller (DW) factor obtained from PEN wire (peak = 600 nm) and 1L WSe₂ (peak = 750 nm) as a function of the temperature. At 77 K the DW factor is much higher in PEN wires as compared to TMDC monolayers confirming an almost zero phonon emission or a quasi-linear PL emission. **e**, Variation of full-width half maximum (FWHM) of excitonic PL emission peaks from PEN wires (peak = 600 nm) and WSe₂ (peak = 750 nm). The FWHM from PEN wire excitonic emission is much lower as compared to TMD monolayer and the reduction in FWHM with temperature to ~ 3 nm, confirms the zero-phonon line emission from PEN wires.

Figure 3 | Polarization angle-dependent PL measurements. **a**, Measured PL intensity as a function of emission polarization angle θ from PEN wire samples at room temperature, revealing the anisotropic excitonic nature of emission from the PEN wires. In experiment, the excitation polarization angle was fixed and the polarization angle of the emission θ was determined by using an angle-variable polarizer located in front of the detector. **b**, Schematic diagram showing the growth morphology and crystalline structure molecular arrangement in PEN wires grown on hBN. The molecular axis as in a conventional triclinic pentacene crystal have been marked as a, b and c. The inset SEM image shows the 001 and 100 face of as grown PEN wires. **c**, Measured polar plot of PL emission spectra peaks as a function of emission polarization angle θ from PEN wires at room temperature revealing the opposite anisotropic excitonic nature of PL emission peaks at 600 nm, 660 nm and 730 nm. **d**, Measured PL intensity as a function of emission polarization angle θ from PEN wire samples at 77 K. **e-f**, Measured polar plot of PL emission spectra peaks as a function of emission polarization angle θ from PEN wires at 77 K revealing the opposite anisotropic excitonic nature of PL emission peaks. For remaining polar plots see Figure S10.

Figure 4 | Time-resolved PL emission from PEN wires. **a-b**, Time-resolved PL emission (normalized) from PEN wires at 298 K (a) and 77 K (b). The orange curve represents the decay curve from bulk thin film pentacene for comparison. An effective long lifetime of 1.24 ns (1.01 ns) was extracted from the orange decay curve at 298 K (77 K), by a fitting with deconvolution using the instrument response function (IRF) (green curve). The red/blue balls represent decay curve from 1L, which is from FR exciton emission. The red (600 nm), blue (660 nm) and green (730 nm) decay curves are from

PEN wires PL emission spectra. The deconvolution using IRF, gives an effective lifetime value of 3.36 ns, 3.07 ns and 2.74 ns respectively at 298 K. Similarly, at 77 K, deconvolution with IRF has been used to extract a long lifetime from various peaks at 77 K. See text for values. **c-d**, Graphical representation (with experimental errors bars) showing the distribution of extracted lifetime from various peaks of PL emission spectra from PEN wires. For peak positions refer to Table S2.

Figure 5 | Back gate dependent modulation of PL emission from PEN wire MOS device. **a**, Schematic diagram of the MOS device used for static doping of charges into the PEN wire. (See optical image in Figure 1a). **b**, Measured PL spectra from PEN wire sample at room temperature under various back gate voltages, showing clear modulation of all emission peaks. **c**, Measured PL spectra from PEN wire sample at 77 K under various back gate voltages, showing similar modulation of all emission peaks as observed at room temperature. **d**, Variation of peak = 600 nm, 654 nm and 747 nm as a function of sweeping back gate voltage at 77 K, demonstrating a clear n-type doping in the PEN wire. The MOS device confirms the external control of the PL emission that can be achieved by modulating back gate voltage.

References

1. O. Sild, K. Haller, *Zero-Phonon Lines: And Spectral Hole Burning in Spectroscopy and Photochemistry*. (Springer Science & Business Media, 2012).
2. A. V. Naumov, Low-temperature spectroscopy of organic molecules in solid matrices: from the Shpol'skii effect to laser luminescent spectromicroscopy for all effectively emitting single molecules. *Physics-Uspekhi* **56**, 605-622 (2013).
3. A. Kiraz *et al.*, in *Photonic Materials, Devices, and Applications*. (International Society for Optics and Photonics, 2005), vol. 5840, pp. 584-592.
4. Y. S. Zhao, A. Peng, H. Fu, Y. Ma, J. Yao, Nanowire waveguides and ultraviolet lasers based on small organic molecules. *Advanced Materials* **20**, 1661-1665 (2008).
5. D. O'carroll, I. Lieberwirth, G. Redmond, Microcavity effects and optically pumped lasing in single conjugated polymer nanowires. *Nature nanotechnology* **2**, 180 (2007).
6. Y. S. Zhao *et al.*, Optical waveguide based on crystalline organic microtubes and microrods. *Angewandte Chemie International Edition* **47**, 7301-7305 (2008).
7. Y. S. Zhao *et al.*, Construction and optoelectronic properties of organic one-dimensional nanostructures. *Accounts of chemical research* **43**, 409-418 (2009).
8. M. Law *et al.*, Nanoribbon waveguides for subwavelength photonics integration. *Science* **305**, 1269-1273 (2004).
9. Y. S. Zhao *et al.*, Tunable emission from binary organic one-dimensional nanomaterials: an alternative approach to white-light emission. *Advanced Materials* **20**, 79-83 (2008).
10. Y. S. Zhao, H. Fu, F. Hu, A. D. Peng, J. Yao, Multicolor emission from ordered assemblies of organic 1D nanomaterials. *Advanced Materials* **19**, 3554-3558 (2007).
11. P. d. Bree, D. A. Wiersma, Application of Redfield theory to optical dephasing and line shape of electronic transitions in molecular mixed crystals. *The Journal of Chemical Physics* **70**, 790-801 (1979).
12. K. K. Rebane, Zero-phonon line as the foundation stone of high-resolution matrix spectroscopy, persistent spectral hole burning, single impurity molecule spectroscopy. *Chemical Physics* **189**, 139-148 (1994).
13. É. V. Shpol'skiĭ, LINE FLUORESCENCE SPECTRA OF ORGANIC COMPOUNDS AND THEIR APPLICATIONS. *Soviet Physics Uspekhi* **3**, 372-389 (1960).
14. Y. S. Zhao, D. Xiao, W. Yang, A. Peng, J. Yao, 2, 4, 5-Triphenylimidazole nanowires with fluorescence narrowing spectra prepared through the adsorbent-assisted physical vapor deposition method. *Chemistry of materials* **18**, 2302-2306 (2006).
15. S. Xiao *et al.*, Transferring self-assembled, nanoscale cables into electrical devices. *Journal of the American Chemical Society* **128**, 10700-10701 (2006).
16. S. Berson, R. De Bettignies, S. Bailly, S. Guillerez, Poly (3-hexylthiophene) fibers for photovoltaic applications. *Advanced Functional Materials* **17**, 1377-1384 (2007).
17. J. A. Merlo, C. D. Frisbie, Field effect transport and trapping in regioregular polythiophene nanofibers. *The Journal of Physical Chemistry B* **108**, 19169-19179 (2004).

18. D. Kim *et al.*, Single-crystal polythiophene microwires grown by self-assembly. *Advanced Materials* **18**, 719-723 (2006).
19. A. L. Briseno, S. C. Mannsfeld, S. A. Jenekhe, Z. Bao, Y. Xia, Introducing organic nanowire transistors. *Materials Today* **11**, 38-47 (2008).
20. A. P. Schenning, E. Meijer, Supramolecular electronics; nanowires from self-assembled π -conjugated systems. *Chemical Communications*, 3245-3258 (2005).
21. H. Fu, D. Xiao, J. Yao, G. Yang, Nanofibers of 1, 3-diphenyl-2-pyrazoline induced by cetyltrimethylammonium bromide micelles. *Angewandte Chemie International Edition* **42**, 2883-2886 (2003).
22. J.-S. Hu, Y.-G. Guo, H.-P. Liang, L.-J. Wan, L. Jiang, Three-dimensional self-organization of supramolecular self-assembled porphyrin hollow hexagonal nanoprisms. *Journal of the American Chemical Society* **127**, 17090-17095 (2005).
23. L. Kang *et al.*, Organic core/diffuse-shell nanorods: fabrication, characterization and energy transfer. *Chemical Communications*, 2695-2697 (2007).
24. B. K. An, S. K. Kwon, S. Y. Park, Photopatterned arrays of fluorescent organic nanoparticles. *Angewandte Chemie* **119**, 2024-2028 (2007).
25. B.-K. An, S.-K. Kwon, S.-D. Jung, S. Y. Park, Enhanced emission and its switching in fluorescent organic nanoparticles. *Journal of the American Chemical Society* **124**, 14410-14415 (2002).
26. M. T. Lloyd, J. E. Anthony, G. G. Malliaras, Photovoltaics from soluble small molecules. *Materials Today* **10**, 34-41 (2007).
27. T. J. Shin *et al.*, Tunable thin-film crystalline structures and field-effect mobility of oligofluorene-thiophene derivatives. *Chemistry of Materials* **19**, 5882-5889 (2007).
28. D. M. DeLongchamp *et al.*, High carrier mobility polythiophene thin films: structure determination by experiment and theory. *Advanced Materials* **19**, 833-837 (2007).
29. F. C. Spano, The Spectral Signatures of Frenkel Polarons in H- and J-Aggregates. *Accounts of Chemical Research* **43**, 429-439 (2010).
30. H. Y. Woo *et al.*, Solvent Effects on the Two-Photon Absorption of Distyrylbenzene Chromophores. *Journal of the American Chemical Society* **127**, 14721-14729 (2005).
31. J. E. Park, M. Son, M. Hong, G. Lee, H. C. Choi, Crystal-Plane-Dependent Photoluminescence of Pentacene 1D Wire and 2D Disk Crystals. *Angewandte Chemie* **124**, 6489-6494 (2012).
32. A. Bloess *et al.*, Microscopic Structure in a Shpol'skii System: A Single-Molecule Study of Dibenzanthanthrene in n-Tetradecane. *The Journal of Physical Chemistry A* **105**, 3016-3021 (2001).
33. V. A. Kizel, M. N. Sapozhnikov, The Interaction of Impurity Centres with the Surroundings and Quasi-Line Spectra. *physica status solidi (b)* **41**, 207-216 (1970).
34. W. Zhang, Y. Yan, J. Gu, J. Yao, Y. S. Zhao, Low-Threshold Wavelength-Switchable Organic Nanowire Lasers Based on Excited-State Intramolecular Proton Transfer. *Angewandte Chemie International Edition* **54**, 7125-7129 (2015).
35. M. Muccini, A bright future for organic field-effect transistors. *Nature Materials* **5**, 605 (2006).
36. X. Duan, Y. Huang, R. Agarwal, C. M. Lieber, Single-nanowire electrically driven

lasers. *Nature* **421**, 241 (2003).

37. J. E. Anthony, Functionalized Acenes and Heteroacenes for Organic Electronics. *Chemical Reviews* **106**, 5028-5048 (2006).

38. Y. Zhang *et al.*, Probing Carrier Transport and Structure-Property Relationship of Highly Ordered Organic Semiconductors at the Two-Dimensional Limit. *Physical Review Letters* **116**, 016602 (2016).

39. F. C. Spano, Optical microcavities enhance the exciton coherence length and eliminate vibronic coupling in J-aggregates. *The Journal of Chemical Physics* **142**, 184707 (2015).

40. D. Beljonne, H. Yamagata, J. L. Brédas, F. C. Spano, Y. Olivier, Charge-Transfer Excitations Steer the Davydov Splitting and Mediate Singlet Exciton Fission in Pentacene. *Physical Review Letters* **110**, 226402 (2013).

41. H. Yamagata, F. C. Spano, Strong Photophysical Similarities between Conjugated Polymers and J-aggregates. *The Journal of Physical Chemistry Letters* **5**, 622-632 (2014).

42. P. Tokousbalides, Observation of quasilinear fluorescence spectra (the "Shpol'skii effect") in matrix-isolated polycyclic aromatic hydrocarbons. *Journal of physical chemistry (1952)* **81**, 1769-1772.

43. D. E. McCumber, M. D. Sturge, Linewidth and Temperature Shift of the R Lines in Ruby. *Journal of Applied Physics* **34**, 1682-1684 (1963).

44. R. H. Silsbee, Thermal Broadening of the Mossbauer Line and of Narrow-Line Electronic Spectra in Solids. *Physical Review* **128**, 1726-1733 (1962).

45. V. F. Sears, Debye-Waller factor for elemental crystals. *Acta crystallographica. Section A, Foundations of crystallography* **47**, 441-446.

46. Y. G. Vainer, M. A. Kol'chenko, A. V. Naumov, R. I. Personov, S. J. Zilker, Photon echoes in doped organic amorphous systems over a wide (0.35–50K) temperature range. *Journal of Luminescence* **86**, 265-272 (2000).

47. A. L. Briseno *et al.*, Perylenediimide Nanowires and Their Use in Fabricating Field-Effect Transistors and Complementary Inverters. *Nano Letters* **7**, 2847-2853 (2007).

48. M. G. Debije *et al.*, Dramatic increase in charge carrier lifetime in a liquid crystalline perylene bisimide derivative upon bay substitution with chlorine. *Journal of Materials Chemistry* **15**, 1270-1276 (2005).

49. E. Aghaei, M. Haghighi, Enhancement of catalytic lifetime of nanostructured SAPO-34 in conversion of biomethanol to light olefins. *Microporous and Mesoporous Materials* **196**, 179-190 (2014).

50. M. Palummo, M. Bernardi, J. C. Grossman, Exciton radiative lifetimes in two-dimensional transition metal dichalcogenides. *Nano letters* **15**, 2794-2800 (2015).

Supplementary Information

Quasi-line spectral emissions from high crystalline 1D Organic Nanowires

Ankur Sharma^{1§}, Ahmed Khan^{1§}, Yi Zhu¹, Robert Halbach¹, Wendi Ma¹ and Yuerui Lu^{1*}

¹Research School of Electrical, Energy and Materials Engineering, College of Engineering and Computer Science, the Australian National University, Canberra, ACT, 2601, Australia.

* To whom correspondence should be addressed: Yuerui Lu (yuerui.lu@anu.edu.au)

§ These authors contributed equally to the work.

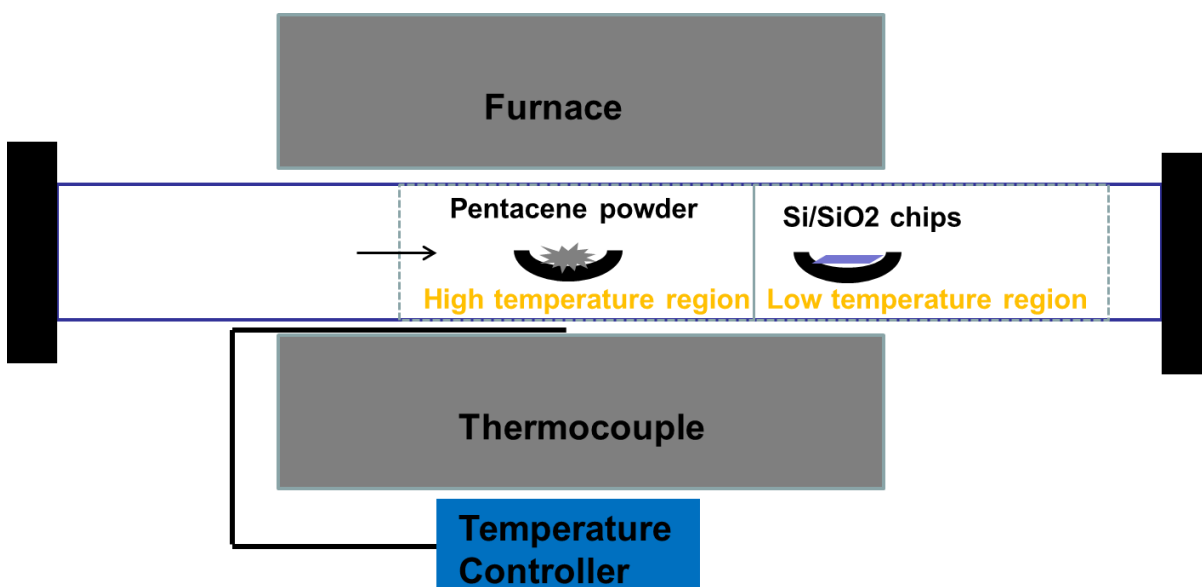


Figure S1 | Schematic diagram of the furnace used for growth of 1D pentacene (PEN) wires.

Supplementary Information Note 1:

1D Pentacene wires were realized on exfoliated h-BN over a Si/SiO₂ substrate by thermal evaporation of Pentacene source. The figure S1 depicts the schematic experimental setup for physical vapor deposition (PVD) of 1D Pentacene. First, we used mechanically exfoliated few-layer hBN sheet on 285nm-thick SiO₂ on Si (SiO₂/Si) as the growth substrate without further annealing. Before growth, the hBN sheets were topographically examined using an optical microscope. The epitaxial growth of pentacene was carried out in a tube furnace. We put the pentacene powder at the centre of the furnace and the hBN sheets a few inches downstream and used a turbo molecular pump to evacuate the quartz tube to $\sim 10^{-4}$ MPa. We then heated up the furnace to 135-180°C to grow pentacene wires. The length of the wires was controlled by the source temperature, the substrate position and growth time. When the growth was finished, we turned off the furnace and let the sample cool down to room temperature under vacuum.

We used 135-180°C temperature range in the growth process. We obtained pentacene wires growth on hBN which grew bigger to achieve the maximum average length around 15 microns at 155°C. The average length followed a reduction in value at higher temperature after 155 °C. (Figure S3). In order to find out the most optimized growth time, we used 1 hr, 3hr, 4 hr and 24 hr growth time. 3 hrs growths were found to be the growth with highest yield including large sized pentacene wires. (Figure S3).

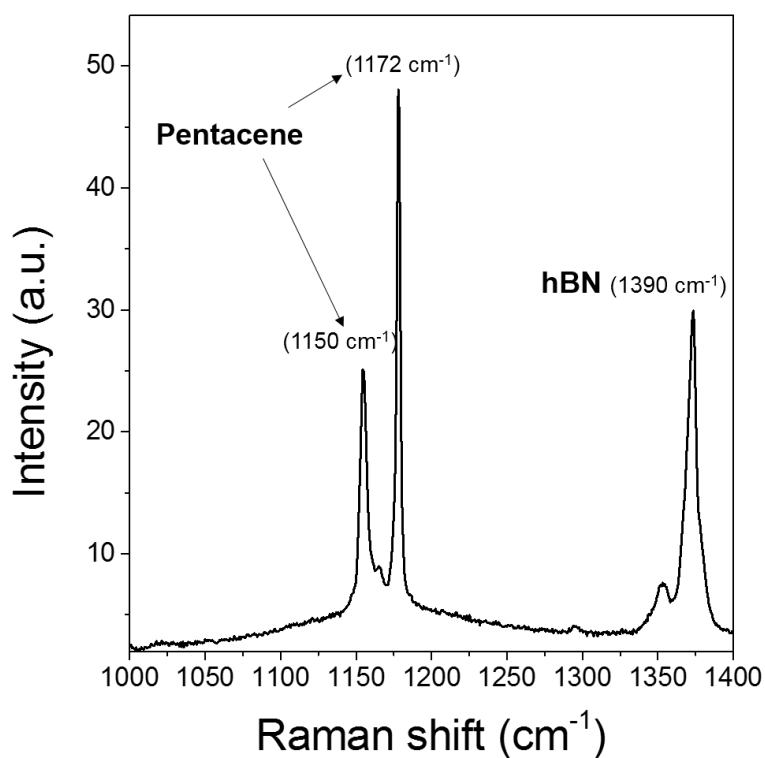


Figure S2 | Measured Raman spectrum from a 1D PEN wire sample grown on a h-BN flake. Peaks at 1150 cm⁻¹ and 1172 cm⁻¹ are for pentacene and peak at 1390 cm⁻¹ is for h-BN.

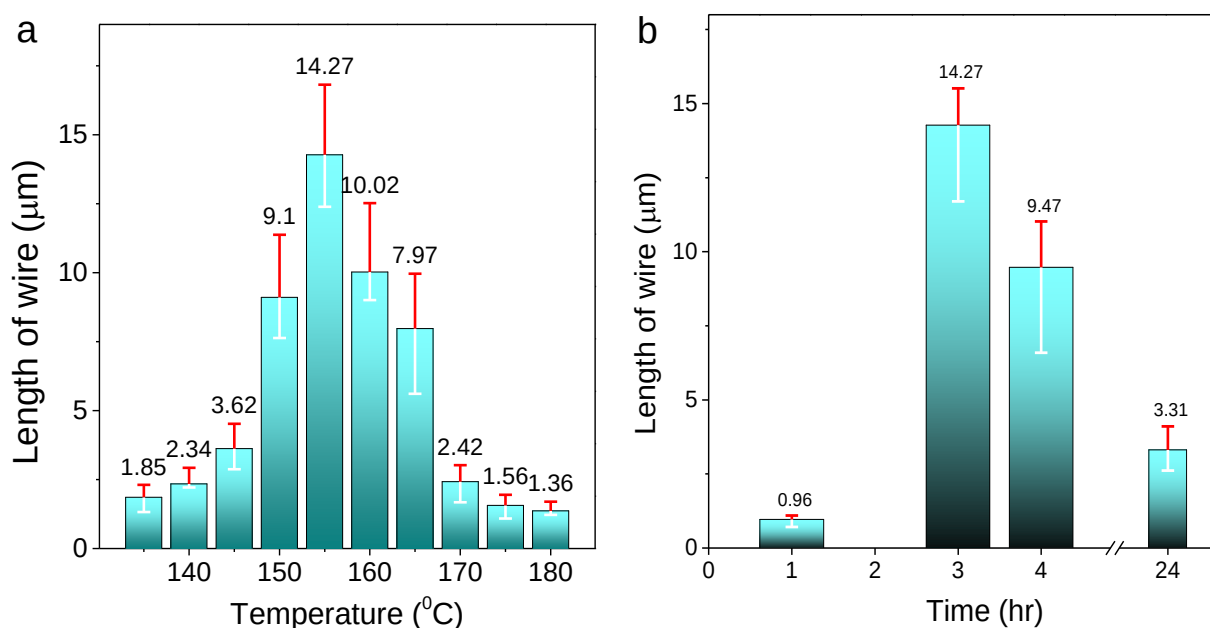


Figure S3 | Growth optimization of PEN wires **a**, Length of PEN wires as a function of growth temperature in the furnace. The maximum length of the wires was obtained at 155 $^{\circ}\text{C}$. The error bars demonstrate the experimental deviation as obtained after several optimization runs. **b**, The length of PEN wires as a function of growth time in the PVD furnace. The longest wires with clear morphology were obtained at 3-hour growth mark.

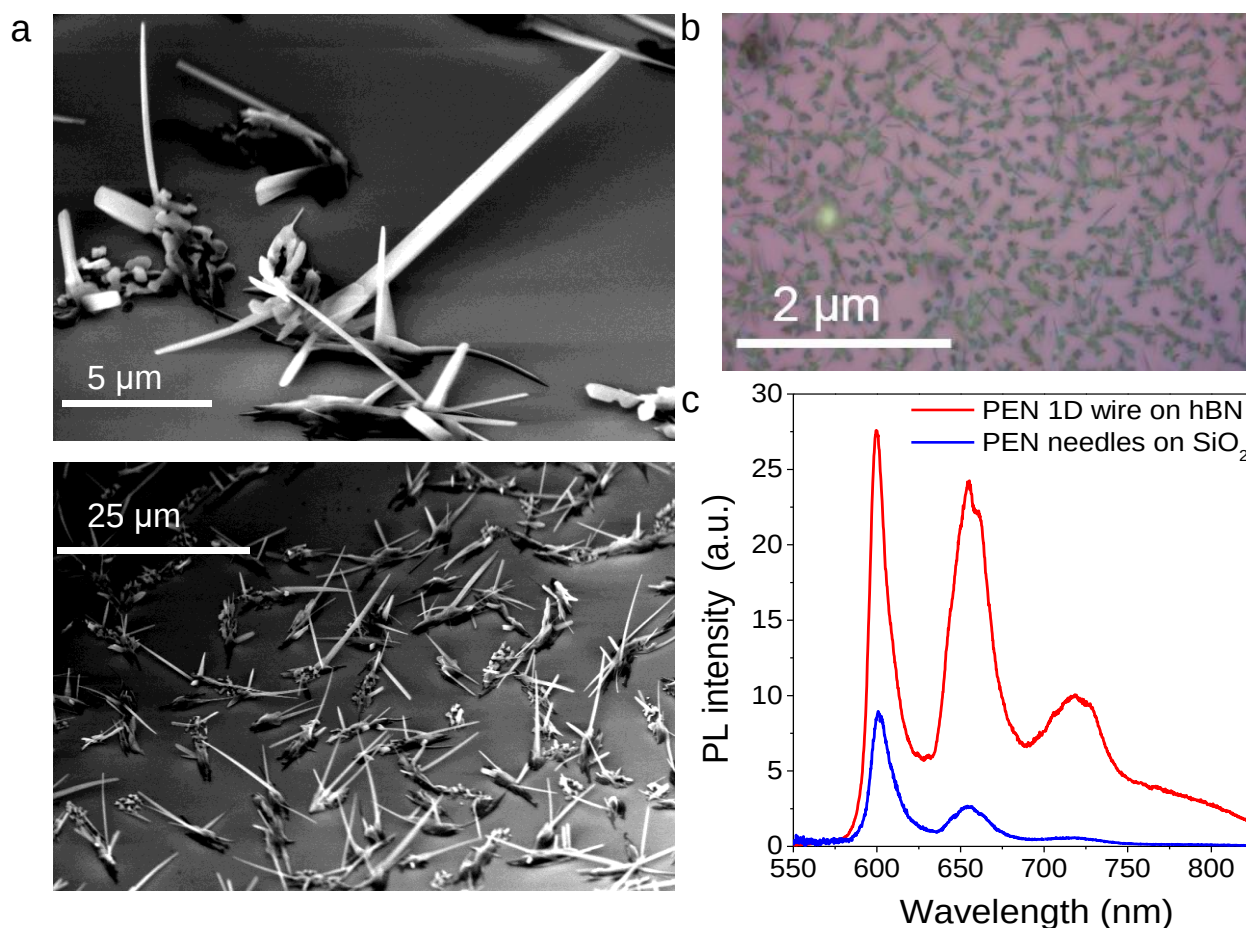


Figure S4 | Comparison between wires and needles **a**, SEM and optical (**b**) images of PEN needle like structures grown under same growth conditions as discussed in FigureS1. The PEN needles on SiO₂ grow out of nucleation sites and diverge into needle-like structures as shown in FigureS2b. Whereas, on hBN the PEN wires follows higher degree of orientation and crystallinity and converge to form tube like wire structures (See Figure1c). hBN serves as a stencil to help ordered growth of PEN H-bonded molecular chains in to wire like cylindrical quasi 1D structures. **c**, PL spectra comparison from PEN wires grown on hBN as compared to the PEN needles grown on SiO₂. The PL emission from PEN wires is much stronger and vibronic levels are well resolved as compared to the needles on SiO₂.

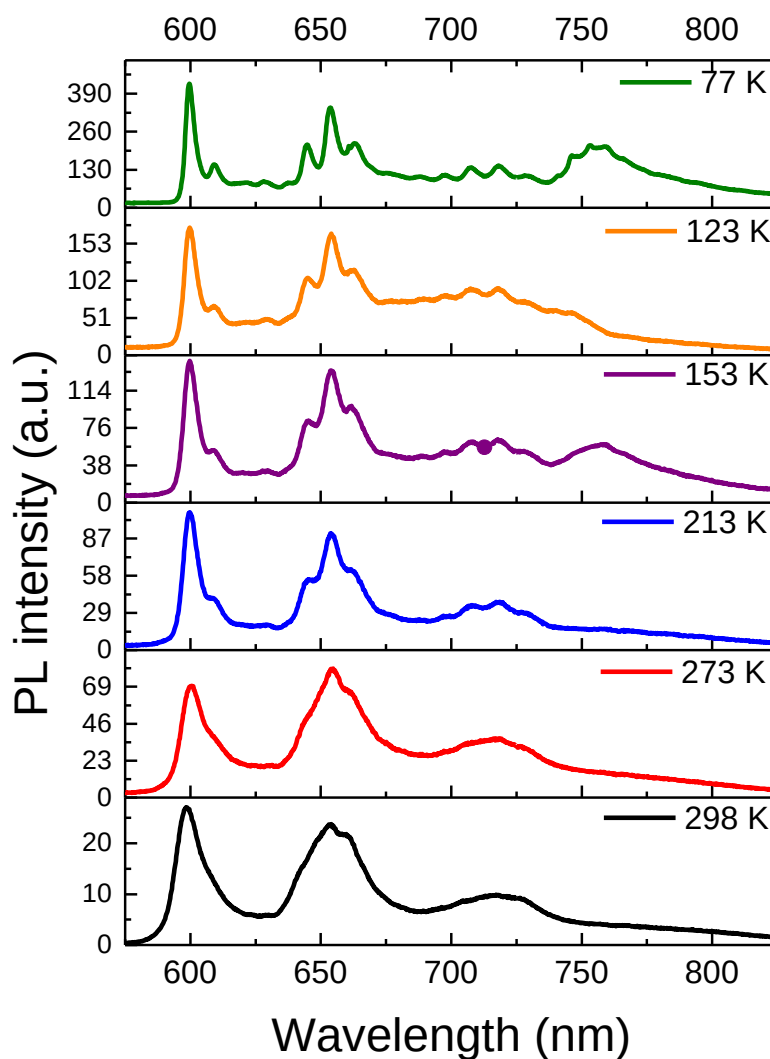


Figure S5 | Temperature dependent PL spectra from PEN wires. PL emission spectra at various temperatures showing the clear resolvable vibronic levels as the temperature is reduced and the emergence of quasi-line Shpol'skii spectra at 77 K. The quasi line spectra start to emerge at 213 K and are fully resolvable as the temperature is further reduced.

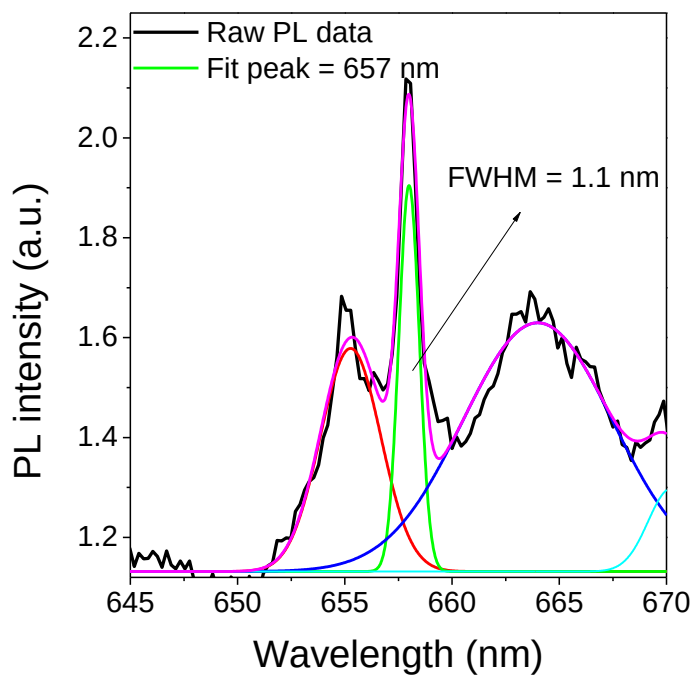


Figure S6 | Narrow line width emission. PL emission from some of the optimal grown PEN wires, where the FWHM ≈ 1 nm. Lorentzian fitting function has been used to fit the PL peaks.

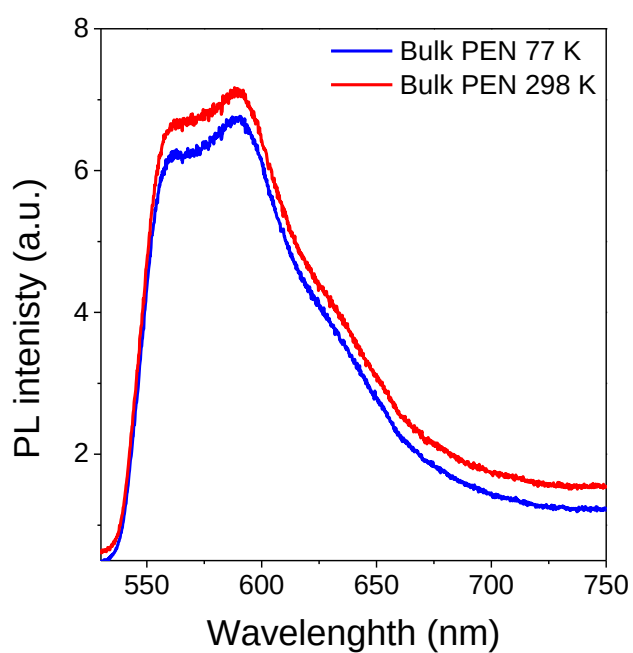


Figure S7 | PL emission from thin film PEN. PL emission peak from thin film bulk crystalline PEN samples grown on hBN at room temperature and 77 K. The average thickness of the films around 70-100 nm.

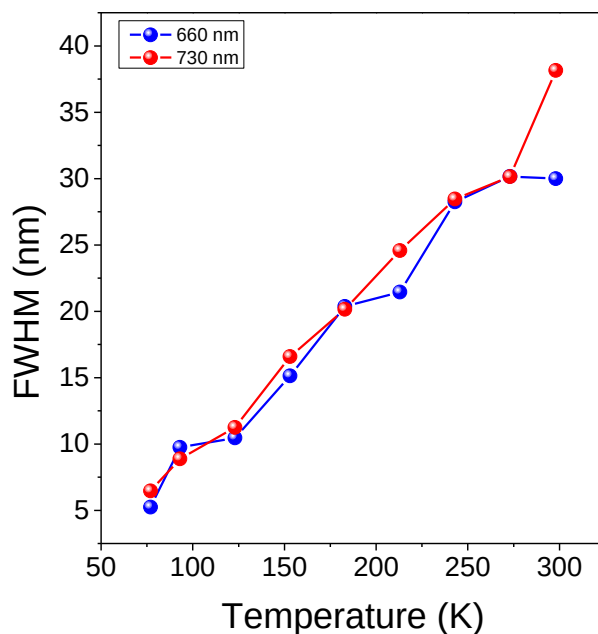


Figure S8 | FWHM vs temperature. Variation of FWHM of peak = 660 nm and peak = 730 nm as a function of temperature. The variation of peak = 600 nm is shown in Main text Figure 2e.

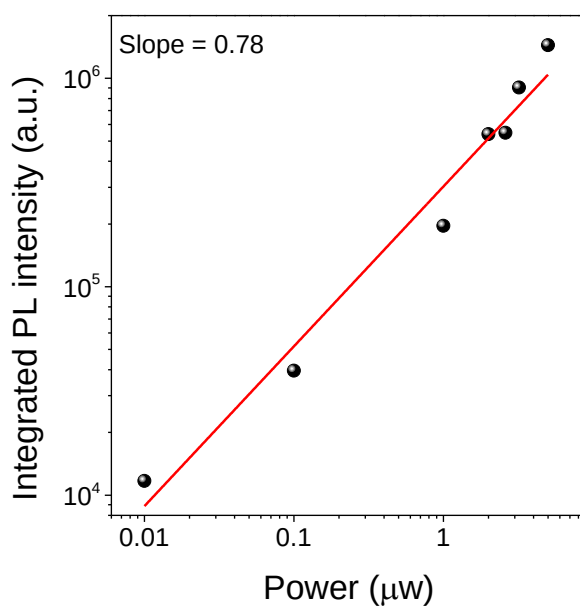


Figure S9 | Pumping power dependent PL measurement. Variation of the 600 nm peak at 77 K with increasing pumping power. The sub-linear slope confirms that it is not lasing at this stage.

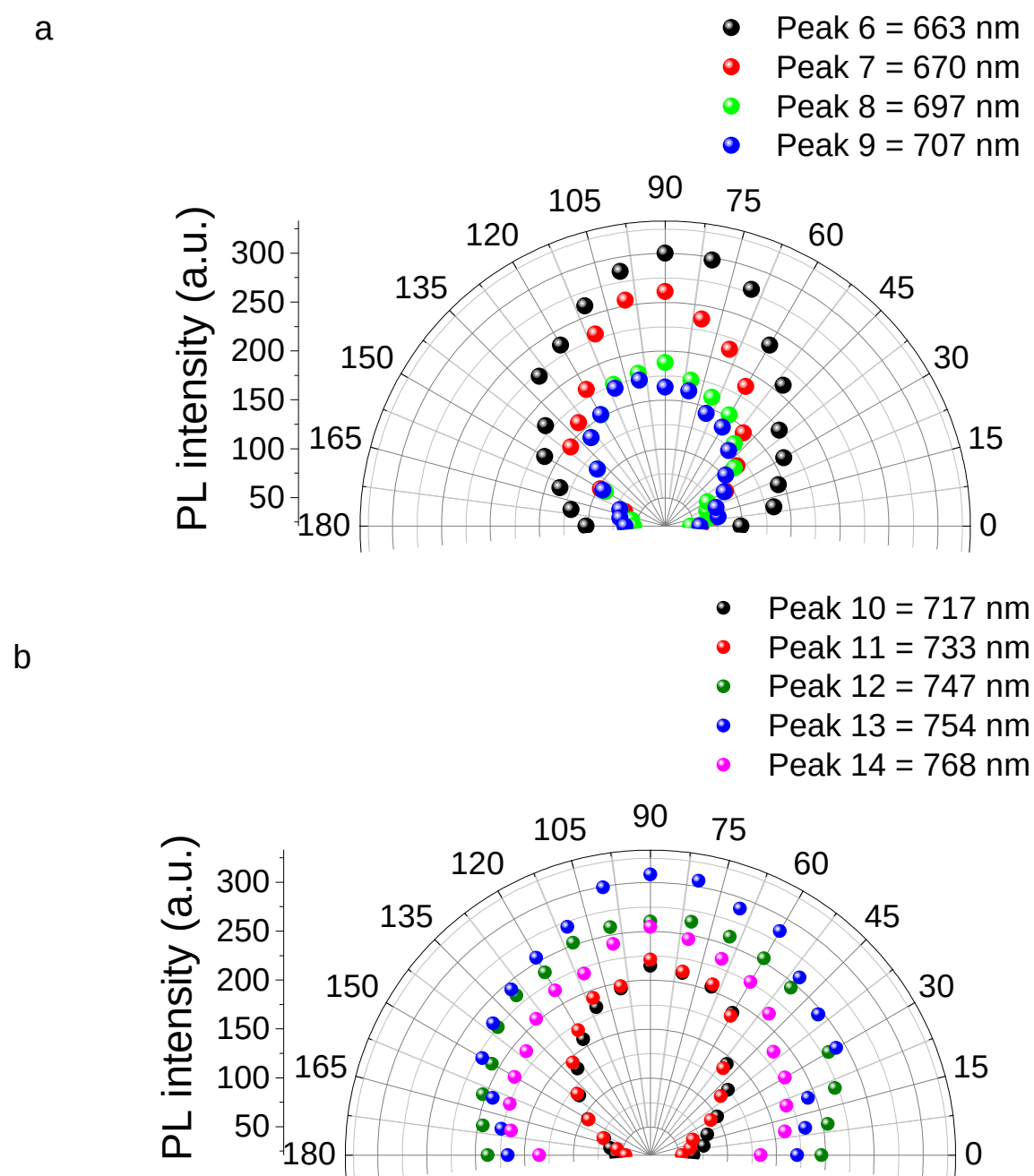


Figure S10 | Polarization angle-dependent PL measurements. Measured polar plot of PL emission spectra peaks (6-14) as a function of emission polarization angle θ from PEN wires at 77 K revealing the opposite anisotropic excitonic nature of PL emission peaks. For polar plots of peaks 1-5, refer to main text Figure 3.

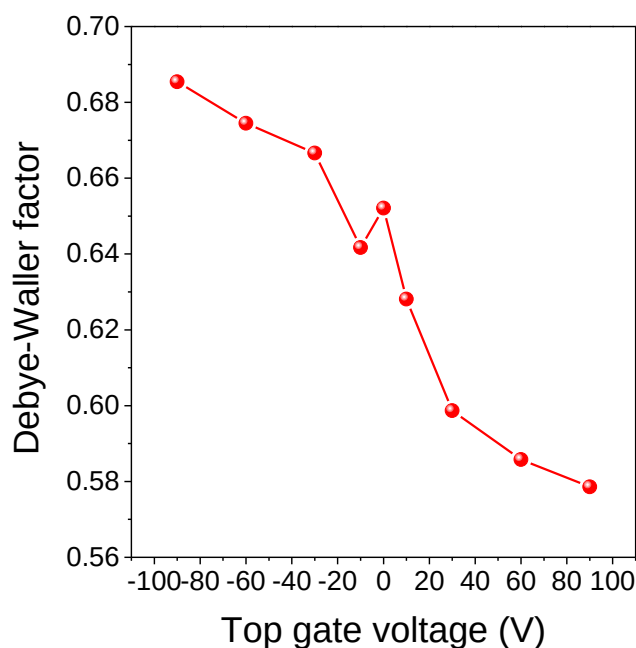


Figure S11 | Debye-Waller factor as a function of back gate voltage. The DW factor has been extracted as a function of back gate voltage. The DW factor shows a clear modulation with change in back gate voltage which can be attributed to the change of doping levels with change in back gate voltage affecting the PL emission efficiency at different back gate voltages. This demonstrates the use of external voltage to control the quasi line spectra or zero-phonon line (ZPL) emissions from 1D PEN wires.

Table S1: Full-width half maximum (FWHM) from other nanowire and Shpol skii matrix solutions

	System	Temperature (K)	FWHM (nm)
Nanowire Systems	GaN(1)	298	12
	CdS single crystal(2)	298	18-24*
	ZnO(3)	10	1.4
	InAsSb(4)	77	40-70
	Rubrene(5)	298	50
	DPBT single crystal(6)	77	2.9
	DMHP(7)	298	82*
	Organic-inorganic Perovskite(8)	298	10-32*
Shpol 'skii Matrices	Single perylene molecules in n-nonane(9)	1.7	1-2
	Terrylene in hexadecane(10)	1.7	0.3
	DBATT in n-tetradecane(11)	1.2	1.1-1.3
	TDI in hexadecane(12, 13)	1.7	1
	Pentacene in n-tetradecane(14)	1.2	0.5-1
	Single Crystal DCNP(15)	5	5

Peak Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Peak Position (nm)	600	609	645	654	657	663	670	697	707	717	733	747	754	768

Table S2 | Peak positions at 77 K. PL emission spectra 77 K was fitted using a Lorentzian function and the resultant 14 peak positions have been tabulated in table above.

References

1. S. Gradečak, F. Qian, Y. Li, H.-G. Park, C. M. Lieber, GaN nanowire lasers with low lasing thresholds. *Applied Physics Letters* **87**, 173111 (2005).
2. X. Duan, Y. Huang, R. Agarwal, C. M. Lieber, Single-nanowire electrically driven lasers. *Nature* **421**, 241-245 (2003).
3. W. I. Park, Y. H. Jun, S. W. Jung, G.-C. Yi, Excitonic emissions observed in ZnO single crystal nanorods. *Applied Physics Letters* **82**, 964-966 (2003).
4. A. C. Farrell *et al.*, High-quality InAsSb nanowires grown by catalyst-free selective-area metal–organic chemical vapor deposition. *Nano letters* **15**, 6614-6619 (2015).
5. J. W. Lee *et al.*, Light-Emitting Rubrene Nanowire Arrays: A Comparison with Rubrene Single Crystals. *Advanced Functional Materials* **19**, 704-710 (2009).
6. C. Zhang *et al.*, Two-Photon Pumped Lasing in Single-Crystal Organic Nanowire Exciton Polariton Resonators. *Journal of the American Chemical Society* **133**, 7276-7279 (2011).
7. X. Wang *et al.*, Tunable Near-Infrared Organic Nanowire Nanolasers. *Advanced Functional Materials* **27**, 1703470 (2017).
8. P. Liu *et al.*, Organic–Inorganic Hybrid Perovskite Nanowire Laser Arrays. *ACS Nano* **11**, 5766-5773 (2017).
9. M. Pirrotta, A. Renn, M. H. Werts, U. P. Wild, Single molecule spectroscopy. Perylene in the Shpol'skii matrix n-nonane. *Chemical physics letters* **250**, 576-582 (1996).
10. W. Moerner *et al.*, Optical probing of single molecules of terrylene in a shpol'kii matrix: A two-state single-molecule switch. *The Journal of Physical Chemistry* **98**, 7382-7389 (1994).
11. A. Bloess *et al.*, Microscopic structure in a Shpol'skii system: A single-molecule study of Dibenzanthanthrene in n-Tetradecane. *The Journal of Physical Chemistry A* **105**, 3016-3021 (2001).

12. A. Kiraz *et al.*, in *Photonic Materials, Devices, and Applications*. (International Society for Optics and Photonics, 2005), vol. 5840, pp. 584-592.
13. A. Kiraz *et al.*, in *Journal of Physics: Conference Series*. (IOP Publishing, 2006), vol. 36, pp. 67.
14. Y. Durand *et al.*, An optical study of single pentacene molecules in n-tetradecane. *Chemical Physics Letters* **317**, 232-237 (2000).
15. O. Morawski, A. L. Sobolewski, B. Kozankiewicz, L. Sznitko, A. Miniewicz, On the origin of fluorescence emission in optically non-linear DCNP crystals. *Physical Chemistry Chemical Physics* **16**, 26887-26892 (2014).

CHAPTER 6

Engineering the Exciton/Trion Dynamics and Transport in Monolayer WS₂

The study of transport and diffusion dynamics of quasi particles such as excitons and trions in two dimensional (2D) semiconductors has opened avenues for their application in functional optoelectronic devices. But long-range transport and ultra-fast diffusion of these quasi particles has not been reported for 2D inorganic materials such as transition metal dichalcogenides (TMDCs), which is significantly lower than their organic counterparts. The thesis discusses the exciton dynamics in detail in organic low dimensional systems in chapter 4 and 5. The thesis focussed on developing a new technique to measure the exciton diffusion using spectrally resolved CCD imaging and time-resolved PL imaging for organic nanomaterials discussed in earlier chapters. While doing a comparison with

inorganic counterparts in Chapter 4, such as monolayer TMDC materials, we observed that the exciton diffusion coefficients in inorganic materials were low as compared to the organic materials. This is a direct consequence of higher dielectric constant in the inorganic materials. But, as described in chapter 3, the binding energies of excitons are very high in monolayer TMDC materials such as WS₂. This motivated me to explore and engineer the exciton dynamics in inorganic monolayer TMDC materials. Additionally, there have been key demonstration of other quasi particles such as trions and biexcitons in these materials recently, which can lead to potential device applications based on these quasi particles.

As discussed in Chapter 1 and 3, the quasi particles, excitons, trions and biexcitons play a key role in determining the suitability of a 2D material for device applications. This chapter focusses on engineering the exciton dynamics in monolayer WS₂ using external back gate voltage by changing the doping in the semiconductor 2D material. This chapter reports the highest exciton diffusion coefficient value in monolayer WS₂ achieved via engineering the radiative lifetime and diffusion lengths using static back gate voltage and substrate engineering. Electrostatic doping is observed to modulate the radiative lifetime of excitons by ~3 times, which in turn can tune the diffusion coefficients to significantly high values, which have not been reported before in TMDCs. At low temperatures, we further report the control of dynamic and spatial diffusion of excitons, trions and biexcitons from WS₂. The electrostatic control of dynamics and transport of these quasi particles in monolayers opens avenues for high-speed excitonic circuits, optoelectronic and photonic device applications. This approach is in contrast to other approaches used to enhance long-range diffusion of excitons like supramolecular assemblies and nanofibers. This technique allows the use of 2D materials and their large interface for enhanced long-range exciton diffusion.

The chapter finally discusses the role of external modulation factors such as substrate screening and doping which determine the overall exciton, trion and biexciton dynamics in inorganic 2D materials, especially electrically tuneable TMDC materials. The approach discussed in this chapter can be extended to their similar TMDC materials and is critical for engineering the devices based on 2D inorganic materials for future optoelectronic and photonics device applications.

Engineering the Dynamics and Transport of Excitons, Trions, and Biexcitons in Monolayer WS₂

Ankur Sharma ¹, Yi Zhu¹, Robert Halbich¹, Linglong Zhang¹, Bowen Wang¹ and Yuerui Lu^{1*}

¹Research School of Electrical, Energy and Materials Engineering, College of Engineering and Computer Science, the Australian National University, Canberra, ACT, 2601, Australia

* To whom correspondence should be addressed: Yuerui Lu (yuerui.lu@anu.edu.au)

ABSTRACT: The study of transport and diffusion dynamics of quasi particles such as excitons, trions and biexcitons in two dimensional (2D) semiconductors has opened avenues for their application in high speed excitonic and optoelectronic devices. But long-range transport and fast diffusion of these quasi particles has not been reported for 2D systems such as transition metal dichalcogenides (TMDCs). The reported diffusion coefficients from TMDCs are low, limiting their use in high speed excitonic devices and other optoelectronic applications. Here, we report the highest exciton diffusion coefficient value in monolayer WS₂ achieved *via* engineering the radiative lifetime and diffusion lengths using static back gate voltage and substrate engineering. Electrostatic doping is observed to modulate the radiative lifetime and in turn the diffusion coefficient of excitons by ~3 times at room temperature. By combining electrostatic doping and substrate engineering, we push the diffusion coefficient to an extremely high value of 86.5 cm²/sec, which have not been reported before in TMDCs and is even higher than the values in some 1D systems. At low temperatures, we further report the control of dynamic and spatial diffusion of excitons, trions and biexcitons from WS₂. The electrostatic control of dynamics and transport of these quasi particles in monolayers opens avenues for high-speed excitonic circuits, optoelectronic and photonic device applications.

Keywords: Exciton diffusion, coefficient, electrostatic doping, suspended monolayer.

Introduction

Atomically thin two-dimensional (2D) layered transition metal dichalcogenides (TMDC)^{[1] [2]} semiconductors have been established recently as promising candidates for various optoelectronic and photonic device applications.^[3] In these 2D semiconductors, due to the reduced screening^[4] and enhanced coulombic coupling^[4-7] between charged particles, various quasi particles, such as excitons,^[4] trions^[5] and biexcitons^[8], have been reported. The binding energy of excitons in some cases has been reported to be >0.5 eV.^[9, 10] This makes them stable even at room temperature and dominates the opto-electronic properties of these semiconductors.^[11] Exciton transport is critical for the operation of the majority of optoelectronic devices such as light emitting diodes,^[12] excitonic lasers,^[13] excitonic transistors,^[14] exciton-polariton devices,^[15] photodetectors^[16] and solar cells.^[17] Particularly, energy transport in 2D materials occurs through motion of these tightly bound quasi-particles.^[18] Therefore, it is crucial to understand/control the dynamics and transport mechanism of these quasi particles in 2D semiconductors.

The diffusion coefficient is a function of the diffusion length (L_D) and the effective radiative lifetime (τ_{eff}) of the excitons. The diffusion length and lifetime are further dependent on three key parameters including doping, ^[19, 20] quantum confinement of charges^[4] due to reduced screening^[10] and surface/thermal scattering of charges.^[21] The doping affects the radiative lifetime of excitons, while the surface/thermal scattering causes non-linear energy loss in energy dissipation of excitons.^[16, 22, 23] The screening and quantum confinement are a resultant of the dimensionality of the system and hence affect the diffusion coefficient.^[24] As shown in Table S1 the values of diffusion coefficients reported increases as the dimensionality decreases from quasi 2D systems down to 1D systems. The value of diffusion coefficient in quasi 2D systems such as quantum wells was reported to be around 0.1 cm²/sec^[25] and around 3-15 cm²/sec in 2D TMDC monolayers.^[26-29] Subsequently, high values of exciton diffusion lengths and coefficients

have been reported recently from quasi-1D systems^[30, 31] such as CNTs ≈ 44 cm²/sec.^[32] However, the application of 1D CNTs for practical optoelectronic applications is intrinsically limited due to their small cross-sectional area. It is also difficult to assemble a large-sized film of CNTs due to diverse distribution of chirality in CNTs.^[33] The trade-off between higher exciton diffusion coefficient and low cross-sectional area has hindered their use for high speed excitonic applications.

Therefore, 2D TMDC materials provide the right alternative with higher cross-sectional area and a defect free surface^[29] to substantiate their applications in high-speed energy transport applications, but their low diffusion coefficients remain a big challenge. Diffusion coefficient has been used recently to quantify the extent of energy transport in TMDC monolayers. The dynamics of excitons and trions have been studied in TMDCs such as WS₂,^[29] WSe₂,^[26] MoTe₂,^[27] MoSe₂,^[28] and MoS₂,^[6, 23] using high resolution pump-probe^[30] and time-resolved photoluminescence (TRPL) studies.^[34] But, the values of the diffusion coefficient in TMDC materials reported (See Table S1) has been low to substantiate their applications for excitonic devices as mentioned above. There have been no reports that demonstrate dynamic control of lifetime and spatial diffusion lengths of excitons/trions in TMDC materials to realize long-range and ultra-fast energy transport. The parameters that we can engineer to enhance the diffusion of excitons in 2D TMDC materials are doping of charges and surface scattering of charges. Therefore, to achieve higher diffusion coefficients we need to engineer the diffusion dynamics excitons and trions in such 2D systems, to push the diffusion coefficient of excitons towards higher values like reported from quasi 1D systems.

Here, we report the engineering of the radiative lifetime and spatial diffusion of the quasi particles at room and cryogenic temperatures using static back gate modulation by incorporating the monolayer in to a metal-oxide semiconductor (MOS) device. We study

the exciton/trion equilibrium transport dynamics in both space and time-domain from a 1L WS₂ using a direct near-field CCD imaging technique [32, 35, 36] and picosecond resolution time-resolved PL detector. The change in doping significantly affects the diffusion dynamics in WS₂, allowing us to demonstrate a back-gate controlled diffusion of neutral and charged quasi particles. In order to realize the ultra-high value of diffusion coefficient in TMDCs comparable to quasi 1D systems as CNTs, we demonstrate the free-standing monolayer combined with a MOS device. We report a value of 86.5 cm²/sec for excitons from the suspended 1L WS₂ device with back gate voltage modulation, which is much higher than previously reported values of exciton diffusion coefficients in TMDCs and is comparable to quasi 1D systems. Our results establish the 2D TMDC materials as robust contenders for various applications in high speed energy transport devices such as excitonic circuits and high quantum yield LEDs utilizing their robustness, high crystallinity, defect free surfaces and visible range band gaps.

Results and Discussion

Modulating the carrier lifetime in 1L WS₂

The effective lifetime of various quasi-particles such as exciton and trions plays a key role in determining the suitability of TMDCs for various optoelectronic applications.^[37, 38] Due to high binding energy, strong oscillation strength of excitons and trions in TMDCs and presence intrinsic defect sites, it is difficult to externally control the carrier lifetime and hence the diffusion dynamics.^[19, 38, 39] In order to manipulate the diffusion dynamics and carrier lifetime of quasi particles in WS₂, we incorporated the monolayer WS₂ in to a MOS device (**Figure 1a**) (See methods section). We chose WS₂ because it has the maximum quantum efficiency across all TMDC materials and has almost a defect free surface, allowing us a greater flexibility to manipulate the charge diffusion dynamics.^[29] The optical microscope image of the MOS structure is shown in Figure 1b.

The photoluminescence (PL) spectra from 1L WS₂ at room temperature is shown in Figure 1c, as the back gate voltage was swept from -60 V to +60 V. The intensity weight of the X and X⁻ peaks can be significantly modulated^[40] as the back gate voltage is swept from -60 V to +60 V (Figure 1c and inset). The doping within the semiconductor affects the PL emission and relative exciton to trion emission ratio.^[40, 41] The measurements from a control monolayer sample with no externally applied voltage are shown in Figure S1 and S2 (See supplementary information note 1).

Interestingly we found the lifetime decay curves to be significantly modulated as the back gate voltage applied was changed, which has not been reported before.^[39] The decay trace curves were deconvoluted with respect to the instrument response function (IRF) and then were fitted using the following equation: $I = A \exp(-\frac{t}{\tau_1}) + B \exp(-\frac{t}{\tau_2}) + C$, where I is the PL intensity, A , B , and C are constants, ' t ' is time, and τ_1 is faster decay rate and τ_2 is the slower decay rate, indicating emission lifetimes for different decay processes.^[42] The short lifetime is effectively considered to represent non-radiative lifetime decay while the longer component is indicative of the radiative recombination time at room temperature.^[38] The longer component (radiative) of the excitonic lifetime changed from 238 ± 4 ps at -60 V to 690 ± 6 ps at +60 V (Figure 1d), while the trion radiative lifetime changed from 241 ± 6 ps to 392 ± 5 ps in the same modulation range (Figure 1e). Figure 1f shows the change in radiative lifetime as a function of back gate voltage. The shorter lifetime components also follow the same trend (Figure S3). We measured several other samples and we observed a similar trend (Figure S4). As the doping increases the PL emission intensity is minimum at +60 V, but the lifetime is the longest and vice-versa. It is important to note here that this trend is reversible and can be retraced if the voltage is swept in opposite direction, thus establishing the reversible doping effect in modulating the effective lifetimes. The change in radiative lifetime with change in doping level can be attributed to the change in relative oscillator strength and kinetic energy of the

excitons/trions as the doping changes due to back gate voltage being applied.^[19, 20] This was theoretically predicted by Rana et al.^[19] who calculated the change in radiative lifetime with decreasing oscillator strength of the excitons due to increase in doping concentration. Band filling effects and Pauli blocking will cause the oscillator strength of the exciton to reduce when the doping increases and hence the PL emission intensity will reduce, and the effective radiative lifetime will increase.^[19, 20] In case of bright trions similar enhancement of lifetime due to reduction in oscillator strength is observed because the phase space for the electron left behind after the trion has combined is either not available or is reduced near the conduction band due to Pauli blocking.^[19] Hence the increase in radiative lifetime observed in these quasi particles due to increase in doping concentration of charges can be explained by reduced oscillator strength and enhanced kinetic energy of the quasi particles.

Engineering the exciton spatial transport

The enhanced lifetime is bound to affect the spatial diffusion of excitons and trions and hence the transport of excitons and trions can be manipulated. Hence, we measured the spatial diffusion profile under various back gate voltages at room temperature (**Figure 2**). The near-field direct imaging technique with a charge-coupled device (CCD) camera was used to detect the diffusion length of bright excitons from 1L WS₂ sample. Figure 2a-c show the contour mapping plot of PL intensity as a function of emission wavelength and space of exciton diffusion from 1L WS₂ at room temperature, at two extreme back gate voltages applied and no voltage applied cases. The spatial distribution of PL intensity can be extracted at the specific energies (shown by dotted lines in Figure 2a-c). Figure 2d shows the extent of spatial diffusion in a steady 1D diffusion model. A gaussian fitting routine was used to quantitatively compare the reflected excitation beam to the emission profile emerging from WS₂. Laser and emission profiles were fitted using a bivariate

normal distribution and their full width half maximums (FWHMs) were recorded. The spatial extent of exciton diffusion (diffusion length L_D) was obtained by taking the square root of the difference between the variances of the emission image and of the passive laser spot.^[32] The L_D for excitons when no voltage is applied was measured to be $1.51 \pm 0.05 \mu\text{m}$ (Figure S5a-b), which is consistent with the values reported from similar measurements on WS₂.^[9] Using the measured lifetimes of excitonic emissions (τ), the effective exciton diffusion coefficient (D_{eff}) in a steady state equilibrium condition can be extracted using the equation $L_D = \sqrt{2D_{eff}\tau}$.^[35, 43] Using the lifetimes (Figure S1d), the extracted diffusion coefficients for excitons at room temperature from a monolayer WS₂ sample on a SiO₂/Si substrate was obtained to be $23.98 \pm 4.06 \text{ cm}^2/\text{sec}$. Exciton-exciton annihilation (EEA) effects while calculating the effective diffusion coefficient can be neglected in our measurements as explained in the later section. Similar values of exciton diffusion coefficients from WS₂ have been reported previously.^[9, 34] The radiative lifetime (τ_2) has been used to determine the effective diffusion coefficient as it is the major component affecting the diffusion dynamics in steady state equilibrium conditions. The exciton (trion) diffusion length (Figure 2d-e) at room temperature can be modulated from $1.41 \pm 0.04 \mu\text{m}$ ($1.15 \pm 0.02 \mu\text{m}$) at -60 V (minimum doping) to $1.69 \pm 0.05 \mu\text{m}$ ($1.26 \pm 0.06 \mu\text{m}$) at +60 V (large doping). Exciton and trion diffusion coefficients can be obtained after combining the variation in radiative lifetime (Figure 1f) and diffusion lengths (Figure 2e). The diffusion coefficients as a function of back gate voltage is shown in Figure 2f. A significant modulation (~ 2 times) in exciton and trion transport diffusion coefficients using static back gate voltage can lead to significant use of TMD materials like WS₂ in various optoelectronic device applications.

To further confirm the role of doping in affecting the radiative lifetime as explained above, we introduced solution based chemical dopants onto the surface of WS₂ monolayers. The surface of the monolayer was treated with 7,7,8,8-

tetracyanoquinodimethane (TCNQ),^[44] which is a p-type dopant. The PL intensity was considerably reduced as expected because of the doping (Figure S6a), but the effective lifetime was significantly enhanced to 1.02 ns (Figure S6b) as compared to 476 ± 5 ps (Figure S1d) from undoped sample. This confirms the role of external doping in enhancing the radiative lifetime of excitons in WS₂. (See Figure S6).

Engineering the dynamics of excitons, trions and bi-excitons in monolayer WS₂ at Low Temperature

At low temperature, higher-order correlated excitonic states such as biexcitons are also detected in TMDCs, which are crucial for quantum and optoelectronic applications at low light intensities.^[45] Hence, we performed the diffusion measurements at low temperature to study the effect of back gate induced doping on transport dynamics of other quasi particles such as trions and biexcitons in 1L WS₂. **Figure 3a** shows the PL spectrum obtained from the MOS device at various back gate voltages at 77 K. At +60 V we can clearly distinguish three peaks. Based on previous literature,^[40] the peak at 590 nm (X peak) and 602 nm (X⁻ peak) can be assigned to excitonic and trionic resonances in WS₂. The third peak at 609 nm has been reported as biexciton (XX) emission in literature.^[40] To confirm the biexciton emission, we performed power dependent measurements at 77 K and plotted the integrated PL from XX peak as a function of X peak (I_B vs I_X ; Figure 3b). We obtained a slope of 1.93, which confirms it to be a biexciton emission.^[7] With change in back gate voltage we could easily modulate the spectral weights of X, X⁻ and XX peaks. At -60 V, the PL emission was clearly dominated by XX peak, with X and X⁻ peaks almost quenched (Figure 3a). The lifetime (Figure 3c and S8) modulated significantly at low temperature with the change in doping in the sample using back gate voltage. The trend is gain reversible here with change in sweeping direction of

the voltage. We obtained diffusion profiles at low temperature as shown in Figure 3d-e at different back gate voltages. The extracted gaussian profiles have been shown in Figure S7. The diffusion lengths (Figure 3f) from X, X⁻ and XX peaks shows a clear modulation with sweeping back gate voltage. EEA effects can be ignored in our diffusion measurements. We confirmed the same by performing power dependent time-resolved PL measurements at 77 K (Figure S9 and associated text). The absolute values of diffusion lengths and modulation for excitons and trions at low temperature is smaller as compared to the room temperature. This can be explained by the thermally activated acoustic phonon scattering and ionized impurity scattering at this temperature range, as detailed in this report.^[36] The diffusion coefficients for X, X⁻ and XX peaks have been extracted in the same way using the diffusion equation and have been plotted as a function of back gate voltage in Figure 3g. Interestingly, the excitons diffuse the farthest followed by trions and biexcitons (Figure 3g). This can be attributed to the net effective masses and radii of these quasi particles.^[36] The excitons have the smallest net effective mass and radii and hence easily diffuse to longer distances as compared to trions and biexcitons. The modulation of the dynamics and diffusion of these quasi particles using external static electric field opens up avenues for designing optoelectronic devices based on these quasi particles.

Substrate and doping engineering for enhanced exciton transport

Substrates have been reported to affect the diffusion of excitons in TMDCs by influencing defect-assisted recombination and enhancing the EEA in supported TMD samples.^[16, 23] To realize high values of diffusion coefficient in inorganic TMD materials which are comparable to large diffusion coefficient values reported quasi 1D systems, we designed a MOS device with free standing monolayer WS₂. The suspended or free standing monolayer was achieved by transferring an exfoliated 1L onto the trench on a patterned

substrate (**Figure 4a**). The optical microscope image of the suspended monolayer is shown in Figure 4b. The role of substrate affecting the diffusion dynamics was observed without even application of external electric field (Figure S10). The intensity of the PL emission from the suspended part was enhanced significantly as compared to the supported part (Figure S10a). The lifetime from the free-standing monolayer excitonic emission enhanced significantly to 805 ± 6 ps as compared to supported monolayer $\sim 476 \pm 5$ ps. (Figure S10b). It is important to note that supported monolayer measurements were carried out on the same monolayer close to the suspended part as shown in the optical microscope image. Near field imaging of the diffusion length from the suspended monolayer revealed an enhanced diffusion length of excitons at room temperature of 3.09 ± 0.05 μm (Figure S10c-d). The effective diffusion coefficient from the suspended monolayer increased to 59.51 ± 5.32 cm^2/sec , which is much higher than what was observed from the supported monolayer sample. A comparison of diffusion coefficients from 1L WS₂ under various conditions without application of any back gate voltage is shown in Figure S10e.

The schematic shown in Figure 4a shows the MOS device with a suspended 1L WS₂. With the sweeping of back gate voltage, the PL spectra from the suspended 1L modulated significantly (Figure 4c). We observed the diffusion length could be further modulated in the suspended sample with the application of back gate voltage (Figure 4d). The maximum diffusion length (3.50 ± 0.01 μm) was observed at -20 V back gate voltage (Figure 4e, f). TRPL measurements were used to determine the lifetime of the exciton emissions at various back gate voltages. The decay curve was again fitted with a double exponential decay as reported earlier in Figure 1. The longer radiative lifetime (τ_2) which is already enhanced in the suspended sample could be further modulated to a value of 985 ± 8 ps with increase in doping of the sample (Figure 4g). The variation in lifetime of the longer (shorter) exciton lifetime with change in back gate voltage is shown in Figure 4h

(S11). It is interesting to note that the diffusion length after reaching a certain maximum value (almost equal to radius of the suspended part) reduces with continuous increase in doping. This effect can be attributed to the energy transfer to the quenching layer as the excitons hit the interface between the suspended and supported monolayer part.^[46] The effect was theoretically predicted by Scully et al.^[46] and explains as to when the exciton diffusion length starts to reach the interface of the supported substrate, the exciton will lose energy exponentially and hence the effective diffusion length will be reduced. Even though, the effective radiative lifetime of excitons increases with increasing doping. (See Figure S12 and associated text for details). The study of trion diffusion parameters on suspended samples is not the focus of this work and will be explored in upcoming publications. The effective variation in diffusion coefficient with different back gate voltage is shown in Figure 4i. The maximum effective diffusion coefficient from the suspended 1L WS₂ device was observed to be 86.5 cm²/sec at -20 V back gate voltage. This is the highest value of exciton diffusion reported from TMDC materials and is comparable to values of diffusion coefficient reported from similar thin film organic systems and quasi 1D systems^[31, 32, 35] (See Table S1). These results provide a foundational method to engineer the spatial and temporal diffusion of excitons and other quasi particles in TMDC materials to enhance their applications in excitonic optoelectronic and photonic device applications.

Conclusion

In conclusion, we successfully engineered the energy carrying quasi-particle diffusion dynamics in 1L WS₂ sample at both room and cryogenic temperatures. To achieve long range energy transport and ultra-fast diffusion we use back gate static doping to significantly modulate the effective diffusion coefficient of excitons and trions at room temperature via control of their radiative lifetime and diffusion lengths. The doping in the

semiconductor is reported to significantly change their oscillator strength and hence leading to change in lifetime and diffusion dynamics. At low temperature we further observe a modulation in diffusion parameters for different quasi particles incusing excitons, trions and biexcitons. The change in diffusion coefficient is reported for exciton, trion and biexciton dominated regions from a 1L WS₂ sample at 77 K. In addition, we further enhanced the diffusion length and pushed the value of diffusion coefficient to the highest reported value by engineering the substrate effects on diffusion. A very high value of $D_{eff} \approx 86.5 \text{ cm}^2/\text{sec}$ is reported for a suspended 1L WS₂ MOS device. This value is the highest reported from all TMDC materials and is comparable to the values reported from CNTs and other quasi 1D systems. Our results provide the important experimental demonstration of engineering the diffusion dynamic in TMDC materials, paving the way for optoelectronic device applications based on diffusion dynamics of excitons, trions and biexcitons. The TMDCs provide a large cross-sectional area combined with high binding energy of quasi-particles to realize optoelectronic devices based on the transport and diffusion of these quasi particles. Our results provide an efficient way to enhance the low diffusion coefficient in TMDCs to achieve long-range and ultra-fast exciton diffusion, making them suitable choice for high speed excitonic circuit and device applications.

Methods

Material growth: WS₂ flakes were mechanically exfoliated onto a thermally grown 290 nm thick SiO₂ layer deposited over silicon substrate. All the samples were characterized, and layer thickness were identified using the standard AFM measurements, which were collected in ambient atmosphere at room temperature with a Bruker Multi-Mode III AFM. The monolayer WS₂ was placed on a gold electrode that was prepatterned on the substrate. Another gold electrode was then transferred to electrically bridge the WS₂ flake and the gold electrode, forming a MOS device (Figure 1a). This fabrication procedure kept the WS₂ free from chemical contaminations by minimizing the postprocesses after the flake was transferred. In the measurement, the gold electrode is grounded, and the n⁺-doped Si substrate functions as a back gate, providing uniform electrostatic doping in the WS₂.

Optical Characterization: PL measurements at room temperature and 77 K were conducted using a Horiba LabRAM system equipped with a confocal microscope, a charge-coupled device (CCD) Si detector, and a 532 nm diode-pumped solid-state (DPSS) laser as the excitation source. For low temperature (upto 77 K) measurements, the sample was placed into a microscope-compatible chamber with a low temperature controller (using liquid nitrogen as the coolant). In the experiment, the incident polarization angle was controlled by an angle-variable half-wave plate and was fixed, and the polarization angle of the emission (θ) was determined by using an angle-variable polarizer located in front of the detector. Time resolved PL measurements were conducted in a setup which incorporates μ -PL spectroscopy and a time-correlated single photon counting (TCSPC) system. A linearly polarized pulse laser (frequency doubled to 522 nm, with 300 fs pulse width and 20.8 MHz repetition rate) was directed to a high numerical aperture (NA= 0.7) objective (Nikon S Plan 603). PL signal was collected by a grating

spectrometer, thereby either recording the PL spectrum through a charge coupled device (CCD; Princeton Instruments, PIXIS) or detecting the PL intensity decay by a Si single-photon avalanche diode (SPAD) and the TCSPC (PicoHarp 300) system. The double exponential decay in the IRF is due to delay in response timings of the MPD SPAD® photon detector and the PicoHarp 300 coupled with it. A similar system response has been reported from an equivalent system.^[47] Similar bi-exponential decay is commonly reported from such systems.^[48] All the measured decay curves have been deconvoluted with the IRF using biexponential decay.

Measurements of exciton diffusion lengths: Exciton diffusion measurements were carried out using the same PIXIS CCD detector coupled with a X100 (NA= 1.49, oil suspended) objective lens. The pulsed 522 nm laser was used for excitation with a beam diameter ~500 nm (confirmed by CCD imaging) with collection time of 1s per measurement. The diffusion mapping direction was well aligned with the polarization of the excitation laser. The collected light was spectrally filtered to remove the pump laser wavelength. Spectral measurements were made using a grating spectrometer (Acton, SpectraPro 2750). The focal plane of the sample was imaged using the zeroth order of the grating and the spectrometer CCD, giving a spatial resolution of about 200 x 200 nm in space, corresponding to a pixel (20 µm x 20 µm) on the CCD. The PL intensity at a particular excitonic emission energy was plotted as a function of the distance from the excitation centre ($x = 0$ in Figures 1-4). The spatial extent of exciton diffusion (diffusion length L_D) was found by taking the square root of the difference between the variances of the emission image and of the passive laser spot.

Author Contributions

Y. L. conceived and supervised the project; Y.Z., B.W and L.Z prepared WS₂ samples and MOS device; A. S. carried out all the optical measurements; A. S, Y. L. and R. H. analysed

the data; A. S. took the AFM imaging; A. S. and Y. L. drafted the manuscript and all authors contributed to the manuscript.

Supporting Information

All additional data and supporting information and methods are presented in the supporting information file.

Acknowledgements

We would like to acknowledge the financial support from ANU PhD student scholarship, China Scholarship Council, Australian Research Council, ANU Major Equipment Committee fund, National Natural Science Foundation of China and Australian Centre for Advanced Photovoltaics. We would also like to thank Professor Chennupati Jagadish and Professor Barry Luther-Davies from the Australian National University for their facility support.

Competing financial interests

The authors declare that they have no competing financial interests.

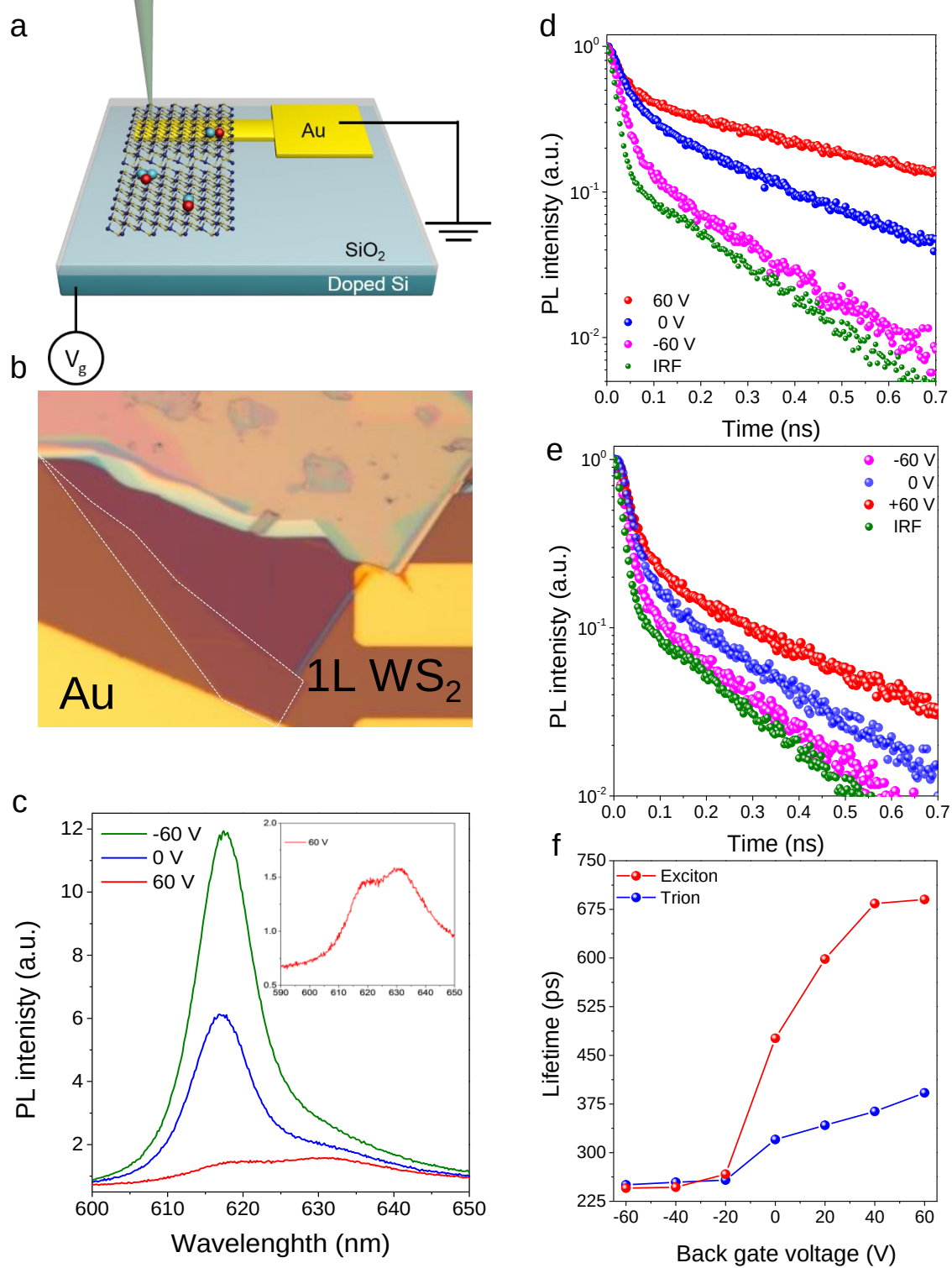


Figure 1

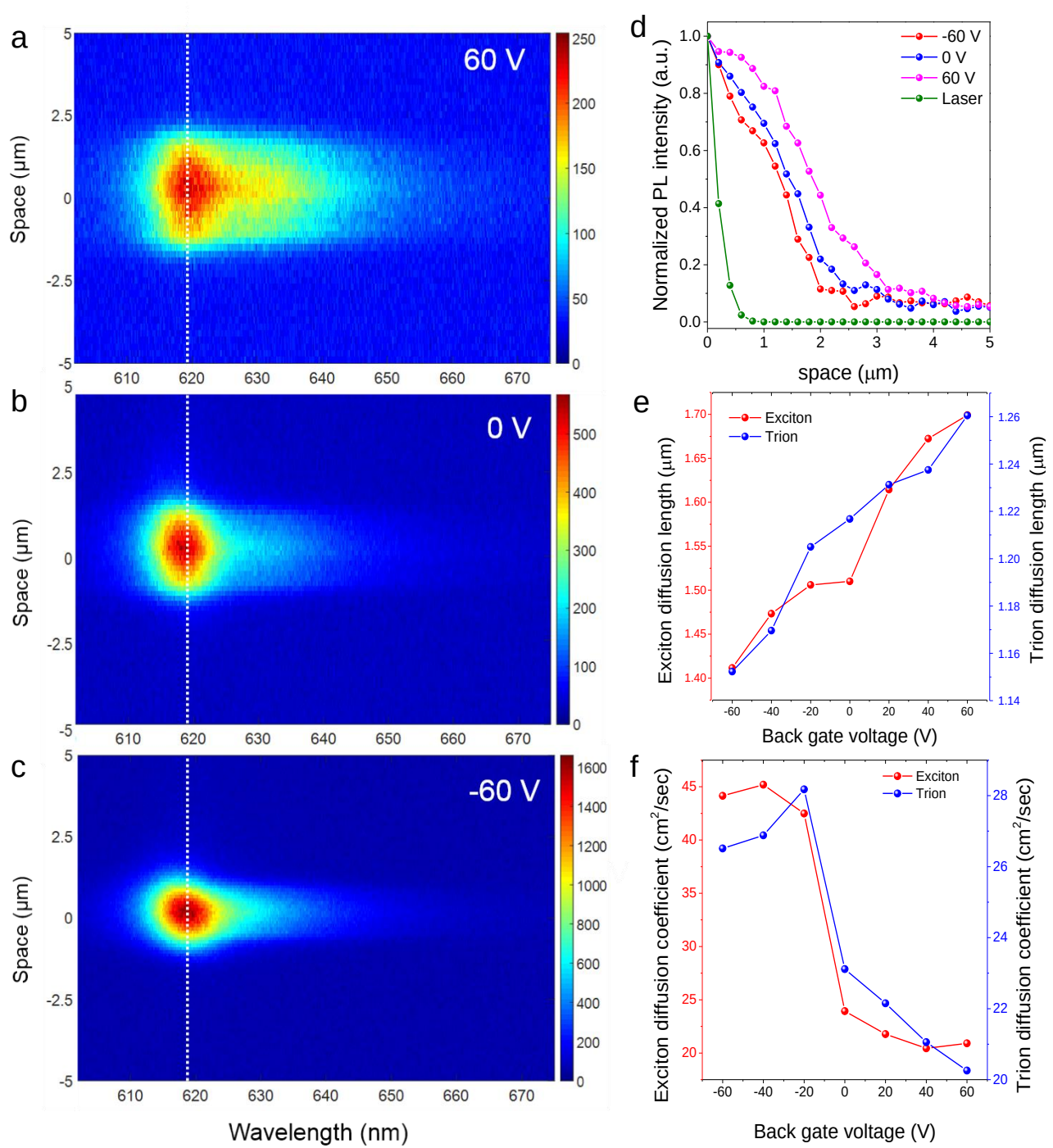


Figure 2

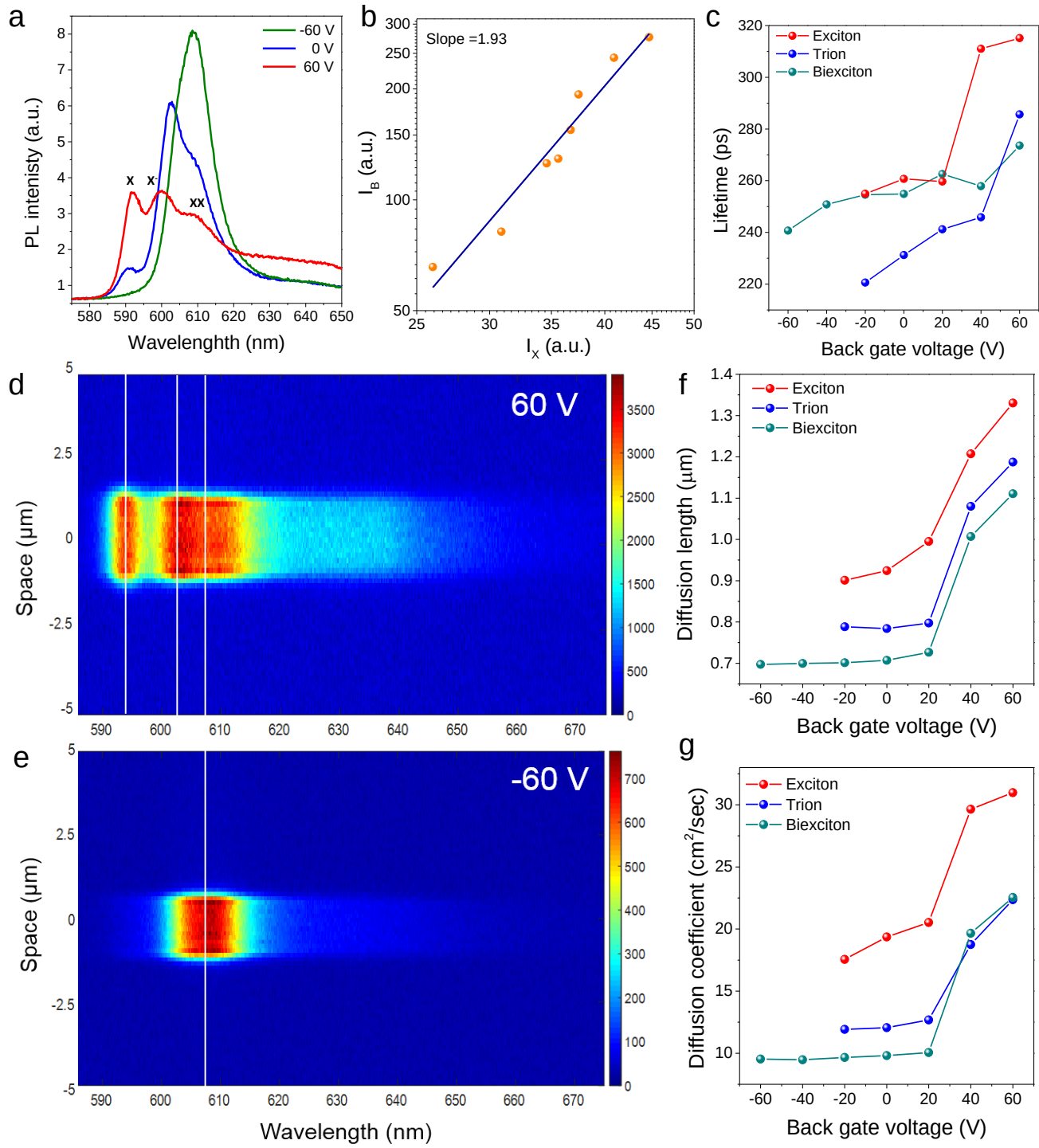


Figure 3

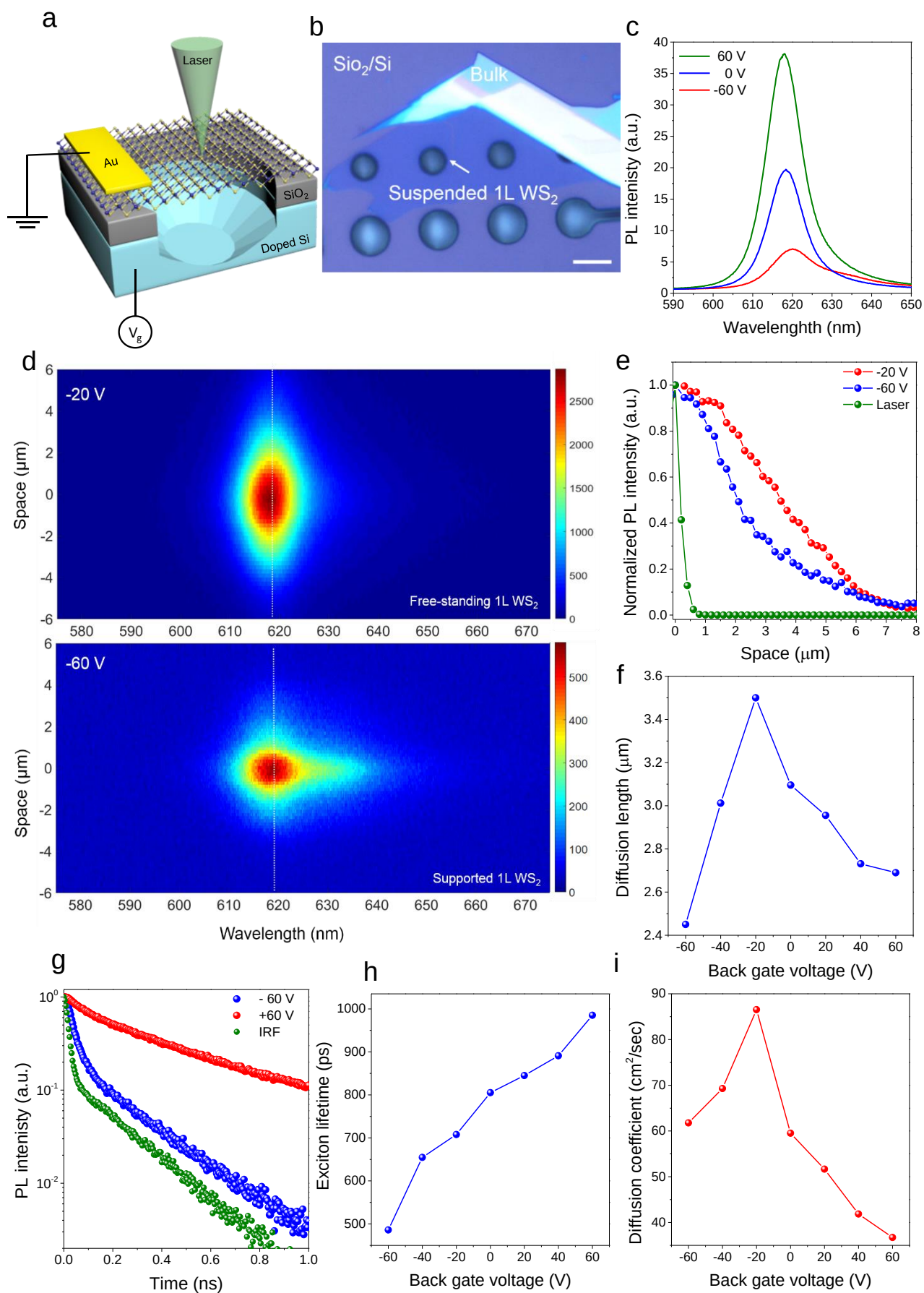


Figure 4

Figure Captions

Figure 1 | Modulating the carrier lifetime in 1L WS₂ **a**, Schematic diagram of the MOS device used for static doping of charges into the monolayer WS₂. **b**, Optical microscope image of the 1L WS₂ used for measurements, coupled into a MOS device with gold electrodes **c**, Measured PL spectra from 1L WS₂ sample at room temperature under various back gate voltages, showing clear modulation of excitonic (617 nm) trionic (626 nm) emissions. Inset shows a zoomed in spectra from +60 V. **d-e**, Time-resolved PL emission (normalized) obtained from exciton (d) and trion (e) emission from 1L WS₂ at various back gate voltages, showing a clear modulation of lifetime as the voltage sweeps from -60 V to +60 V. The decay curves were fitted by two slopes using equation (1) after deconvoluting the data from instrument function response (IRF) and the lifetimes were classified as short (τ_1) and long (τ_2). **f**, The modulation of long lifetime τ_2 as a function of back gate voltage for both exciton (red) and trionic emissions (blue). For τ_1 see Figure S3.

Figure 2 | Engineering the exciton transport in 1L WS₂ **a-c**, Exciton diffusion direct measurements at 60V, 0 V and -60 V using near-field CCD imaging. The white dotted line shows the exciton resonance peak where the diffusion profiles were extracted in 2d. **d**, the spatial distribution of exciton diffusion from the two back gate biases and no voltage case plotted along the with the laser diffusion profile. **e**, the variation in diffusion length of exciton/trions as a function of back gate voltage applied obtained by direct near-field imaging of excitonic PL emission on to a CCD detector. **f**, Exciton/Trion diffusion coefficient variation as a function of back gate voltage at room temperature.

Figure 3 | Engineering the dynamics of excitons, trions and bi-excitons in monolayer WS₂ at Low Temperature. **a**, Measured PL spectra at 77 K from 1L WS₂ showing a clear modulation of exciton (X), trion (X⁻) and biexciton (XX) peaks with application of back gate voltage. **b**, Log-log plot showing the variation of integrated PL intensity of peak B as a function of peak E. From the fitting curve (blue solid line) the PL intensity of peak X grows super-linearly ($\alpha \sim 1.93$), with the increase of the excitation power, thus confirming it to be a biexciton emission. **c**, Variation in exciton, trion and biexciton lifetimes as a function of back gate voltage at 77 K. **d-e**, Near field imaging of diffusion at various back gate voltages; PL intensity as a function of emission wavelength and space of exciton/trion and biexciton diffusion from 1L WS₂ at 77 K. The white lines are exciton, trion and biexciton resonances where the spatial profiles were extracted. **f**, Exciton, trion and biexciton diffusion length variation as a function of back gate voltage

at 77 K. **g**, Variation of exciton/trion diffusion coefficient with sweeping back gate voltage at 77 K.

Figure 4 | Substrate and doping engineering for enhanced exciton transport. a, Schematic diagram showing the device used for modulating the doping in a free-standing monolayer using back gate voltage. **b**, Microscope image of monolayer WS₂ suspended on a circular cavity used for diffusion measurements. The scale is 10 μm . **c**, PL spectra from the free-standing 1L WS₂ at different back gate voltages at room temperature. **d**, Direct exciton diffusion measurements at -20 V and -60 V using near-field CCD imaging from a suspended 1L WS₂ sample at room temperature. **e**, the spatial distribution from the two extreme cases, plotted along the with the laser diffusion profile. **f**, the variation in diffusion length as a function of back gate voltage applied from a suspended 1L WS₂ sample at room temperature. **g**, Time-resolved PL measurements at -60 V and +60 V at room temperature showing the huge variation in lifetime as a function of voltage at two extreme cases of back gate voltage applied. **h**, Variation of exciton (617 nm) decay long lifetime as a function of sweeping back gate voltage. **i**, Exciton diffusion coefficient variation as a function of back gate voltage at room temperature.

References

- [1] J. Yang, T. Lu, Y. W. Myint, J. Pei, D. Macdonald, J.-C. Zheng, Y. Lu, ACS nano 2015, 9, 6603; M. Chhowalla, Z. Liu, H. Zhang, Chemical Society Reviews 2015, 44, 2584.
- [2] K. F. Mak, J. Shan, Nature Photonics 2016, 10, 216; M. Xu, T. Liang, M. Shi, H. Chen, Chemical reviews 2013, 113, 3766.
- [3] A. Rodin, A. Carvalho, A. C. Neto, Physical Review B 2014, 90, 075429.
- [4] A. Chernikov, T. C. Berkelbach, H. M. Hill, A. Rigosi, Y. Li, O. B. Aslan, D. R. Reichman, M. S. Hybertsen, T. F. Heinz, Physical review letters 2014, 113, 076802.
- [5] K. F. Mak, K. He, C. Lee, G. H. Lee, J. Hone, T. F. Heinz, J. Shan, Nature materials 2013, 12, 207.
- [6] D. Sun, Y. Rao, G. A. Reider, G. Chen, Y. You, L. Brézín, A. R. Harutyunyan, T. F. Heinz, Nano letters 2014, 14, 5625.
- [7] Y. You, X.-X. Zhang, T. C. Berkelbach, M. S. Hybertsen, D. R. Reichman, T. F. Heinz, Nature Physics 2015, 11, 477.
- [8] J. Pei, J. Yang, X. Wang, F. Wang, S. Mokkapat, T. Lü, J.-C. Zheng, Q. Qin, D. Neshev, H. H. Tan, ACS nano 2017, 11, 7468.
- [9] J. He, D. He, Y. Wang, Q. Cui, F. Ceballos, H. Zhao, Nanoscale 2015, 7, 9526.
- [10] Y. Lin, X. Ling, L. Yu, S. Huang, A. L. Hsu, Y.-H. Lee, J. Kong, M. S. Dresselhaus, T. Palacios, Nano letters 2014, 14, 5569.
- [11] A. Thilagam, Journal of Applied Physics 2014, 116, 053523.
- [12] S. Hofmann, T. C. Rosenow, M. C. Gather, B. Lüssem, K. Leo, Physical Review B 2012, 85, 245209.
- [13] Y. Ye, Z. J. Wong, X. Lu, X. Ni, H. Zhu, X. Chen, Y. Wang, X. Zhang, Nature Photonics 2015, 9, 733.
- [14] A. A. High, E. E. Novitskaya, L. V. Butov, M. Hanson, A. C. Gossard, Science 2008, 321, 229; G. Grosso, J. Graves, A. Hammack, A. High, L. Butov, M. Hanson, A. Gossard, Nature Photonics 2009, 3, 577.
- [15] S. Dufferwiel, S. Schwarz, F. Withers, A. Trichet, F. Li, M. Sich, O. Del Pozo-Zamudio, C. Clark, A. Nalitov, D. Solnyshkov, Nature communications 2015, 6, 8579; N. Lundt, S. Klemmt, E. Cherotchenko, S. Betzold, O. Iff, A. V. Nalitov, M. Klaas, C. P. Dietrich, A. V. Kavokin, S. Höfling, Nature communications 2016, 7, 13328.
- [16] S. Mouri, Y. Miyauchi, M. Toh, W. Zhao, G. Eda, K. Matsuda, Physical Review B 2014, 90, 155449.
- [17] R. R. Lunt, N. C. Giebink, A. A. Belak, J. B. Benziger, S. R. Forrest, Journal of Applied Physics 2009, 105, 053711.
- [18] G. M. Akselrod, P. B. Deotare, N. J. Thompson, J. Lee, W. A. Tisdale, M. A. Baldo, V. M. Menon, V. Bulović, Nature communications 2014, 5, 3646; M. Pope, C. E. Swenberg, *Electronic processes in organic crystals and polymers*, Vol. 2, Oxford University Press New York, 1999.
- [19] H. Wang, C. Zhang, W. Chan, C. Manolatou, S. Tiwari, F. Rana, Physical Review B 2016, 93, 045407.
- [20] C. Zhang, H. Wang, W. Chan, C. Manolatou, F. Rana, Physical Review B 2014, 89, 205436.
- [21] A. Slobodeniuk, D. Basko, Physical Review B 2016, 94, 205423.

- [22] F. Cadiz, C. Robert, E. Courtade, M. Manca, L. Martinelli, T. Taniguchi, K. Watanabe, T. Amand, A. Rowe, D. Paget, *Applied Physics Letters* 2018, 112, 152106.
- [23] Y. Yu, Y. Yu, C. Xu, A. Barrette, K. Gundogdu, L. Cao, *Physical Review B* 2016, 93, 201111.
- [24] H. Marciniak, X.-Q. Li, F. Würthner, S. Lochbrunner, *The Journal of Physical Chemistry A* 2010, 115, 648.
- [25] Z. Vörös, R. Balili, D. Snoke, L. Pfeiffer, K. West, *Physical review letters* 2005, 94, 226401.
- [26] Q. Cui, F. Ceballos, N. Kumar, H. Zhao, *ACS nano* 2014, 8, 2970.
- [27] G. Froehlicher, E. Lorchat, S. Berciaud, *Physical Review B* 2016, 94, 085429.
- [28] N. Kumar, Q. Cui, F. Ceballos, D. He, Y. Wang, H. Zhao, *Nanoscale* 2014, 6, 4915.
- [29] L. Yuan, L. Huang, *Nanoscale* 2015, 7, 7402.
- [30] L. Yuan, T. Wang, T. Zhu, M. Zhou, L. Huang, *The journal of physical chemistry letters* 2017, 8, 3371.
- [31] J. R. Caram, S. Doria, D. r. M. Eisele, F. S. Freyria, T. S. Sinclair, P. Rebentrost, S. Lloyd, M. G. Bawendi, *Nano letters* 2016, 16, 6808.
- [32] K. A. Clark, E. L. Krueger, D. A. Vanden Bout, *The journal of physical chemistry letters* 2014, 5, 2274.
- [33] R. Xu, S. Zhang, F. Wang, J. Yang, Z. Wang, J. Pei, Y. W. Myint, B. Xing, Z. Yu, L. Fu, *ACS nano* 2016, 10, 2046.
- [34] M. Kulig, J. Zipfel, P. Nagler, S. Blanter, C. Schüller, T. Korn, N. Paradiso, M. M. Glazov, A. Chernikov, *Physical review letters* 2018, 120, 207401.
- [35] A. T. Haedler, K. Kreger, A. Issac, B. Wittmann, M. Kivala, N. Hammer, J. Köhler, H.-W. Schmidt, R. Hildner, *Nature* 2015, 523, 196.
- [36] T. Kato, T. Kaneko, *ACS nano* 2016, 10, 9687.
- [37] V. A. Fonoberov, A. A. Balandin, *Physical Review B* 2004, 70, 195410.
- [38] M. Palummo, M. Bernardi, J. C. Grossman, *Nano letters* 2015, 15, 2794.
- [39] C. Robert, D. Lagarde, F. Cadiz, G. Wang, B. Lassagne, T. Amand, A. Balocchi, P. Renucci, S. Tongay, B. Urbaszek, *Physical Review B* 2016, 93, 205423.
- [40] G. Plechinger, P. Nagler, J. Kraus, N. Paradiso, C. Strunk, C. Schüller, T. Korn, *physica status solidi (RRL)–Rapid Research Letters* 2015, 9, 457.
- [41] J. S. Ross, S. Wu, H. Yu, N. J. Ghimire, A. M. Jones, G. Aivazian, J. Yan, D. G. Mandrus, D. Xiao, W. Yao, *Nature communications* 2013, 4, 1474.
- [42] X. Liu, H. Yu, Q. Ji, Z. Gao, S. Ge, J. Qiu, Z. Liu, Y. Zhang, D. Sun, *2D Materials* 2016, 3, 014001.
- [43] O. V. Kozlov, F. de Haan, R. A. Kerner, B. P. Rand, D. Cheyns, M. S. Pshenichnikov, *Physical review letters* 2016, 116, 057402; O. V. Mikhnenko, P. W. Blom, T.-Q. Nguyen, *Energy & Environmental Science* 2015, 8, 1867.
- [44] P. Hu, J. Ye, X. He, K. Du, K. K. Zhang, X. Wang, Q. Xiong, Z. Liu, H. Jiang, C. Kloc, *Scientific reports* 2016, 6, 24105.
- [45] Z. Ye, L. Waldecker, E. Y. Ma, D. Rhodes, A. Antony, B. Kim, X.-X. Zhang, M. Deng, Y. Jiang, Z. Lu, D. Smirnov, K. Watanabe, T. Taniguchi, J. Hone, T. F. Heinz, *Nature Communications* 2018, 9, 3718.
- [46] S. R. Scully, M. D. McGehee, *Journal of applied physics* 2006, 100, 034907.

- [47] T. Burgess, D. Saxena, S. Mokkaapati, Z. Li, C. R. Hall, J. A. Davis, Y. Wang, L. M. Smith, L. Fu, P. Caroff, *Nature communications* 2016, 7, 11927.
- [48] L. Bergmann, G. J. Hedley, T. Baumann, S. Bräse, I. D. Samuel, *Science advances* 2016, 2, e1500889.

Supplementary Information

Engineering the Dynamics and Transport of Excitons, Trions, and Biexcitons in Monolayer WS₂

Ankur Sharma¹, Yi Zhu¹, Robert Halbich¹, Linglong Zhang^{1,2}, Bowen Wang¹ and Yuerui Lu^{1*}

¹Research School of Electrical, Energy and Materials Engineering, College of Engineering and Computer Science, the Australian National University, Canberra, ACT, 2601, Australia

* To whom correspondence should be addressed: Yuerui Lu (yuerui.lu@anu.edu.au)

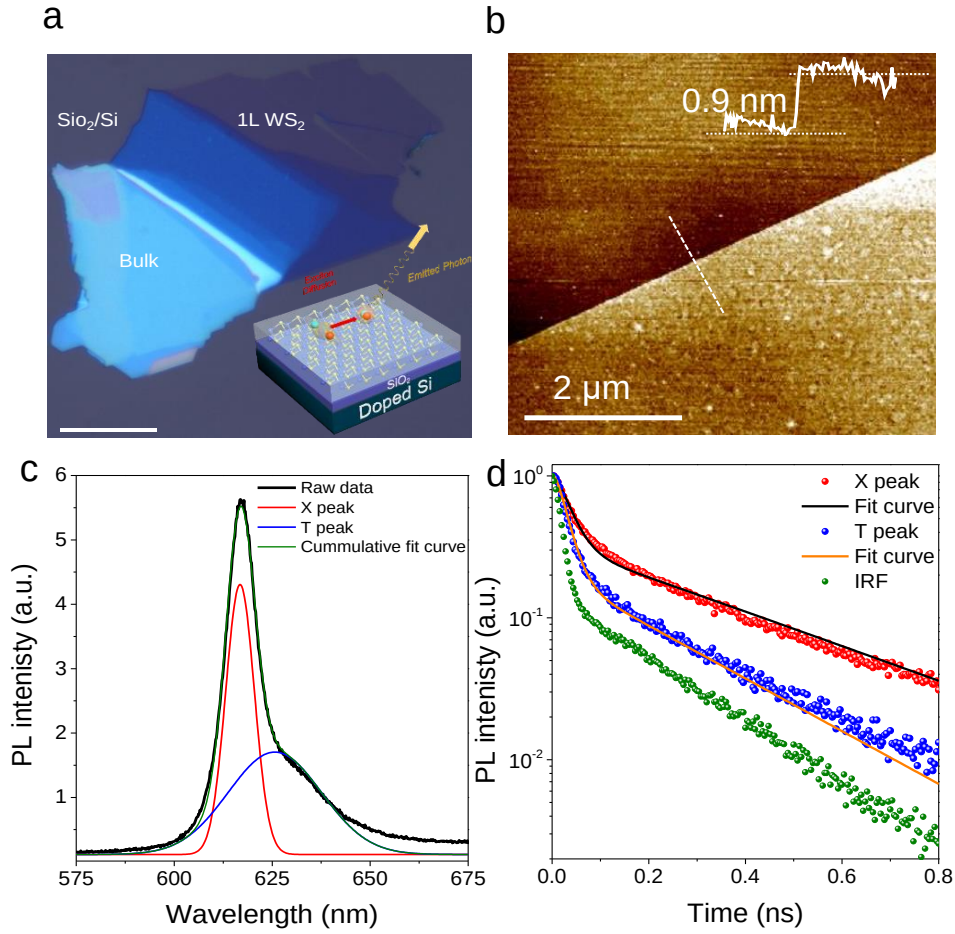


Figure S1 | Characterization of monolayer WS₂ **a**, Optical micrograph image of the 1L WS₂ used for measurements. The scale bar is 20 μm. Inset: Schematic diagram of a 1L WS₂ on top of SiO₂/Si substrate showing exciton diffusion along the monolayer and annihilation into a photon. **b**, Zoomed Atomic force microscope (AFM) image of the WS₂ sample confirming the thickness to be ~ 0.9 nm. **c**, Measured PL spectra from 1L WS₂ at room temperature. The spectrum is fitted by two Lorentzian peaks at 617 and 626 nm, designated as exciton (X peak) (red) and trion (X⁻ peak) (blue) emissions. **d**, Time-resolved PL emission (normalized) from 1L WS₂. The blue/red balls represent measured decay curve from excitonic/trionic emissions respectively. The decay curve was fitted by two slopes using equation (1) after deconvoluting the data from instrument function response (green balls). An effective short lifetime of $\tau_1 = 21 \pm 7$ ps and long lifetime of $\tau_2 = 476 \pm 5$ ps was extracted from the fitted curve (orange) from exciton emission at 617 nm. Similarly, an effective lifetime of $\tau_1 = 12 \pm 4$ ps and $\tau_2 = 320 \pm 6$ ps was extracted (black curve for the trionic emission at 626 nm).

Supplementary Information Note 1:

The monolayer WS₂ was mechanically exfoliated from a bulk crystal onto a thermally grown 290 nm SiO₂/Si substrate. Figure S1a shows the optical microscope image of the sample. The thickness of the exfoliated layer was confirmed using atomic force microscopy to be 0.9 nm (Figure S1b), which confirmed it to be a monolayer. Raman spectroscopy was further used to confirm the monolayer WS₂ (Figure S2). The sample was excited with a 300fs pulsed laser to collect the PL spectrum. Figure S1c shows the PL spectrum from monolayer WS₂ at room temperature. The spectrum is fitted with two Lorentzian peaks. The peaks at 617 (X peak) and 626 nm (X⁻ peak) are consistent with excitonic and trionic resonances from monolayer WS₂ reported in the literature.^[1] The lifetime traces from X and X⁻ peaks were recorded using a picosecond resolved TRPL setup (Figure S1d). An effective short lifetime of $\tau_1 = 21 \pm 7$ ps and long lifetime of $\tau_2 = 476 \pm 5$ ps was extracted from the fitted curve from the exciton emission at 617 nm. Similarly, an effective lifetime of $\tau_1 = 12 \pm 4$ ps and $\tau_2 = 320 \pm 6$ ps was extracted from the trion emission at 626 nm. The values of lifetime obtained are in close agreement with the lifetime values reported from monolayer WS₂.^[2]

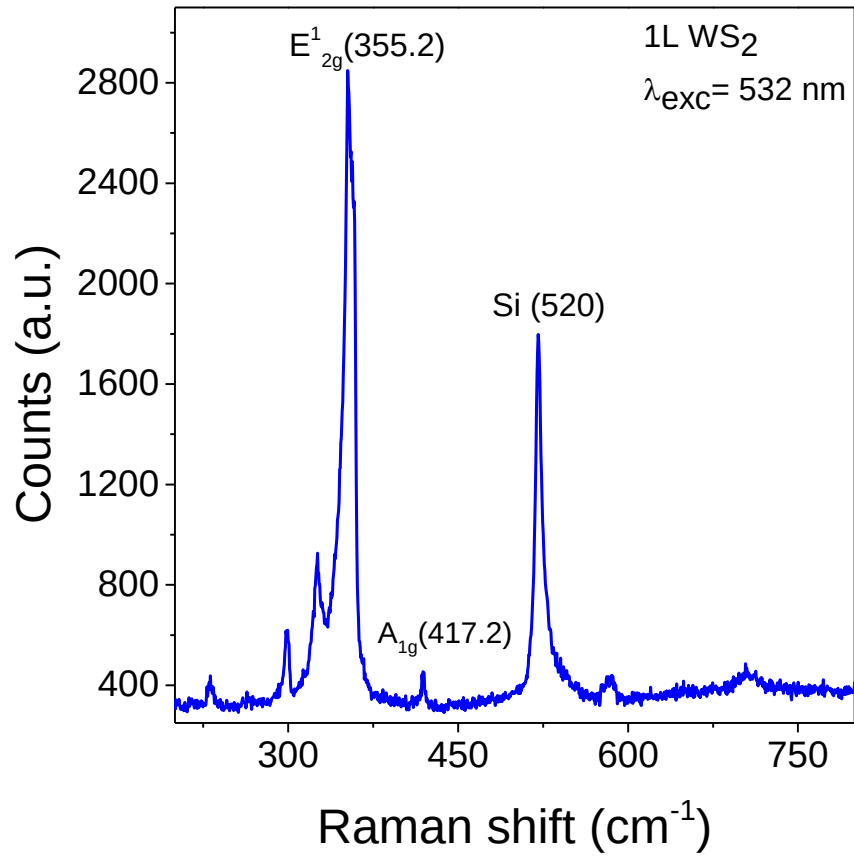


Figure S2 | Measured Raman spectrum from 1L WS₂ on SiO₂/Si substrate. Peaks at 355.2 cm⁻¹ and 417.2 cm⁻¹ are for WS₂ and the peak at 520 cm⁻¹ is for silicon.

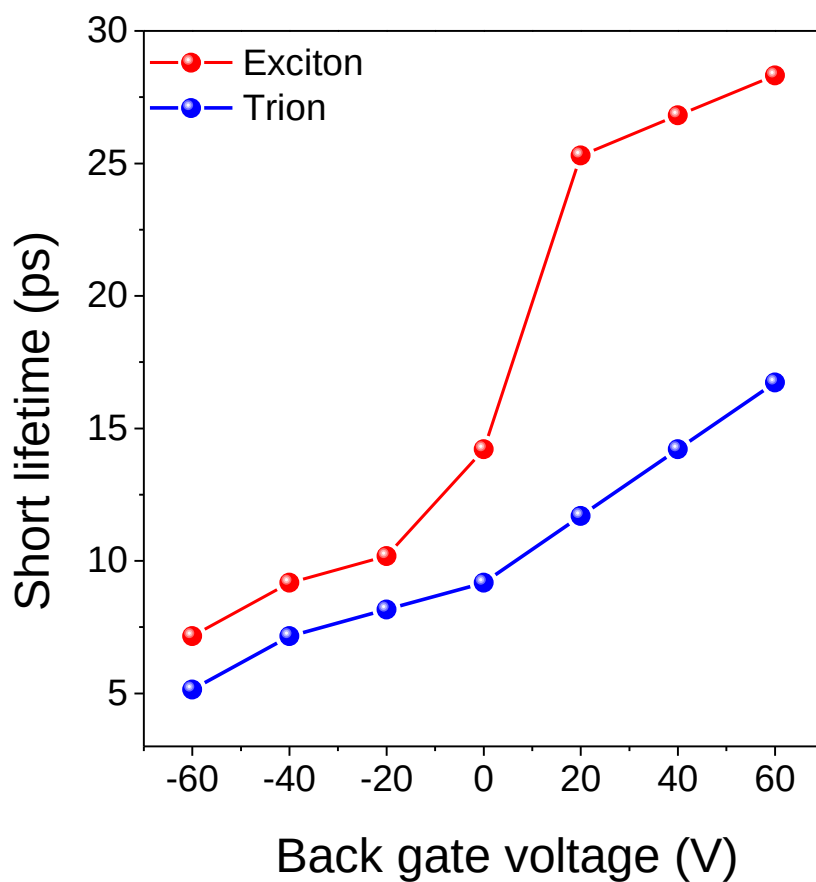


Figure S3 | Deconvoluted short lifetime as a function of back gate voltage for excitons (617 nm) and trion (626 nm) peaks at room temperature. The decay curve has been shown in Figure 2d. The curve is then deconvoluted with the instrument response function (IRF) and fitted with two slopes. The short lifetime as a function is shown here, while the long lifetime is shown in Figure 2e.

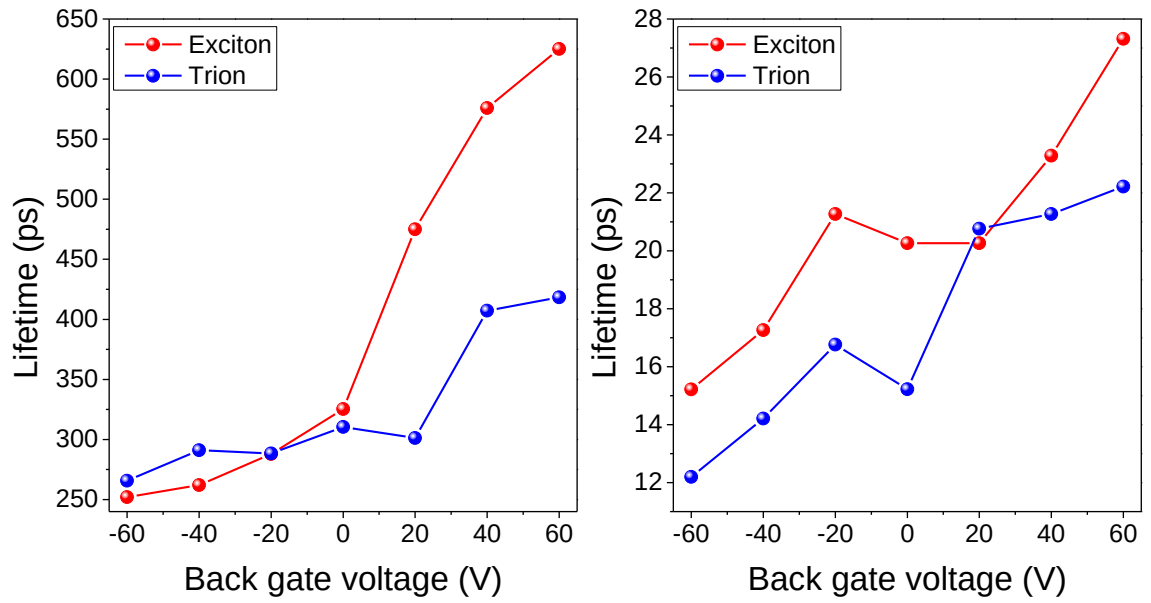


Figure S4 | a-b, Long lifetime component (a) (τ_2) and short lifetime (b) (τ_1) from excitons and trions in 1L WS₂ as a function of the back-gate voltage measured from a different sample from the ones used in main text.

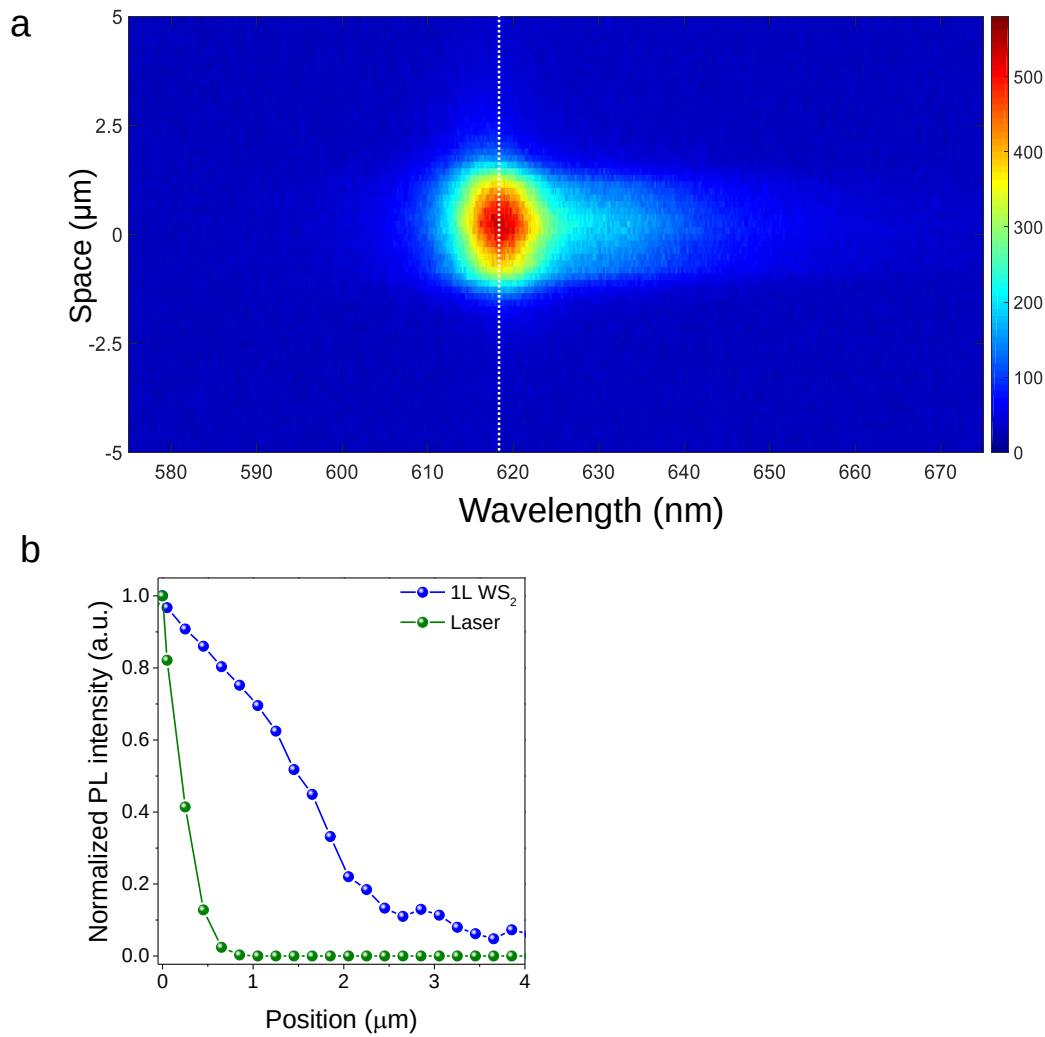


Figure S5 | **a**, Near-field imaging of spatial exciton diffusion, resolved as a function of emission wavelength and space from 1L WS_2 at room temperature. The middle of laser spot is at $x = 0$. **b**, spatial profile of exciton diffusion plotted against the dotted line in the contour plot. The deconvolution from the laser profile gives an effective exciton diffusion length of $1.51 \pm 0.05 \mu\text{m}$.

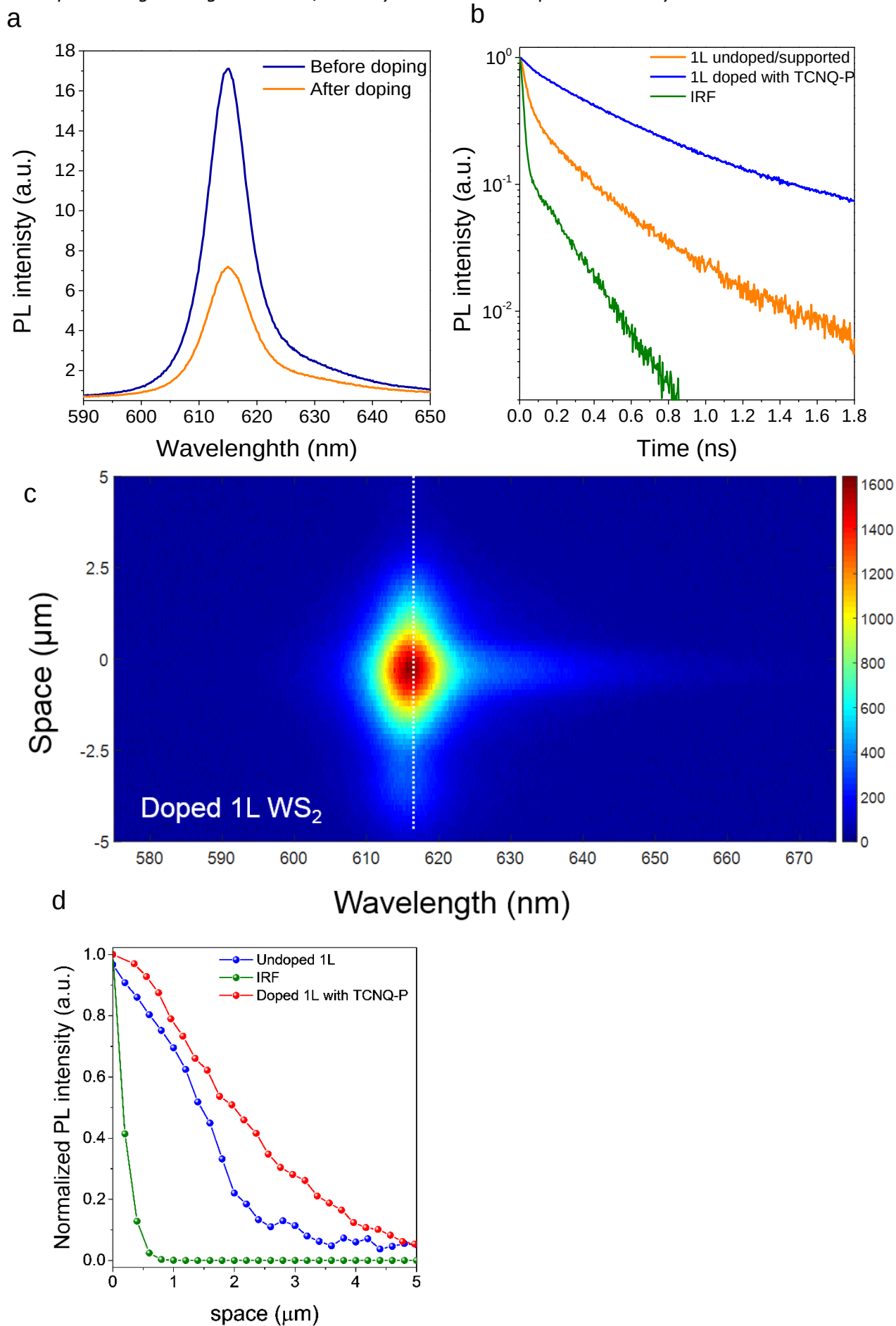


Figure S6 | Chemical doping effect on exciton diffusion. **a**, Measured PL spectra from 1L WS₂ sample at room temperature from a doped 1L WS₂ sample with TCNQ-P compared with PL emission from an undoped 1L WS₂ sample. **b**, Measured time-resolved PL spectra of exciton emission (617 nm) from an undoped 1L sample (orange curve) (See Figure 1) as compared to elongated lifetimes from chemically doped 1L (blue curve) at room temperature. The effective lifetime from doped sample is fitted with only one slope with a value of 1.02 ns. **d**, Direct imaging of exciton diffusion lengths using a near-field CCD imaging technique from chemically doped 1L WS₂. **e**, Spatial distribution of exciton diffusion plotted against the white dotted line in figure d. The diffusion length from chemically doped samples is higher (1.86 μm) as compared to undoped supported 1L WS₂ samples. (1.51 μm ; Figure 1). The L_D obtained after extracting the spatial profile from the contour diffusion plot (Figure S3c-d) is 1.95 μm , which is also significantly higher than what was reported from the undoped samples. The diffusion coefficient $D_{\text{eff}} \approx 18.58 \text{ cm}^2/\text{sec}$ is slightly low as compared to the undoped samples which can be due to the surface adsorption effects in the solution doped sample.

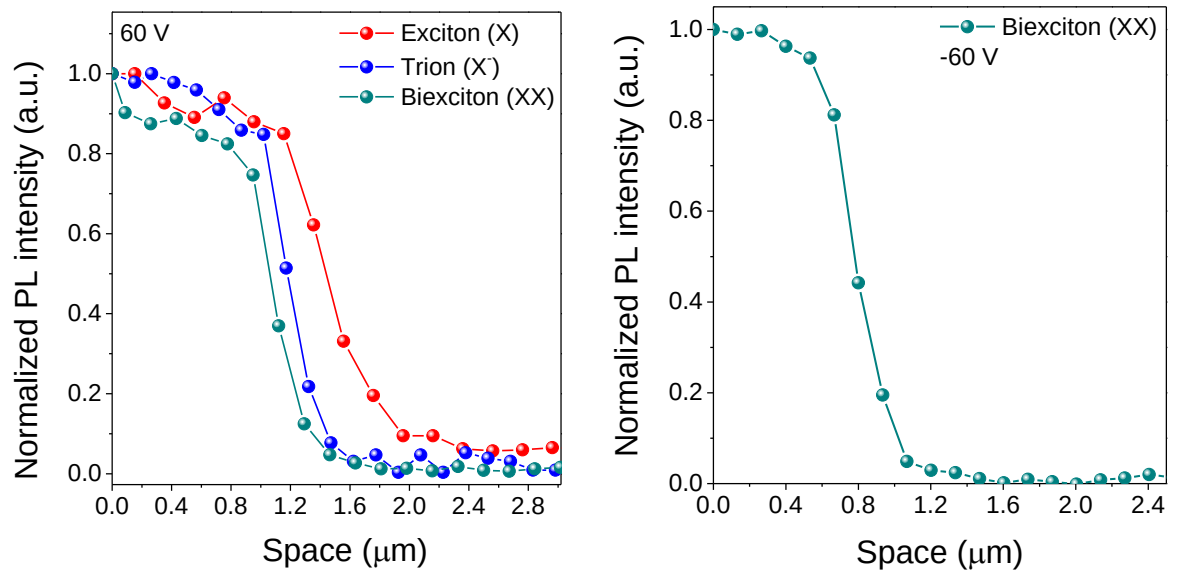


Figure S7 | Spatial diffusion profiles at 77 K. a, Extracted gaussian profiles of excitons, trion and biexciton diffusion at +60 V and -60 V **(b)** respectively. The profiles have been extracted from the spatial mapping shown in main text Figure 3d-e.

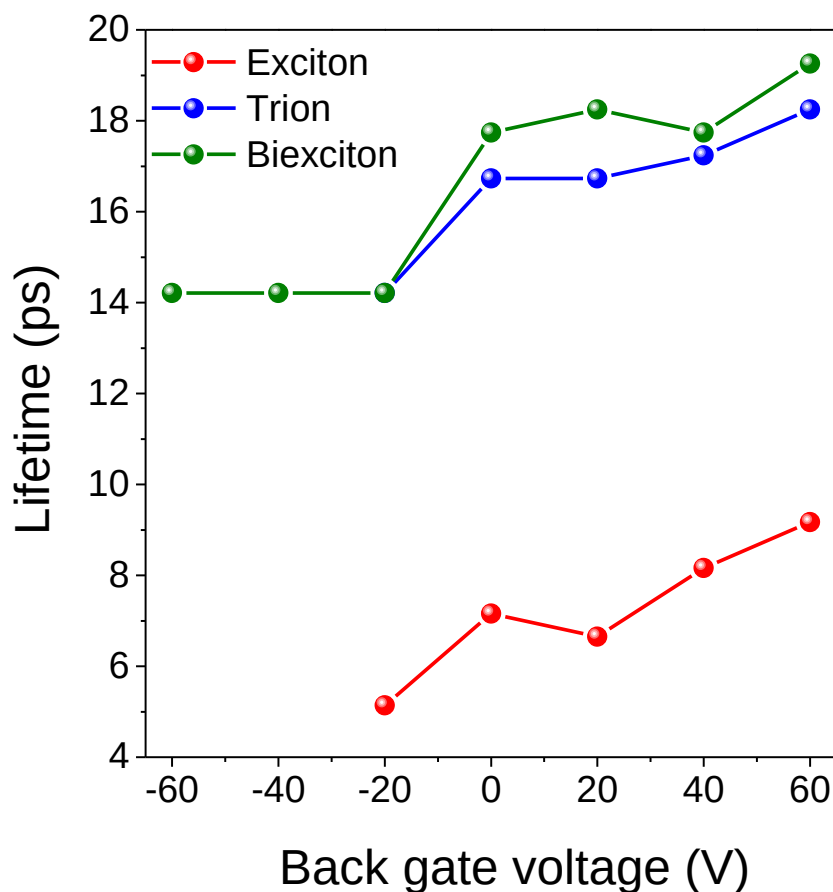


Figure S8 | Deconvoluted short lifetime as a function of back gate voltage for excitons (590 nm), trions (602 nm) and biexcitons (609 nm) peaks at room temperature. The decay curve is deconvoluted with the instrument response function (IRF) and fitted with two slopes. The short lifetime as a function is shown here, while the long lifetime is shown in Figure 3c.

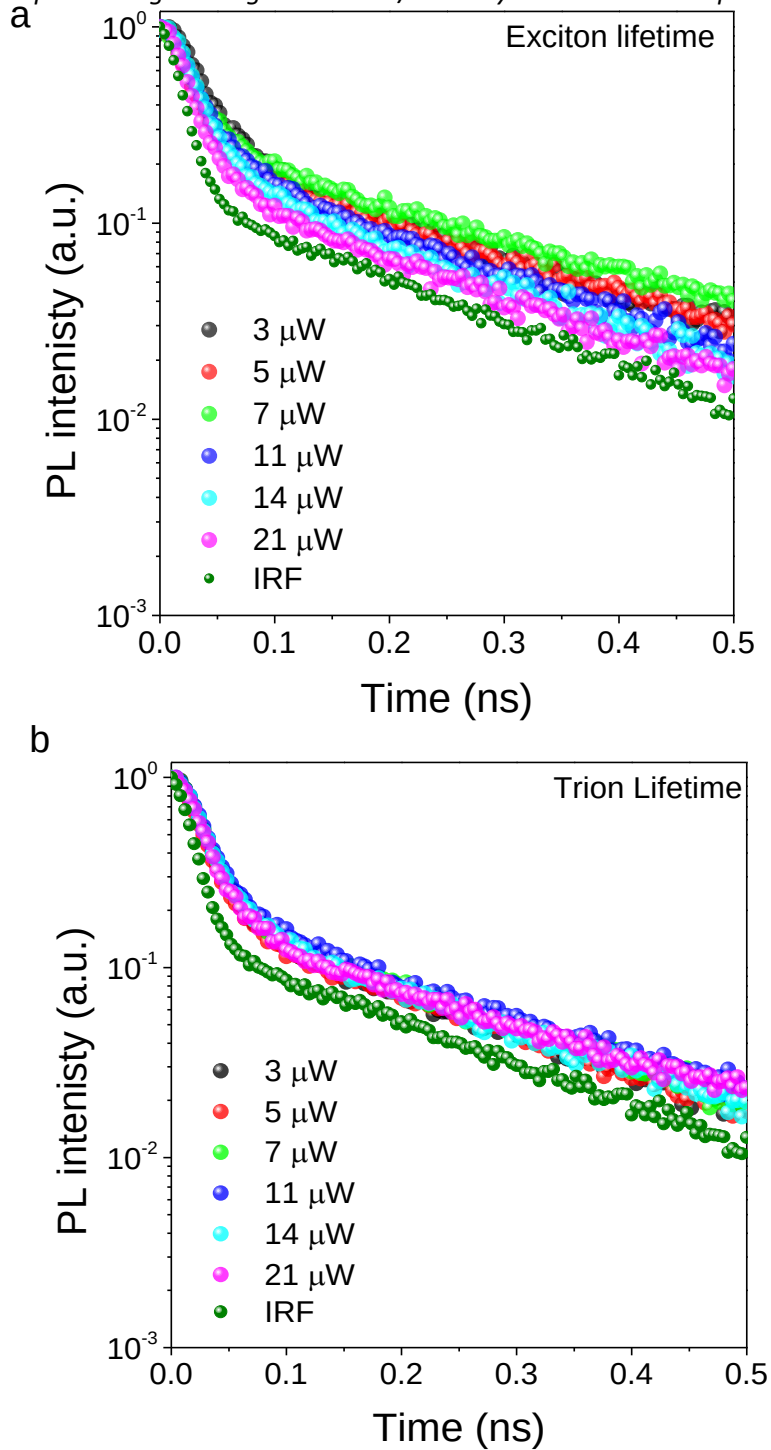


Figure S9 | Power dependent time-resolved PL at 77 K. Power dependent measurements at 77 K were carried out on 1L WS₂ samples, to confirm the exciton-exciton annihilation effects for both excitonic and trionic emission peaks. We observed an almost constant excitonic lifetime (263 -284 ps) and trionic lifetime (254-264 ps) ranging from a very low laser power to a high laser power ranging from 3 μ W to 21 μ W. The consistent lifetime suggest that the EEA does not play a key role in defining the exciton diffusion characteristics in our sample as shown in the figure below.

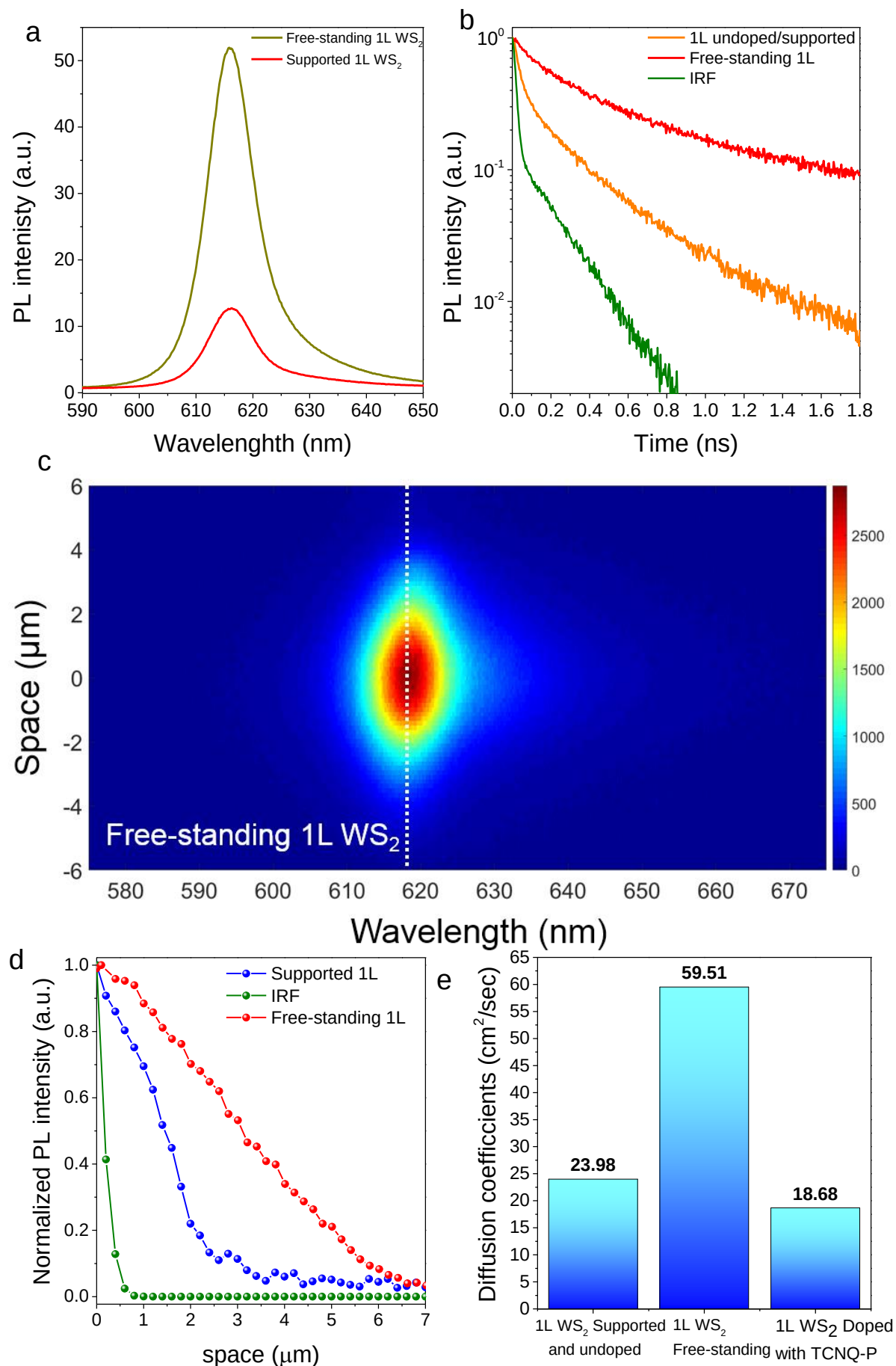


Figure S10 | Substrate induced defect scattering effect on exciton diffusion. **a**, Measured PL spectra from 1L WS₂ sample at room temperature from a free-standing 1L WS₂ sample as compared to PL emission from a supported 1L WS₂ sample. **b**, measured time-resolved PL spectra of exciton emission (617 nm) from a supported 1L sample (orange curve) (See Figure 1) as compared to elongated lifetimes from free-standing 1L sample (red curve) at room temperature. The effective lifetime from doped sample is fitted with only one slope with a value of 805 ± 15 ps. **d**, Direct imaging of exciton diffusion lengths using a near-field CCD imaging technique from free standing 1L WS₂. **e**, Spatial distribution of exciton diffusion plotted against the white dotted line in figure d. The diffusion length from chemically doped samples is higher ($3.09 \mu\text{m}$) as compared to undoped supported 1L WS₂ samples. ($1.51 \mu\text{m}$; Figure 1). **f**, Diffusion coefficient comparison between undoped/supported and chemically doped and free standing 1L WS₂ samples at room temperature under same excitation conditions.

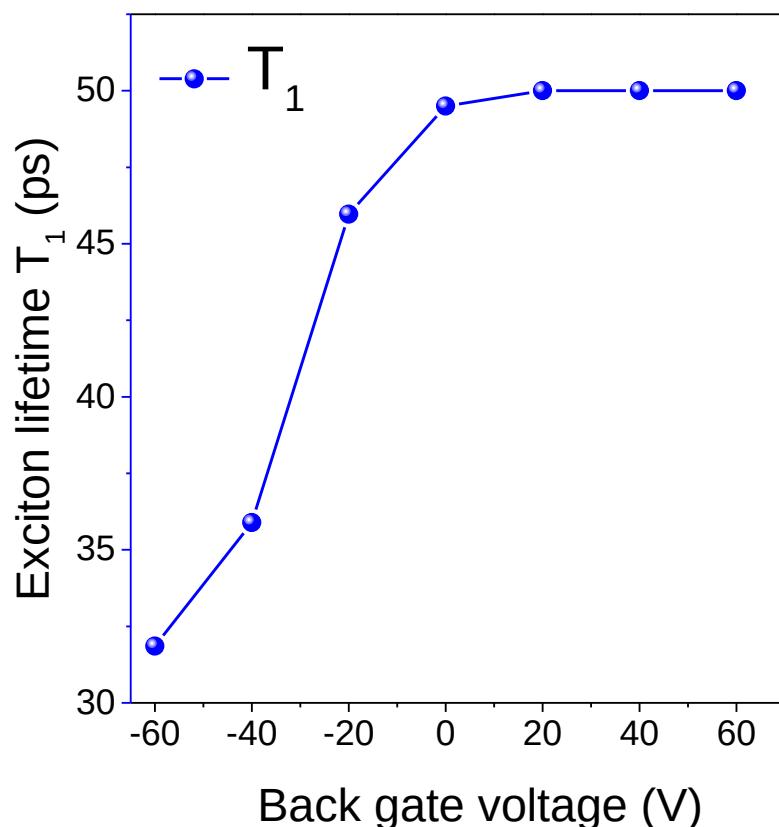


Figure S11 | Deconvoluted short lifetime as a function of back gate voltage for exciton peak (617 nm) at room temperature. The decay curves are shown in Figure 4g and are deconvoluted with IRF and fitted with two slopes. The decay curve is deconvoluted with the instrument response function (IRF) and fitted with two slopes. The short lifetime as a function is shown here, while the long lifetime is shown in Figure 4h.

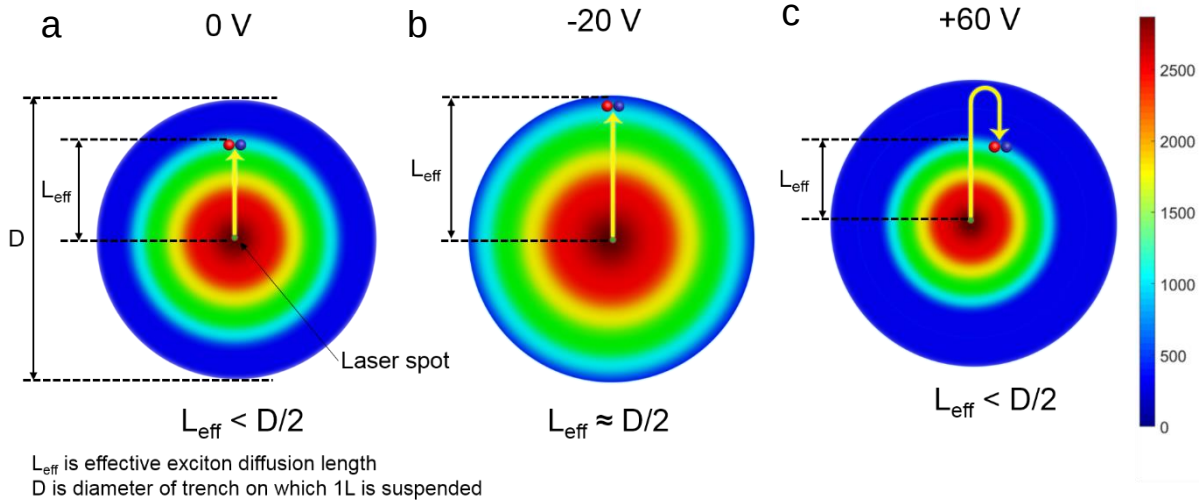


Figure S12 | Schematic showing the variation in diffusion length of excitons from a suspended 1L WS₂ sample. **a**, Exciton diffusion on a suspended 1L WS₂ when no back-gate voltage is applied. The diffusion length in all cases is calculated by the method described in the main text. **b**, Exciton diffusion pattern when the back-gate voltage is -20 V. The effective diffusion length of exciton is almost similar to the radius if the trench on which the 1L is suspended. **c**, Exciton diffusion pattern when the back-gate voltage is +60 V (more doping). The effective diffusion length decreases due to annihilation of excitons, attributed to non-linear loss of energy of excitons at the interface.

In the third case, when the exciton diffusion length starts to increase beyond the suspended part of the monolayer (> -20 V, due to continuous enhanced doping in the MOS device), the excitons will encounter the air-SiO₂ interface and lose their energy exponentially into the exciton quencher layer as predicted by Scully et al.^[3] Some of the excitons will return (as shown in Figure S12c) and annihilate with the incoming excitons from the laser spot, which is a common phenomenon reported with different substrates and different optical interference offered by various substrates.^[4] Hence, the effective diffusion length will be decreased (Figure 4f). However, the effective radiative lifetime as captured by our time-resolved PL (TRPL) photon counter will continue to increase with increasing doping (Figure 4h), due to the same reason which was explained in the main text. The excitons in the high-doping case are still long-lived, thus turn back from the interface to annihilate with the incoming excitons. Hence the TRPL setup will capture the longer lifetime of excitons as they will recombine radiatively to generate photons, which are captured by the TRPL counter. However, the effective diffusion length is captured by integrating the total photon emission in space onto a CCD detector after 1

second. The effective length will then be much smaller due to non-radiative recombination of exciton-exciton annihilation. It is important to note that this annihilation is not due to enhanced pumping power, but due to enhanced diffusion length of excitons and bouncing back of excitons from the optical boundary created by air-SiO₂ interface.

Table S1: Exciton diffusion coefficients from various materials.

Material Name	Diffusion Coefficient (cm ² /sec)	Temperature (K)
GaAs Quantum wells ^[5]	0.1-10	4.2
1L MoS ₂ ^[6]	0.1	298
1L WSe ₂ ^[7]	14.5	298
1L WS ₂ ^[8]	3.5	298
1L MoTe ₂ ^[9]	0.1	70
1L MoSe ₂ ^[10]	19	298
Phosphorene ^[11]	5 E-3	4
WS ₂ -tetracene heterostructure ^[12]	1	298
Wse ₂ -thin film/bulk ^[13]	15/9	298
Carbon Nanotubes ^[14]	44	298

References

- [1] G. Plechinger, P. Nagler, J. Kraus, N. Paradiso, C. Strunk, C. Schüller, T. Korn, *physica status solidi (RRL)*–Rapid Research Letters 2015, 9, 457.
- [2] J. He, D. He, Y. Wang, Q. Cui, F. Ceballos, H. Zhao, *Nanoscale* 2015, 7, 9526.
- [3] S. R. Scully, M. D. McGehee, *Journal of applied physics* 2006, 100, 034907.
- [4] T. Stübinger, W. Brütting, *Journal of Applied Physics* 2001, 90, 3632.
- [5] Z. Vörös, R. Balili, D. Snoke, L. Pfeiffer, K. West, *Physical review letters* 2005, 94, 226401.
- [6] D. Sun, Y. Rao, G. A. Reider, G. Chen, Y. You, L. Brézin, A. R. Harutyunyan, T. F. Heinz, *Nano letters* 2014, 14, 5625.
- [7] F. Cadiz, C. Robert, E. Courtade, M. Manca, L. Martinelli, T. Taniguchi, K. Watanabe, T. Amand, A. Rowe, D. Paget, *Applied Physics Letters* 2018, 112, 152106.
- [8] L. Yuan, L. Huang, *Nanoscale* 2015, 7, 7402.
- [9] G. Froehlicher, E. Lorchat, S. Berciaud, *Physical Review B* 2016, 94, 085429.
- [10] N. Kumar, Q. Cui, F. Ceballos, D. He, Y. Wang, H. Zhao, *Nanoscale* 2014, 6, 4915.
- [11] A. Surrente, A. Mitioglu, K. Galkowski, L. Klopotoski, W. Tabis, B. Vignolle, D. Maude, P. Plochocka, *Physical Review B* 2016, 94, 075425.
- [12] T. Zhu, L. Yuan, Y. Zhao, M. Zhou, Y. Wan, J. Mei, L. Huang, *Science Advances* 2018, 4, eaao3104.
- [13] Q. Cui, F. Ceballos, N. Kumar, H. Zhao, *ACS nano* 2014, 8, 2970.
- [14] S. Moritsubo, T. Murai, T. Shimada, Y. Murakami, S. Chiashi, S. Maruyama, Y. Kato, *Physical review letters* 2010, 104, 247402.

CHAPTER 7

Defect Engineering in Few-Layer Phosphorene

In chapter 3 of this thesis, I have discussed in detail the unique properties of phosphorene- another unique inorganic 2D material. While utilizing the substrate engineering for exciton dynamics modulation in TMDC materials reported in chapter 6, I also utilized the same approach with this unique 2D material because of its potential applications and interesting anisotropic optical properties. This chapter focusses on interesting excitonic emissions from defect sites in few-layer phosphorene (2L-4L) for applications in near infrared (NIR) emissions displays and LEDs. The chapter further introduces a combination of 2D-1D-0D system that enables high efficiency excitonic emissions from phosphorene in the NIR regime.

2D phosphorene with a quasi-1D excitonic nature provides a unique 2D platform for investigation of the dynamics of excitons in reduced dimensions and fundamental many-body interactions as explained in Chapter 3. This could lead to the development of many novel electronic and optoelectronic devices. However, on the other hand, the quasi-1D excitonic nature of phosphorene can significantly limit its luminescence quantum yield, primarily because of the quenching of mobile excitons caused by the rapid collision of these excitons with local quencher states in the quasi-1D space. Thus, the luminescence quantum yield has been successfully improved through reduction of the defect quenching of excitons in 1D carbon nanotubes. Conversely, instead of acting as exciton quenchers, some local states can function as zero-dimensional (0D) photoluminescent centers, which capture mobile excitons and convert them into photons with a very high radiative relaxation rate. This rate may even lie beyond that of intrinsic 1D excitons. Therefore, the embedding of local 0D-like luminescent states in monolayer phosphorene can lead to brightening of the excitons, which has implications for future optoelectronic and photonics devices.

In this chapter we demonstrate a method of brightening the excitons in three-layer (3L) phosphorene via the introduction of luminescent local states to monolayer phosphorene using PECVD oxide substrate, a commonly used material in photonic devices. Owing to the interfacial luminescent local states, 0D-like localized excitons are formed, resulting in efficient photon emissions at a new wavelength of ~ 1430 nm at elevated temperature in monolayer phosphorene; this contrast markedly with defect-induced photon emission from TMD semiconductor monolayers that can only be observed at cryogenic temperatures. We find that the luminescence quantum yield of 0D-like localized excitons can be 3 times larger than that of the intrinsic quasi-1D free excitons in 3L phosphorene, mainly caused by the reduction of non-radiative decay rate and possibly the enhanced radiative recombination probability. Phosphorene, with relatively lower bandgaps, is a perfect candidate to hold defect emissions in infrared wavelength ranges. Particularly, defect emission at the telecommunication band ~ 1550 nm is critical for future chip-based quantum communication technologies. The emission peak energy in phosphorene shows a red shift with increase of layer number; therefore, defect engineering in few-layered phosphorene

samples could further push localized exciton emissions to infrared range, which can enable exciting applications, such as chip-based optical telecommunication.

In this chapter, this thesis explores another interesting exciton engineering aspect which involves the role of substrate in introducing defect sites in the puckered structure of few layer phosphorene to obtain high efficiency defect excitonic emissions. This technique developed in this chapter can be critical to design devices such as single photon emitters, exciton-polariton devices and LEDs operating in the visible and NIR regime.

Defect Engineering in Few-Layer Phosphorene

Ankur Sharma, Bo Wen, Boqing Liu, Ye Win Myint, Han Zhang,* and Yuerui Lu*

Defect engineering in 2D phosphorene samples is becoming an important and powerful technique to alter their properties, enabling new optoelectronic applications, particularly at the infrared wavelength region. Defect engineering in a few-layer phosphorene sample via introduction of substrate trapping centers is realized. In a three-layer (3L) phosphorene sample, a strong photoluminescence (PL) emission peak from localized excitons at ≈ 1430 nm is observed, a much lower energy level than free excitonic emissions. An activation energy of ≈ 77 meV for the localized excitons is determined in temperature-dependent PL measurements. The relatively high activation energy supports the strong stability of the localized excitons even at elevated temperature. The quantum efficiency of localized exciton emission in 3L phosphorene is measured to be approximately three times higher than that of free excitons. These results could enable exciting applications in infrared optoelectronics.

semiconductors^[15–18] and will enable several promising novel optoelectronic and excitonic devices. Defect engineering has been demonstrated to be an important technique to modulate the properties of semiconductors for various applications.^[19,20] Particularly, defect engineering in 2D materials is critical and promising for the development of novel optoelectronic devices.^[21–23] Recently, single-photon emitters have been reported from the defect states in atomically thin TMDs and h-BN.^[24,25] Extrinsic defects have also been inducted into TMD materials for enhanced photoluminescence (PL) emission and doping sensitive modulation of the emissions.^[26,27] However, defect engineered emissions from TMDs have been reported in visible range with energies >1 eV.^[28] In contrast, phosphorene, with relatively lower bandgaps, is a perfect candidate to hold defect emissions in infrared wavelength ranges. Particularly, defect emission at the telecommunication band ≈ 1550 nm is critical for future chip-based quantum communication technologies.^[29] Recently, we successfully realized the defect engineering and triggered the defect emissions at ≈ 920 nm from monolayer phosphorene samples.^[30,31] The emission peak energy in phosphorene shows a red shift with increase of layer number; therefore, defect engineering in few-layered phosphorene samples could further push localized exciton emissions to infrared range, which can enable exciting applications, such as chip-based optical telecommunication.^[1,3–5,8,13,32–34]

1. Introduction

Phosphorene has been demonstrated as a viable option for the 2D material-based devices and optoelectronic applications because of its universal direct bandgap nature and wide-ranging bandgaps from 0.3 eV (bulk) to 1.7 eV (monolayer).^[1–8] Phosphorene serves as a perfect alternative material to bridge the gap between zero-bandgap graphene and large-bandgap transition metal dichalcogenide (TMD)^[9,10] semiconductors for suitable applications in the infrared wavelength range. Owing to its puckered lattice configuration,^[11,12] phosphorene possesses quasi-1D excitons and trions with highly enhanced binding energies,^[13,14] which is in contrast to other TMD 2D

phosphorene, with relatively lower bandgaps, is a perfect candidate to hold defect emissions in infrared wavelength ranges. Particularly, defect emission at the telecommunication band ≈ 1550 nm is critical for future chip-based quantum communication technologies.^[29] Recently, we successfully realized the defect engineering and triggered the defect emissions at ≈ 920 nm from monolayer phosphorene samples.^[30,31] The emission peak energy in phosphorene shows a red shift with increase of layer number; therefore, defect engineering in few-layered phosphorene samples could further push localized exciton emissions to infrared range, which can enable exciting applications, such as chip-based optical telecommunication.^[1,3–5,8,13,32–34]

In this work, we explored the defect engineering in few-layer phosphorene samples, by incorporating extrinsic defects using plasma-enhanced chemical vapor deposition (PECVD) grown oxide substrate. We observed a strong PL peak at ≈ 1430 nm, from localized excitons in three-layer (3L) phosphorene samples. Incident power dependent PL measurements were performed to confirm the emission nature of localized excitons, which shows a sublinear growth with increasing excitation power. Temperature-dependent PL measurements were also carried out to explore the thermal stability and activation energy (E_a) of the localized excitons with increasing temperatures. E_a in 3L phosphorene was measured to be ≈ 77 meV, which is a large value indicating relative stability of localized excitons even at higher temperatures (≈ 263 K). This is in sharp contrast to defect states in TMDs, where defect emissions are only visible at cryogenic temperatures.^[28] The overall quantum efficiency of localized exciton emission in 3L phosphorene was measured to approximately three times higher than that of free exciton peak.

A. Sharma, Dr. B. Wen, B. Liu, Y. W. Myint, Prof. Y. Lu
 Research School of Engineering
 College of Engineering and Computer Science
 the Australian National University
 Canberra, ACT 2601, Australia
 E-mail: yuerui.lu@anu.edu.au

Dr. B. Wen, Prof. H. Zhang
 SZU-NUS Collaborative Innovation Center for Optoelectronic
 Science and Technology
 Key Laboratory of Optoelectronic Devices and Systems of
 Ministry of Education and Guangdong Province
 College of Optoelectronic Engineering
 Shenzhen University
 Shenzhen 518060, P. R. China
 E-mail: hzhang@szu.edu.cn

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/smll.201704556>.

DOI: 10.1002/smll.201704556

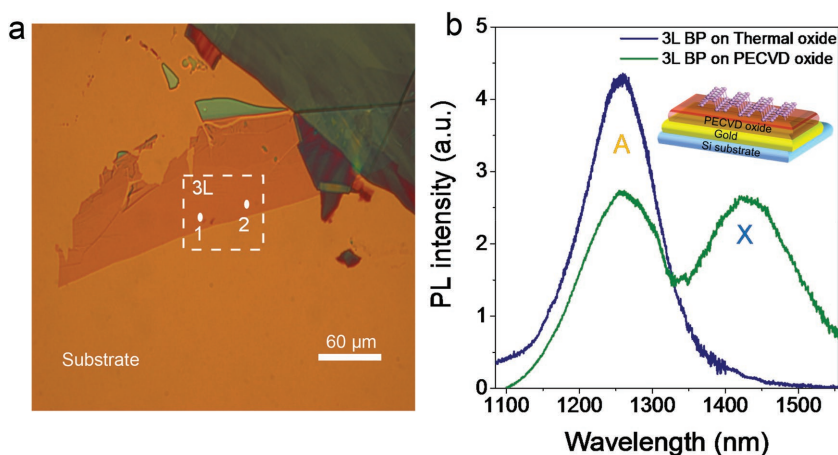


Figure 1. Characterization of 3L phosphorene samples. a) Optical microscope image of the sample used for measurements deposited over PECVD grown oxide layer underneath gold. The dotted square shows the area scanned by PSI to determine the thickness of the sample, hence the layer number (Figure S1b–d, Supporting Information). b) Measured PL spectra from 3L phosphorene at room temperature deposited over thermally grown oxide (blue) and 3L phosphorene sample deposited over PECVD grown oxide (green). Designated free (A) and localized (X) exciton peaks have been marked. Inset shows the schematic diagram of the sample.

2. Results and Discussion

Phosphorene flakes were mechanically exfoliated on to the thermal oxide and PECVD oxide/gold substrates, respectively, under dry conditions. The layer number was first determined by the optical contrast of the layer deposited over the substrate (Figure 1a). The sample was then immediately analyzed by a phase-shifting interferometer (PSI) to precisely determine the layer number^[35] (Figure S1 and associated text, Supporting Information). PL emission from the two samples on thermal oxide (blue) and PECVD oxide (green) was then measured as shown in the Figure 1b. During the PL measurements, the phosphorene sample was kept at -10°C in a Linkam microscope-compatible low-temperature chamber, with a continuous flow of liquid nitrogen to sustain the low temperature. At the temperature of -10°C , the moisture tends to freeze and the photooxidation of phosphorene slows down, which enhances the lifetime of the sample considerably and prevents degradation.^[35,36] Also, the sample on PECVD oxide substrate was observed to sustain longer than 24 h as compared to the one on thermal oxide which we observed started to degrade in a few hours. PECVD oxide has a more hydrophobic nature as compared to thermal oxide, which slows down the degradation of phosphorene.^[37] According to Andres et al.^[38] the degradation rate of phosphorene decreases with increasing thickness. 1L sample can survive up to 30 min in ambient conditions but a 2L, 3L, and 4L sample can survive up to much longer durations. As the layer number increases, the phosphorene samples become mechanically stronger and more stable and can thus survive much higher excitation power. This allowed us to measure PL spectrum at higher excitation power detailed in the following section.^[38]

The 3L phosphorene sample on thermal oxide showed a PL peak at $\approx 1250\text{ nm}$ (designated as A peak, Figure 1b), which is

consistent with our previous reports.^[14,30,33] In contrast, the 3L phosphorene sample showed two clearly distinctive peaks at 1250 and 1430 nm, assigned as A and X peak, respectively. The peak at 1250 nm was again attributed to the free excitons as it repeats itself from the first case, hence designated as A peak. The peak at 1430 nm (assigned as X peak) is a new feature caused by new PECVD oxide substrate. Also, the PL emission from A peak is reduced as compared to the PL intensity from thermal oxide. We moved the laser excitation spot over the same sample in at least 15 different closely spaced points using a manual piezo-stage controller. The “X” peak is repeatable in all the measurements. However, different PL intensity was observed for “X” peak from different locations, suggesting a nonuniform distribution of defect states, which has been discussed in the later sections.

In order to further study the nature of this new X peak observed, we performed excitation power dependent PL measurements at 263 K. Figure 2a shows the various spectrum obtained at various excitation power of the exciting laser from 20 to 110 μW . The PL spectra were fitted by Lorentzian function using two peaks: orange (A peak) and blue (X peak). For further quantitative analysis, the integrated PL intensities of both the peaks were plotted with respect to each other on a log–log scale (Figure 2b). This technique has been described in several previous reports by Yu and co-workers^[39] and Heinz and co-workers^[40] to determine the nature of excitonic emissions. By fitting the data with a power-law $I_X \propto I_A^\alpha$, where I_X is the integrated PL intensity of X peak and I_A is the integrated PL intensity of A peak, it is found that peak X grows sublinearly with the excitation power ($\alpha \approx 0.62$). The sublinear rise in the PL intensity for the ‘X’ peak was confirmed to be not arising from laser-induced damage of the sample. The PL intensity was repeatable after two cycles of power increase and decrease, suggesting no major damage of the sample. Based on the measured α value, peak X is attributed to the emission of localized excitons. Figure 2c shows the variation of peak energies of both the peaks with increasing laser power. The free exciton peak (peak A) shows a slight blue-shift with increasing laser power. This can be explained by an increase in the quasi-fermi energy level of the exciton pairs due to injection of extra charge carriers at higher excitation power, similar to the phenomenon observed in other 2D quantum well structures.^[41] In contrast, the defect peak (peak X) energy does not change with increasing power. The defect energy level in the energy bandgap remains independent of the injection power, possibly due to much lower density of states as compared to the free exciton state.^[42] The absolute integrated PL values are plotted as a function of laser power in Figure 2d. The FWHM (Figure 2e) of the A peak increases with the increasing excitation power, which could be attributed to thermal phonon scattering causing the broadening of the PL peak for the free excitons.^[43] The X peak is repeatable, as we measured several samples of 3L phosphorene on PECVD

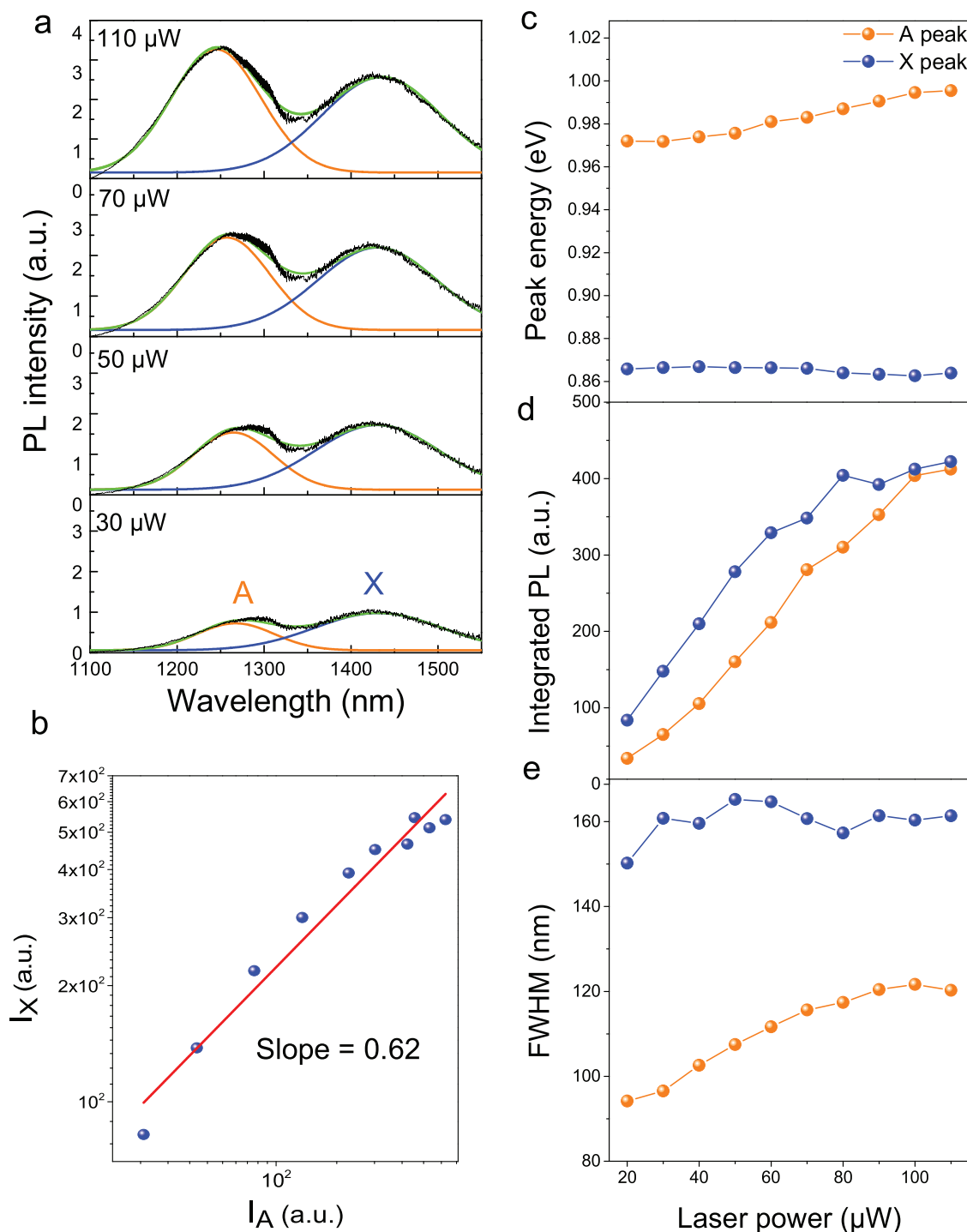


Figure 2. Power-dependent PL measurements. a) Measured PL spectra from 3L phosphorene samples over PECVD grown oxide layer at various excitation powers of the 532 nm laser. Spectra have been fitted using 2 Lorentz peaks at ≈ 1250 nm (orange) and ≈ 1430 nm (blue). Green line shows the cumulative fit. b) Log–log plot showing the variation of integrated PL intensity of peak X as a function of peak A. From the fitting curve (red solid line) the PL intensity of peak X grows sublinearly ($\alpha \approx 0.62$), with the increase of the excitation power. c) Variation of A and X peak positions with the increase in laser power. d) Integrated PL intensity values plotted against laser power. e) Full width at half maximum (FWHM) variation with laser power. X peak's FWHM is independent of the laser power. A peak's FWHM (free excitons) shows an increase with increasing laser power due to enhanced thermal and phonon scattering at higher laser power.

oxide substrate with X peak appearing in all of them regardless of the material on which PECVD oxide substrate was sitting on (gold, silicon, and transparent quartz). We attribute the

X peak to be from the localized excitons induced by the surface trapping centers from the PECVD substrate. Based on our Fourier-transform infrared (FTIR) spectroscopy measurements on

both PECVD and thermal oxides,^[30] there are many dangling oxygen bonds on the PECVD oxide surface. The adatoms of O being absorbed on the surface of phosphorene can serve as exciton trapping centers, leading to the origin of sublevels and gap states in the bandgap of 3L phosphorene and giving rise to intermittent PL emission at lower energy levels.^[44]

To study the thermal stability and activation energy of these localized states, we also performed the temperature-dependent PL measurements on the sample under the same excitation conditions. With the decreasing temperature, peak A was compromised for the enhancement of the X peak (Figure 3a). This trend can be explained with the schematic diagram shown in the Figure 3b. At low temperature, the localized and free excitons exist in their respective energy levels as shown. The thermal energy at low temperature is not enough to avoid the trapping of the free mobile excitons in defect sites and hence they can be localized/trapped and recombine radiatively to emit photons at 1430 nm.^[45] At elevated temperatures (≈ 263 K), the thermal energy starts to increase which provides sufficient kinetic energy to the localized excitons to avoid trapping.^[45] As shown in the Figure 3c, the peak positions are independent to the change of temperature. Whereas, the PL intensity of the X peak decays exponentially with the increasing temperature (Figure 3d). This trend can be explained by a theoretical model, which we used to fit the data for X peak in Figure 3d (solid red line). The localized excitons show a constant decay through a thermally activated dissociation channel, corresponding to the following decay equation^[40]

$$\gamma = 1 / [A \exp\{-E_a/k_B T\}] \quad (1)$$

where, γ is the PL intensity value observed, E_a is the activation energy of the localized excitons, k_B is the Boltzmann constant, A is an arbitrary fitting constant and T is temperature. The localized-state related PL emission shows characteristic thermal behavior, as shown in Figure 3. At low temperature, the generated excitons can get trapped by surface defects and impurities, due to relatively low kinetic energy of the excitons. Whereas, at high temperature the trapping efficiency decreases because of thermal activation of free excitons. Kato and Kaneko^[46] and Xu et al.^[45] suggested this relation between trapping efficiency and temperature. Therefore, it is expected that the intensity of localized exciton emission decreases monotonically with increasing temperature, which is exactly what we observed for the ones labeled as peak "X." The PL intensity of the "X" peak decreases with increasing temperature, which is because the excitons are not tightly bound to defects, and such weak interaction (shallow defect states) can be easily perturbed by thermal stimulation. E_a describes the necessary energy of thermal perturbation that prevents the free excitons from being trapped by localized defect sites.

The fitting equation gives the value of $E_a \approx 77.2 \pm 0.1$ meV. The extracted value for activation energy is smaller than the trapping potential demonstrated by the energy difference between the "A" and "X" peaks (≈ 130 meV). Similar observations have been made in other TMD and semiconducting materials as well (see Note S1 and associated Table S1, Supporting Information). The obtained activation energy of localized states in phosphorene is higher than what has been reported

in localized emissions from 2D TMD materials such as WSe₂ (43 meV),^[47] WS₂ (44.3 meV),^[48] and other semiconducting materials such as InAs quantum dots (27 meV),^[45] GaAs–AlGaAs nanowires (15 meV),^[49] and GaN (27 meV).^[50] Compared to a 2D system, the free excitons in phosphorene are confined in a quasi-1D space,^[25,26] thus resulting in enhanced interactions with the defect sites.^[51] The increased interaction requires higher activation energy correspondingly to overcome the trapping into defect states, because of which there is a greater stability of these localized exciton emissions even at temperatures close to room temperature ($E_a > k_B T$). High activation energy for the defect was simulated for phosphorene^[52] and demonstrated for 1D CNTs recently.^[51] For the free exciton peak (A peak), FWHM decreases at lower temperature again due to decrease in thermal and phonon scattering as explained earlier. Whereas, the FWHM of the X peak is again independent of the temperature, further suggesting its different nature with free excitons (Figure 3e). The total linewidth obtained can be theoretically explained by the following equation^[53] which taken in to account the temperature independent intrinsic term and temperature electron–phonon and surface defect scattering

$$\dot{\Gamma}(T) = \dot{\Gamma}_0 + \sigma T + \dot{\Gamma}_{LO} (\exp(E_{LO}/K_B T) - 1)^{-1} \quad (2)$$

Here, $\dot{\Gamma}_0$ is the dominantly electron–electron scattering representing term, which is independent of the temperature. Whereas σ is the electron–acoustic/thermal phonon coupling coefficient. LO is the longitudinal optical phonon term. $\dot{\Gamma}_{LO}$ represents the strength of exciton–LO phonon coupling. E_{LO} is the LO phonon energy.^[53,54] In case of the free excitons due to higher degree of freedom the electron–phonon coupling plays a dominant role, which is temperature dependent as shown in the second and third terms of the equation. Hence, the linewidth will increase as the temperature increases. While, in the case of localized excitons trapped in defect states the movement is further confined to a quasi 0D state, thus limiting their degree of freedom. This results in weaker phonon coupling and hence the electron–electron scattering dominates which is independent of the temperature. Hence for localized excitons the FWHM does not change with increasing temperature. This effect has been explained in detail in defect states in quantum carbon dots,^[53] CdSe nanodots,^[55] Au nanoclusters.^[56]

To further explore the nature of the localized excitons, we performed incident polarization dependent PL measurements on these peaks by changing the incident angle Θ . Interestingly, both the A and X peaks exhibited anisotropic behavior and showed the same polarization direction along the armchair direction of the phosphorene crystal (Figure S2a,b, Supporting Information).^[8,14,30,34,35] This further suggests that the localized states are caused by point-defects, like O adatoms^[57] absorbed on the phosphorene PECVD interface, since point-defects would not change the polarization of the exciton emissions.^[58,59]

In order to determine the overall quantum efficiency of the X peak in comparison to the A peak, we measured the PL spectra at several different spots, where there were different amounts of trapping centers caused by the nonuniformity of PECVD deposition. Large changes were observed in the PL spectra obtained from various locations. Figure 4a,b shows the variation in PL

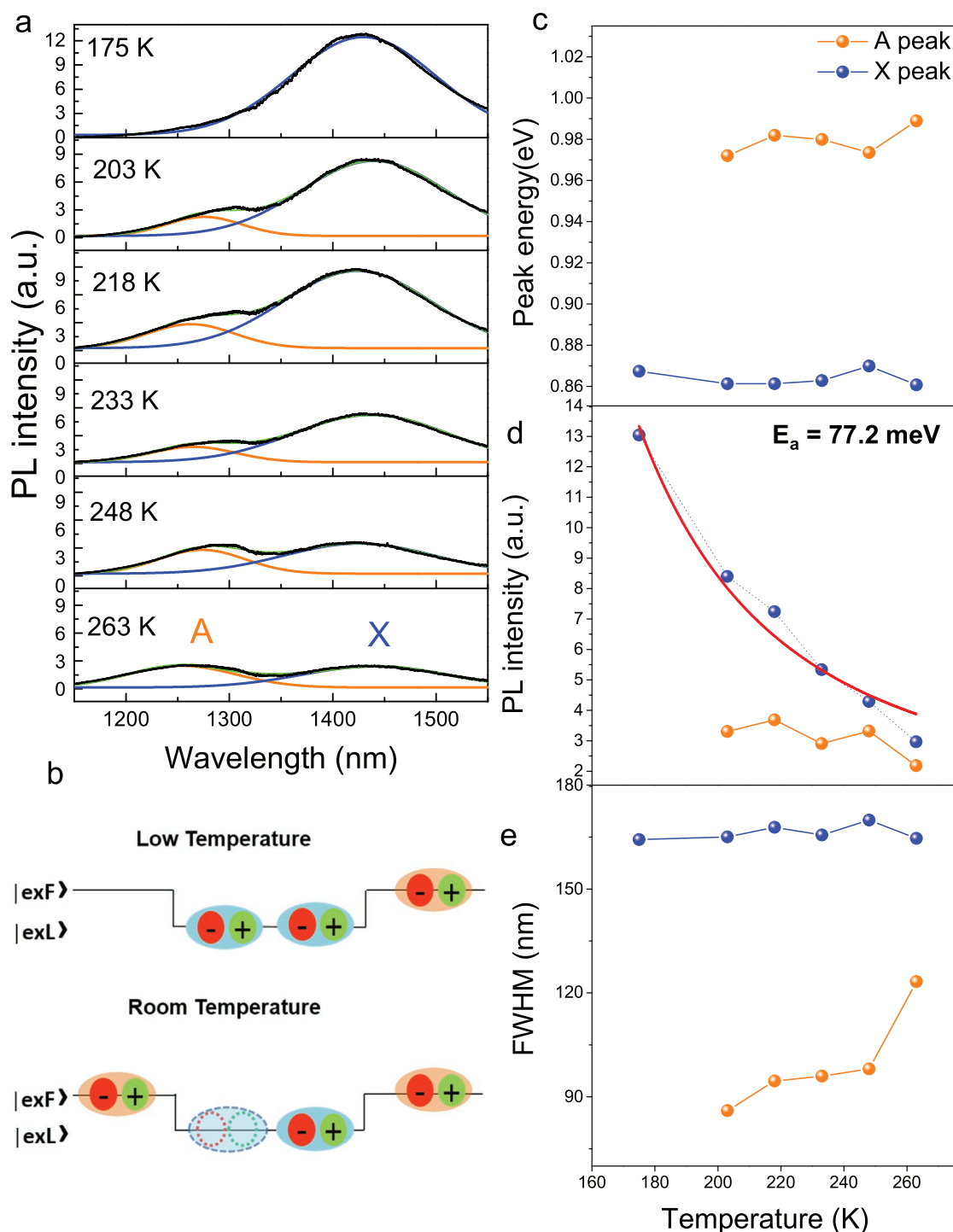


Figure 3. Temperature-dependent PL measurements. a) Measured PL spectra at various temperatures for phosphorene sample. b) Schematic diagram showing the position of localized (low energy) and free (high energy) excitons at low temperature and elevated temperatures. At higher temperature, the localized excitons gain sufficient thermal activation energy to move up to the free exciton energy level. c–e) Measured c) peak position, d) peak intensity and e) FWHM of PL peaks A and X as a function of temperature in 3L phosphorene. The PL intensity of peak X in (e) has been fit (red solid line) using the thermal exponential exciton decay equation (see main text) to calculate the thermal activation energy for localized excitons to be $\approx 77.2 \text{ meV}$.

spectrum obtained from two different positions. As the integrated PL intensity of peak A decreased, the integrated PL intensity for X peak increased considerably (Figure 4c). To determine the quantum efficiency of peak X as compared to the quantum

emission efficiency of peak A, we followed the approach suggested by Miyauchi et al.^[60] This approach is applicable to 1D matrix systems, and as shown above the free excitons in anisotropic phosphorene are confined to a quasi-1D space in nature

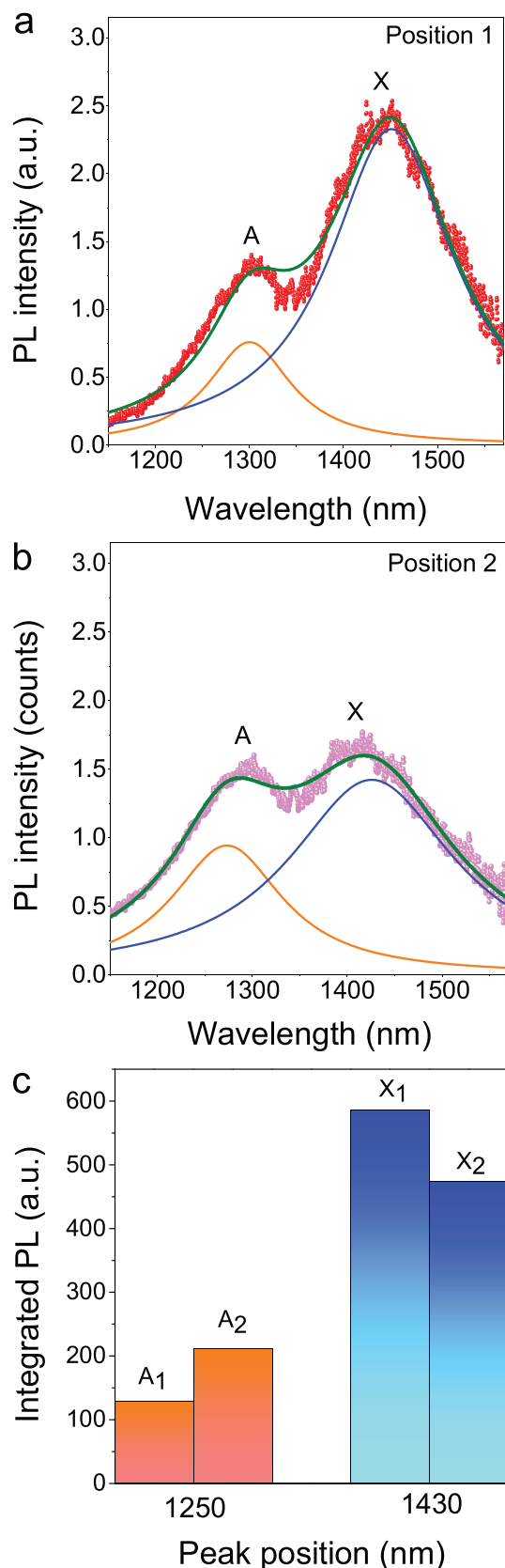


Figure 4. Internal quantum efficiency characterization. a,b) PL spectrum obtained from two different positions on the 3L phosphorene flake (See

(see Figure S2, Supporting Information). Thus, we can apply the same approach to determine overall quantum efficiency ratio between free excitons and localized excitons in case of phosphorene. Here, ΔI_X was defined in terms of the difference of two integrated PL intensities $\Delta I_X = |I_{X1} - I_{X2}|$, where, I_{X1} and I_{X2} are the two integrated PL intensities for localized exciton states measured at two separate locations. ΔI_A is the counterpart for free excitons. Matsuda and co-workers^[60] suggested an equation relating the $\Delta I_X/\Delta I_A$ ratio the internal quantum efficiency yield of the free excitons (η_A) and localized excitons (η_X) emissions as follows

$$\frac{\Delta I_X}{\Delta I_A} \sim \frac{1}{2} \left(\frac{\eta_X}{\eta_A} \right) \left(\frac{E_X}{E_A} \right) \quad (3)$$

We determined the value of $\frac{\eta_X}{\eta_A}$ to be ≈ 3.0 . This indicates that the internal quantum efficiency of the localized excitons is slightly higher than that of free excitons. The enhancement is not as high as compared with what we observed from 1L phosphorene samples ($\frac{\eta_X}{\eta_A} \approx 33.6$) in our previous report.^[30] This indicates layer-dependent defect emissions from phosphorene samples.

In addition, we also deposited bilayer (2L) phosphorene samples on PECVD substrate and measured the PL emissions, but we did not observe any defect peaks from 2L phosphorene samples. This could be depending on the electronic structure of the phosphorene layer and the properties of the adatoms. Similarly, 4L phosphorene samples were also prepared and measured. The free exciton peak emission from 4L is ≈ 1450 nm^[35] which is close to the cutoff range of our InGaAs detector (900–1550 nm). Hence, we were unable to record any possible lower energy defect PL emission peaks from 4L sample, which would lie in the range >1550 nm. (see Figure S3 and associated text, Supporting Information). This opens avenues for further studies to confirm the layer-dependent extrinsic defect nature in mono- and few-layer phosphorene samples.

3. Conclusions

We have demonstrated an infrared PL emission at ≈ 1430 nm from 3L phosphorene, in addition to a free exciton emission at ≈ 1250 nm, by engineering the phosphorene–substrate interfacial states. The localized exciton emission is attributed to the extrinsic defect states caused by the adsorption of O adatoms on the surface of phosphorene. We confirmed the nature of these localized excitonic emissions using power-dependent

Figure 1), showing a varied ratio of peak A/peak X PL intensity. The orange peak shows the fitted peak “A” and blue peak shows the fitted peak “X.” The green curve shows the cumulative fit peak. c) Integrated PL comparisons from the peaks at 1250 nm (blue) and 1430 nm (orange) respectively. The intensity of peak “A” increases while the intensity of peak “X” decreases in position 2 as compared to position 1. The change in integrated PL value was used to calculate the overall quantum efficiency enhancement of peak “X” with respect to peak “A.”

and polarization-dependent PL measurements. Temperature-dependent PL measurements were used to determine the activation energy (≈ 77 meV) of the localized excitons. This relatively high activation energy leads to the thermal stability of localized states in phosphorene, allowing them to be observed at elevated temperatures, in sharp contrast with other TMD materials. Our results have promising potential applications in future optoelectronic devices, such as chip-based optical telecommunication and photodetection devices.

4. Experimental Section

Few-layer phosphorene samples (2L–4L) were mechanically exfoliated onto the PECVD oxide (223 nm) on gold substrate with the thickness of gold ≈ 300 nm. Other sample were grown on normal silicon substrate covered with 280 nm of thermally grown SiO_2 respectively. The Au layer was used to fully block the influence of PL emissions from Si substrate in the first case, in order to avoid any discrepancy coming from the intrinsic defects in silicon being used. Due to high reflective nature of gold, it prevents any emission coming from underneath the gold surface to affect the PL emission detected from the phosphorene sample deposited over the other side of gold surface. This was necessary to understand the exclusive effect PECVD oxide in introducing stimulated defect emissions from few-layered phosphorene. PECVD oxide was deposited at 200 °C with SiH_4 and N_2O as reacting precursors, using the Plasmalab 100 dual frequency system. 3L phosphorene samples were put into a temperature-controlled chamber. All PL spectra, power-dependent PL and polarization-dependent PL measurements were conducted at a temperature of 263 K in the same microscope compatible chamber (LINKAM THMS 600), using a 532 nm Nd:YAG laser as the excitation source. Our PL system (T64000) uses two liquid nitrogen cooled detectors, one charge-coupled device (CCD) detector and one InGaAs detector.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

A.S., B.W., and B.L. contributed equally to this work. The authors thank Professor Chennupati Jagadish and Professor Barry Luther-Davies from Australian National University, for their facility support. The authors acknowledge financial support from ANU PhD student scholarship, China Scholarship Council, Australian Research Council, and ANU Major Equipment Committee.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

activation energy, defect emissions, infrared, localized excitons, phosphorene

Received: December 29, 2017

Revised: February 6, 2018

Published online: March 23, 2018

- [1] M. Buscema, D. J. Groenendijk, S. I. Blanter, G. A. Steele, H. S. J. van der Zant, A. Castellanos-Gomez, *Nano Lett.* **2014**, *14*, 3347.
- [2] R. Fei, L. Yang, *Nano Lett.* **2014**, *14*, 2884.
- [3] X. Hong, J. Kim, S.-F. Shi, Y. Zhang, C. Jin, Y. Sun, S. Tongay, J. Wu, Y. Zhang, F. Wang, *Nat. Nanotechnol.* **2014**, *9*, 682.
- [4] L. Li, Y. Yu, G. J. Ye, Q. Ge, X. Ou, H. Wu, D. Feng, X. H. Chen, Y. Zhang, *Nat. Nanotechnol.* **2014**, *9*, 372.
- [5] H. Liu, A. T. Neal, Z. Zhu, Z. Luo, X. Xu, D. Tománek, P. D. Ye, *ACS Nano* **2014**, *8*, 4033.
- [6] F. Xia, H. Wang, Y. Jia, *Nat. Commun.* **2014**, *5*, 4458.
- [7] A. Chaves, T. Low, P. Avouris, D. Çakır, F. Peeters, *Phys. Rev. B* **2015**, *91*, 155311.
- [8] R. Xu, J. Yang, Y. Zhu, H. Yan, J. Pei, Y. W. Myint, S. Zhang, Y. Lu, *Nanoscale* **2016**, *8*, 129.
- [9] J. Pei, J. Yang, R. Xu, Y.-H. Zeng, Y. W. Myint, S. Zhang, J.-C. Zheng, Q. Qin, X. Wang, W. Jiang, Y. Lu, *Small* **2015**, *11*, 6384.
- [10] J. Pei, J. Yang, X. Wang, F. Wang, S. Mokkaleti, T. Lü, J.-C. Zheng, Q. Qin, D. Neshev, H. H. Tan, C. Jagadish, Y. Lu, *ACS Nano* **2017**, *11*, 7468.
- [11] J. Lu, J. Yang, A. Carvalho, H. Liu, Y. Lu, C. H. Sow, *Acc. Chem. Res.* **2016**, *49*, 1806.
- [12] J. Pei, J. Yang, Y. Lu, *IEEE J. Sel. Top. Quantum Electron.* **2017**, *23*, 206.
- [13] V. Tran, R. Soklaski, Y. Liang, L. Yang, *Phys. Rev. B* **2014**, *89*, 235319.
- [14] R. Xu, S. Zhang, F. Wang, J. Yang, Z. Wang, J. Pei, Y. W. Myint, B. Xing, Z. Yu, L. Fu, *ACS Nano* **2016**, *10*, 2046.
- [15] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, *Nat. Nanotechnol.* **2011**, *6*, 147.
- [16] J. S. Ross, S. Wu, H. Yu, N. J. Ghimire, A. M. Jones, G. Aivazian, J. Yan, D. G. Mandrus, D. Xiao, W. Yao, X. Xu, *Nat. Commun.* **2013**, *4*, 1474.
- [17] J. Yang, R. Xu, J. Pei, Y. W. Myint, F. Wang, Z. Wang, S. Zhang, Z. Yu, Y. Lu, *Light: Sci. Appl.* **2015**, *4*, e312.
- [18] Z. Yi, Y. Jiong, Z. Shuang, M. Salman, P. Jiajie, W. Xinghua, L. Yuerui, *Nanotechnology* **2016**, *27*, 135706.
- [19] H. Nan, Z. Wang, W. Wang, Z. Liang, Y. Lu, Q. Chen, D. He, P. Tan, F. Miao, X. Wang, *ACS Nano* **2014**, *8*, 5738.
- [20] Z. Lin, B. R. Carvalho, E. Kahn, R. Lv, R. Rao, H. Terrones, M. A. Pimenta, M. Terrones, *2D Mater.* **2016**, *3*, 022002.
- [21] H. Chen, J. Yang, E. Rusak, J. Straubel, R. Guo, Y. W. Myint, J. Pei, M. Decker, I. Staude, C. Rockstuhl, Y. Lu, Y. S. Kivshar, D. Neshev, *Sci. Rep.* **2016**, *6*, 22296.
- [22] H. Chen, V. Corbaliou, A. S. Solntsev, D.-Y. Choi, M. A. Vincenti, D. de Ceglia, C. de Angelis, Y. Lu, D. N. Neshev, *Light: Sci. Appl.* **2017**, *6*, e17060.
- [23] X. Zai-Quan, Z. Yupeng, W. Ziyu, S. Yuting, H. Wenchao, X. Xue, Y. Wenzhi, X. Yunzhou, S. Litao, Z. Changxi, L. Yuerui, L. Lei, B. Qiaoliang, *2D Mater.* **2016**, *3*, 041001.
- [24] I. Aharonovich, D. Englund, M. Toth, *Nat. Photonics* **2016**, *10*, 631.
- [25] Y.-M. He, ClarkGenevieve, R. SchaibleyJohn, Y. He, C. ChenMing, J. WeiYu, DingXing, Q. Zhang, W. Yao, X. Xu, C.-Y. Lu, J.-W. Pan, *Nat. Nanotechnol.* **2015**, *10*, 497.
- [26] S. Tongay, J. Zhou, C. Ataca, J. Liu, J. S. Kang, T. S. Matthews, L. You, J. Li, J. C. Grossman, J. Wu, *Nano Lett.* **2013**, *13*, 2831.
- [27] S. Mouri, Y. Miyauchi, K. Matsuda, *Nano Lett.* **2013**, *13*, 5944.
- [28] S. Tongay, J. Suh, C. Ataca, W. Fan, A. Luce, J. S. Kang, J. Liu, C. Ko, R. Raghunathanan, J. Zhou, F. Ogletree, J. Li, J. C. Grossman, J. Wu, *Sci. Rep.* **2013**, *3*, 2657.
- [29] A. Martin, O. Alibart, M. De Micheli, D. Ostrowsky, S. Tanzilli, *New J. Phys.* **2012**, *14*, 025002.
- [30] R. Xu, J. Yang, Y. W. Myint, J. Pei, H. Yan, F. Wang, Y. Lu, *Adv. Mater.* **2016**, *28*, 3493.
- [31] J. Pei, X. Gai, J. Yang, X. Wang, Z. Yu, D.-Y. Choi, B. Luther-Davies, Y. Lu, *Nat. Commun.* **2016**, *7*, 10450.

- [32] J. Qiao, X. Kong, Z.-X. Hu, F. Yang, W. Ji, *Nat. Commun.* **2014**, *5*, 4475.
- [33] S. Zhang, R. Xu, F. Wang, J. Yang, Z. Wang, J. Pei, Y. W. Myint, B. Xing, Z. Yu, L. Fu, Q. Qin, Y. Lu, *arXiv:1411.6124*, **2014**.
- [34] S. Zhang, J. Yang, R. Xu, F. Wang, W. Li, M. Ghufuran, Y.-W. Zhang, Z. Yu, G. Zhang, Q. Qin, Y. Lu, *ACS Nano* **2014**, *8*, 9590.
- [35] J. Yang, R. Xu, J. Pei, Y. W. Myint, F. Wang, Z. Wang, S. Zhang, Z. Yu, Y. Lu, *Light: Sci. Appl.* **2015**, *4*, e312.
- [36] A. Favron, E. Gaufres, F. Fossard, A.-L. Phaneuf-Lheureux, N. Y. W. Tang, P. L. Levesque, A. Loiseau, R. Leonelli, S. Francoeur, R. Martel, *Nat. Mater.* **2015**, *14*, 826.
- [37] Y. Yun, T. Yoshida, N. Shimazu, N. Nanba, Y. Inoue, N. Saito, O. Takai, *J. Surf. Finish. Soc. Jpn.* **2007**, *58*, 307.
- [38] J. O. Island, G. A. Steele, H. S. van der Zant, A. Castellanos-Gomez, *2D Mater.* **2015**, *2*, 011002.
- [39] J. Shang, X. Shen, C. Cong, N. Peimyoo, B. Cao, M. Eginligil, T. Yu, *ACS Nano* **2015**, *9*, 647.
- [40] Y. You, X.-X. Zhang, T. C. Berkelbach, M. S. Hybertsen, D. R. Reichman, T. F. Heinz, *Nat. Phys.* **2015**, *11*, 477.
- [41] P. Perlin, C. Kisielowski, V. Iota, B. Weinstein, L. Mattos, N. A. Shapiro, J. Kruger, E. R. Weber, J. Yang, *Appl. Phys. Lett.* **1998**, *73*, 2778.
- [42] J. I. Pankove, *Optical Processes in Semiconductors*, Courier Corporation, New York, NY : Dover **1971**, p. 422.
- [43] Y. I. Mazur, G. G. Tarasov, G. J. Salamo, in *Self-Assembled Quantum Dots, Lecture Notes in Nanoscale Science and Technology*, vol 1, Springer, New York, NY **2008**, pp. 67–128.
- [44] X. Yang, S. Guo, F. Chan, K. Wong, W. Ching, *Phys. Rev. A* **1991**, *43*, 1186.
- [45] Z. Xu, Z. Lu, Z. Yuan, X. Yang, B. Zheng, J. Xu, W. Ge, Y. Wang, J. Wang, L. L. Chang, *Superlattices Microstruct.* **1998**, *23*, 381.
- [46] T. Kato, T. Kaneko, *ACS Nano* **2014**, *8*, 12777.
- [47] Z. Wu, Z. Luo, Y. Shen, W. Zhao, W. Wang, H. Nan, X. Guo, L. Sun, X. Wang, Y. You, *Nano Res.* **2016**, *9*, 3622.
- [48] C. Backes, A. Mitoglu, V. Vega-Mayoral, D. Hanlon, J. Coleman, V. Ivanov, D. Maude, P. Plochocka, *Nanotechnology* **2016**, *27*, 425701.
- [49] D. Rudolph, L. Schweickert, S. Morkötter, L. Hanschke, S. Hertenberger, M. Bichler, G. Koblmüller, G. Abstreiter, J. J. Finley, *New J. Phys.* **2013**, *15*, 113032.
- [50] C. Wetzel, S. Fischer, J. Krüger, E. Haller, R. Molnar, T. Moustakas, E. Mokhov, P. Baranov, *Appl. Phys. Lett.* **1996**, *68*, 2556.
- [51] Y. Miyauchi, M. Iwamura, S. Mouri, T. Kawazoe, M. Ohtsu, K. Matsuda, *Nat. Photonics* **2013**, *7*, 715.
- [52] A. Ziletti, A. Carvalho, D. K. Campbell, D. F. Coker, A. C. Neto, *Phys. Rev. Lett.* **2015**, *114*, 046801.
- [53] P. Yu, X. Wen, Y.-R. Toh, J. Tang, *J. Phys. Chem. C* **2012**, *116*, 25552.
- [54] B. T. Diroll, C. B. Murray, *ACS Nano* **2014**, *8*, 6466.
- [55] X. Wen, A. Sitt, P. Yu, Y.-R. Toh, J. Tang, *Phys. Chem. Chem. Phys.* **2012**, *14*, 3505.
- [56] P. Yu, X. Wen, Y.-R. Toh, J. Tang, *J. Phys. Chem. C* **2012**, *116*, 6567.
- [57] A. Carvalho, M. Wang, X. Zhu, A. S. Rodin, H. Su, A. H. C. Neto, *Nat. Rev. Mater.* **2016**, *1*, 16061.
- [58] A. K. Arora, A. Ramdas, *Phys. Rev. B* **1987**, *35*, 4345.
- [59] L. Eaves, D. Halliday, *J. Phys. C: Solid State Phys.* **1984**, *17*, L705.
- [60] Y. Miyauchi, M. Iwamura, S. Mouri, T. Kawazoe, M. Ohtsu, K. Matsuda, *Nat. Photonics* **2013**, *7*, 715.



Supporting Information

for *Small*, DOI: 10.1002/sml.201704556

Defect Engineering in Few-Layer Phosphorene

Ankur Sharma, Bo Wen, Boqing Liu, Ye Win Myint, Han Zhang, and Yuerui Lu**

Supplementary Information

Defect Engineering in Few-Layer Phosphorene

Ankur Sharma^{1§}, Bo Wen^{1,2§}, Boqing Liu^{1§}, Ye Win Myint¹, Han Zhang,^{2*} and Yuerui Lu^{1*}

¹Research School of Engineering, College of Engineering and Computer Science, the Australian National University, Canberra, ACT, 2601, Australia

²SZU-NUS Collaborative Innovation Center for Optoelectronic Science and Technology, Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Optoelectronic Engineering, Shenzhen University, Shenzhen, 518060, PR China

* To whom correspondence should be addressed: Yuerui Lu (yuerui.lu@anu.edu.au) and Han Zhang (hzhang@szu.edu.cn)

§ These authors contributed equally to the work.

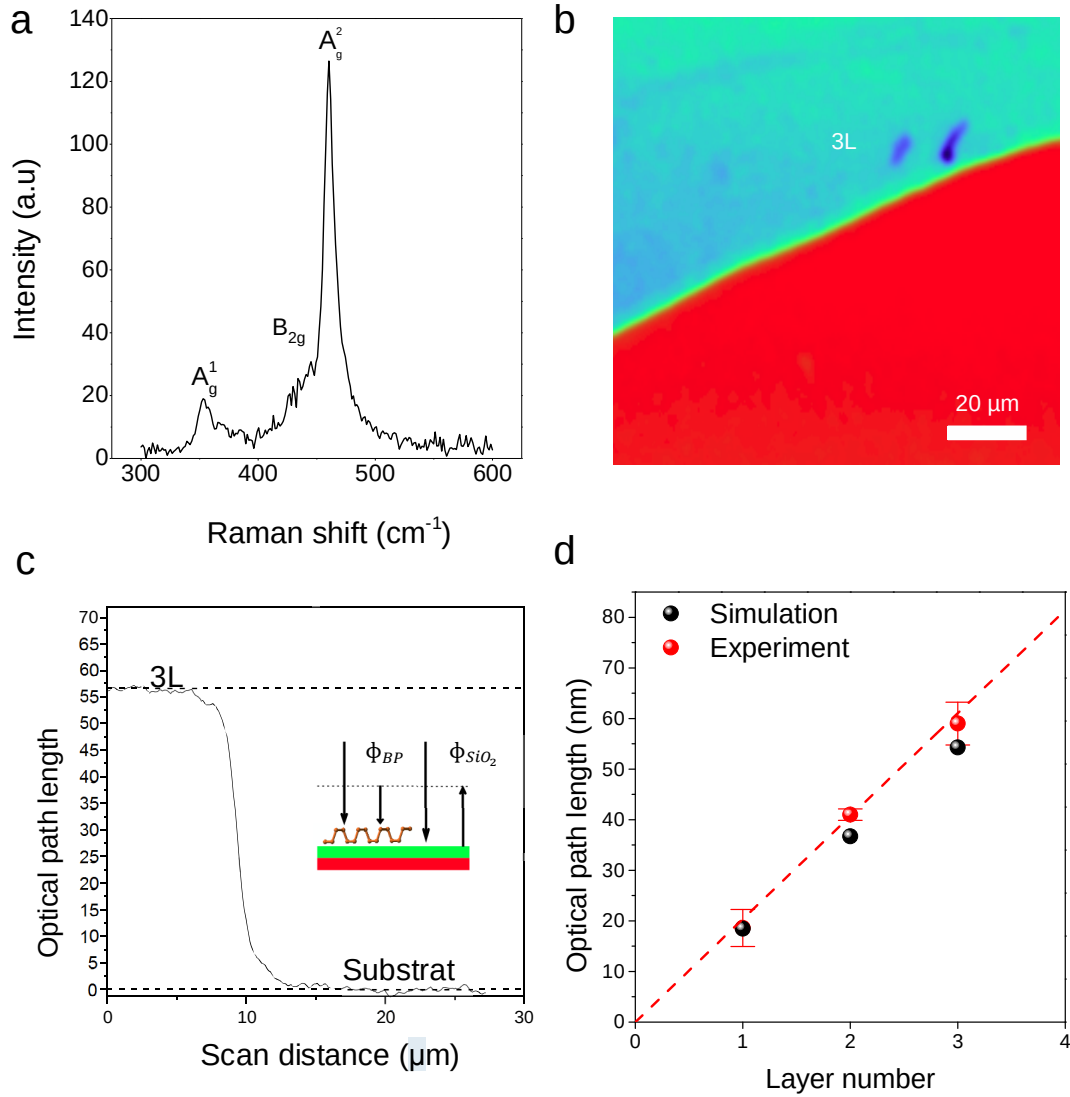


Figure S1 | Characterization of the 3L phosphorene samples. **a**, Raman spectra of the 3L phosphorene sample deposited over PECVD enhanced oxide. **b**, PSI image of the sample area marked in dotted square in Figure 1a. **c**, Measured PSI value of the 3L phosphorene flake as compared to the substrate. The actual thickness can be then derived from the optical path length as reported in our previous report ^[1]. **d**, Statistical data representation of the simulated and calculated optical path lengths (OPL) from various layers of phosphorene samples using PSI on the PECVD enhanced oxide substrates. The values were then used to calibrate the thickness of each layer using at least two sets of measurements on each sample. The actual thickness of each layer was confirmed using AFM ^[1]. Red dots show the experimentally

observed values of the OPL and black dots show the calculated values. The red dotted line represents the linear trend for the measured values of OPL obtained from simulation results.

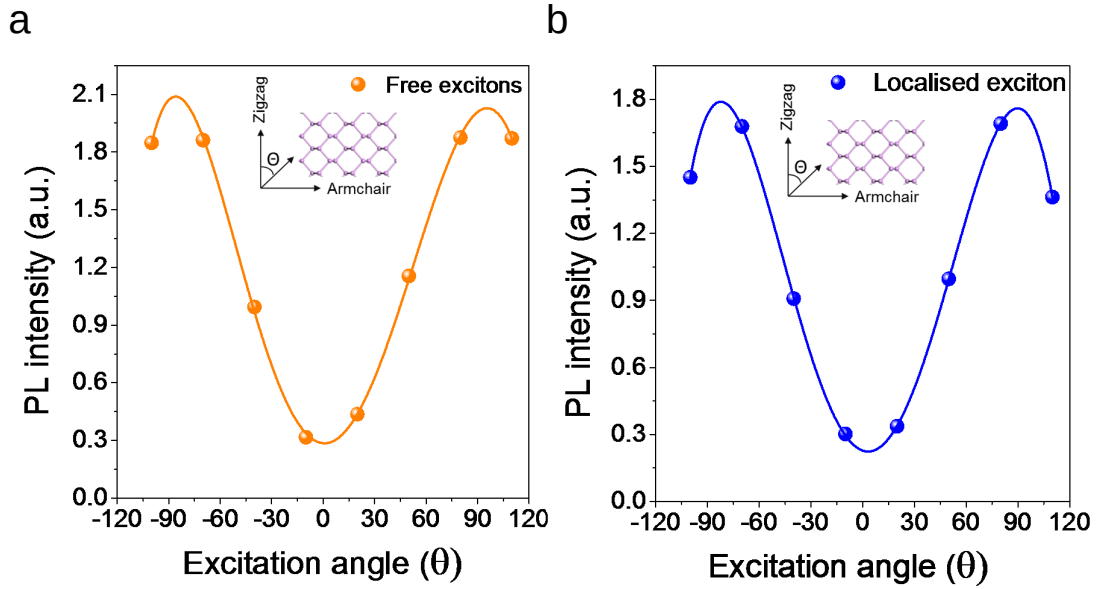


Figure S2 | Angle-resolved PL spectra for excitation polarization, revealing the excitonic nature of emission from the 3L phosphorene on PECVD oxide at room temperature. a-b, Measured angle-resolved PL intensity of the A peak (a) and X peak (b) plotted as a function of the incident laser excitation angle. In experiment, the incident angle (θ) was controlled using an angle variable half-wave plate. Both the exciton peaks show the characteristic anisotropic nature of phosphorene with a period $\sim 180^\circ$, sharing the same polarization direction. The excitons are highly anisotropic and aligned towards the armchair direction of the puckered phosphorene (see inset).

Supplementary Note 1:

“Activation energy” and “Trapping potential”:

The fitting parameter that we have extracted from temperature dependent PL measurements physically signifies the thermal activation energy of localized excitons trapped in the defect states and is thus referred to as ‘Activation energy’. Activation energy is defined as the necessary energy of thermal perturbation that prevents the free excitons from being trapped

by localized defect sites. ^[2] On the other hand, trapping potential is generally the energy difference between free excitonic PL peak and localized exciton peak. ^[3] Though several references have clearly pointed to a co-relation between the two.

Therefore, it is possible that activation energy is lower or comparable to the value of the trapping potential. We have tabulated values of Thermal activation energies and trapping potentials from other TMD materials and semiconducting systems for a simple comparison in Table 1. Generally, the value of activation energy is much lower than the value of the trapping potential, which is also the same in our case. The possible reason for that can be that activation energy apart from being a function of the trapping potential is also a function of the defect state (deep or shallow), defect size and distribution of defect densities across the sample. This has been stated by several similar measurements as tabulated below.

Table S1: Thermal activation energy and Trapping potential for defect states in various semiconducting materials.

Material	Trapping Potential or E_A-E_X (Energy difference between free and localized exciton peaks) (meV)	Thermal Activation Energy (E_a) (meV)	References
1L WSe₂	110.0	43.0	[4]
1L WS₂	100.0	44.3	[5]
ZnO/ (Mg, Zn)O multiple Quantum Wells	47.7	28	[6]
Quasi 1D Mixed-valence platinum complexes	320.0	70.0	[7]
GaAs-AlGaAs nanowires	4.8	5.8	[8]
GaN (1L)	140.0	27.0	[9]
InAs Quantum Dots	27.0	28.0	[10]

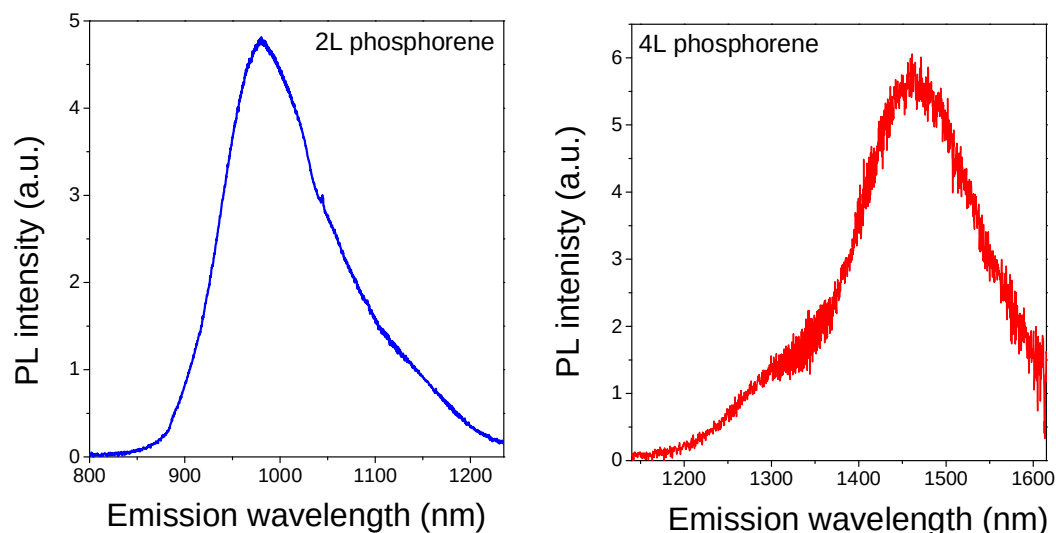


Figure S3 | a(b), PL emission from 2L(4L) phosphorene deposited over PECVD oxide at 263 K showing the free excitonic emission peak.

Figure S3a-b shows the PL spectra obtained from 2L and 4L phosphorene deposited over the PECVD oxide substrate respectively. From 2L sample, we could only observe the free excitonic emission at ~ 975 nm. Any low energy defect emission was not observed in over 7 different samples prepared.

Interestingly, the energy difference between free and localized excitonic emission in case of 1L phosphorene was ~ 0.42 eV^[1], which is much higher as compared to the energy difference in the 3L phosphorene sample in this case ~ 0.12 eV. Thus, clearly indicating layer dependent defect states in phosphorene. Layer dependent defect band gap for oxygen induced defects was reported by using first principle DFT calculations by Doganov, R. A. et al.^[11] and Wang et al.^[12] The studies suggest that in monolayer phosphorene the defect states induced by the defects do not hybridize with the valance band minimum (VBM) of the phosphorene band gap and hence remain unoccupied, acting as charge trapping centers. Whereas as the layer thickness increases as the band gap decreases the defect band states hybridize with the VBM of phosphorene. Thus, the defect states are now occupied and do not affect the conduction of electrons, which possible leads to ineffective trapping. This possibly explains why we did not observe the defect emission peak from 2L phosphorene. Whereas, for 3L sample additional defect bands have been reported by first order DFT calculations which can still act as

potential charge trapping centers, due to possible unoccupied orbital states ^[11] leading to the radiative PL emission in this case. For the 4L sample, we observed the free exciton peak emission at ~ 1450 nm, which is close to the detection limit of our InGaAs detector. Thus, not enabling us to observe any further low energy defect emission that would lie in the region >1550 nm. This opens further avenues for layer dependent defect emissions from phosphorene with further experimental evidence.

References

1. Yang, J., et al., *Optical tuning of exciton and trion emissions in monolayer phosphorene*. Light Sci Appl, 2015. **4**: p. e312.
2. Kato, T. and T. Kaneko, *Optical detection of a highly localized impurity state in monolayer tungsten disulfide*. ACS nano, 2014. **8**(12): p. 12777-12785.
3. Saleh, A.A. and J.A. Dionne, *Toward efficient optical trapping of sub-10-nm particles with coaxial plasmonic apertures*. Nano letters, 2012. **12**(11): p. 5581-5586.
4. Wu, Z., et al., *Defects as a factor limiting carrier mobility in WSe₂: a spectroscopic investigation*. Nano Research, 2016. **9**(12): p. 3622-3631.
5. Backes, C., et al., *Revealing the nature of excitons in liquid exfoliated monolayer tungsten disulphide*. Nanotechnology, 2016. **27**(42): p. 425701.
6. Makino, T., et al., *Temperature quenching of exciton luminescence intensity in ZnO/(Mg, Zn) O multiple quantum wells*. Journal of applied physics, 2003. **93**(10): p. 5929-5933.
7. Kurita, S., M. Haruki, and K. Miyagawa, *Photo-induced defect states in a quasi one-dimensional mixed-valence platinum complex*. Journal of the Physical Society of Japan, 1988. **57**(5): p. 1789-1796.
8. Rudolph, D., et al., *Probing the trapping and thermal activation dynamics of excitons at single twin defects in GaAs-AlGaAs core-shell nanowires*. New Journal of Physics, 2013. **15**(11): p. 113032.
9. Wetzell, C., et al., *Strongly localized excitons in gallium nitride*. Applied physics letters, 1996. **68**(18): p. 2556-2558.
10. Xu, Z., et al., *Thermal activation and thermal transfer of localized excitons in InAs self-organized quantum dots*. Superlattices and microstructures, 1998. **23**(2): p. 381-387.
11. Doganov, Rostislav A., et al. "Transport properties of pristine few-layer black phosphorus by van der Waals passivation in an inert atmosphere." Nature communications 6 (2015): 6647.
12. Wang, V., Y. Kawazoe, and W. T. Geng. "Native point defects in few-layer phosphorene." Physical Review B 91.4 (2015): 045433.

CHAPTER 8

Efficient and Layer-dependent Exciton Pumping Across Atomically-thin Organic-Inorganic Type-I Heterostructures

This thesis has focused on establishing the exciton dynamics and properties of 2D materials for various optoelectronics applications. Chapters 4 and 5 have discussed in detail all the organic 2D materials, whereas chapters 6 and 7 have been dedicated to inorganic 2D materials and their physical properties useful for device applications. In this final technical chapter of this thesis, we explore the dynamics of excitons when organic and inorganic materials are combined to achieve highly functional devices and how it alters the fundamental charge properties within the atomically thin 2D materials.

Van der Waals (vdW) heterostructures have been demonstrated in the literature recently where stacking of two similar layered nanomaterials leads to novel design architectures, optical properties and on demand device designs. One of the key advantages of 2D layered materials is their flexibility to offer flexibility of stacking with similar other materials for required applications and properties. There have been demonstrations recently where two inorganic materials such as two TMDC materials have been stacked together to form vertical vdW heterojunctions. The constituent layers interact weakly with out of plane layers and this weak vdW interaction enables the stacking of these atomically thin layers over each other with precision. This results in interesting electronic and optical properties of these heterostructures and has resulted in demonstration of optoelectronic devices based on tunable band gaps such as photodiodes, light emitting diodes, resonant tunneling diodes and solar cells. Several combinations of 2D materials have been used to synthesize vdW heterostructures these days, but it started with the use of specific inorganic materials such as hBN and graphene to create functional interfaces between two different materials. Since then various vdW heterostructures have been synthesized and reported. Specifically, junctions of various transition metal dichalcogenides (TMDs) (inorganic-inorganic) have been demonstrated extensively to quantify ultra-fast charge transfer across the interacting layers and long lived dissociated charges. Ultrafast charge transfer also has been established in organic-organic vdW coupled junctions. Literature predicts that organic-inorganic interfaces can combine to give such heterojunctions with epitaxially grown materials such as graphene or h-BN. All the organic-inorganic heterostructures that have been reported are far from the 2D limit. Also, the recently demonstrated heterostructures have been all Type-II heterostructures with focus on charge separation for solar cell efficiency enhancements.

As a final device demonstration in the thesis, I explored the possibility of combining the organic 2D material demonstrated in Chapter 4-5 and inorganic 2D materials demonstrated in chapter 3, 6 and 7 to obtain a new function device for enhanced charge transfer and light emitting device applications. The aim was to demonstrate a first of its kind 2D organic-inorganic

heterojunction where both the components are atomically thin and study the interesting exciton dynamics change in the junction.

This chapter demonstrates an inorganic-organic 2D van der Waals heterostructure, comprising of an ultrathin organic film down to the limit of monolayer organic semiconductors, which can provide a powerful platform to explore intrinsic charge transfer and band engineering within 2D plane. The atomically sharp and clean interface of the heterostructure is free from any dangling bonds and native surface oxides which provides an ideal platform to study the charge transfer and doping characteristics in such I-O vdW heterostructures. The 2D inorganic-organic (I-O) hybrid heterojunction exhibit pentacene layer dependent PL enhancement, suggesting a type-I band alignment where photo-excited electron hole pairs are transferred rapidly to from pentacene to MoSe₂ and recombine radiatively to give enhanced PL emission close to 3 times as observed from a 1L MoSe₂. Fundamental asymmetric charge transfer in hetero-interfaces is explained using temperature-dependent PL measurements. This chapter finally emphasizes on using these demonstrated results for various specific optoelectronic device applications such as high efficiency light emitting diodes. Moreover, this technique demonstrated here opens doors for further exploration of heterostructure devices to achieve precise control of molecular deposition over other atomically thin materials for a new class of hybrid functional materials which cater to a specific application.

Efficient and Layer-Dependent Exciton Pumping across Atomically Thin Organic–Inorganic Type-I Heterostructures

Linglong Zhang, Ankur Sharma, Yi Zhu, Yuhan Zhang, Bowen Wang, Miheng Dong, Hieu T. Nguyen, Zhu Wang, Bo Wen, Yujie Cao, Boqing Liu, Xueqian Sun, Jiong Yang, Ziyuan Li, Arara Kar, Yi Shi, Daniel Macdonald, Zongfu Yu, Xinran Wang,* and Yuerui Lu*

The fundamental light–matter interactions in monolayer transition metal dichalcogenides might be significantly engineered by hybridization with their organic counterparts, enabling intriguing optoelectronic applications. Here, atomically thin organic–inorganic (O–I) heterostructures, comprising monolayer MoSe₂ and mono-/few-layer single-crystal pentacene samples, are fabricated. These heterostructures show type-I band alignments, allowing efficient and layer-dependent exciton pumping across the O–I interfaces. The interfacial exciton pumping has much higher efficiency (>86 times) than the photoexcitation process in MoSe₂, although the pentacene layer has much lower optical absorption than MoSe₂. This highly enhanced pumping efficiency is attributed to the high quantum yield in pentacene and the ultrafast energy transfer between the O–I interface. Furthermore, those organic counterparts significantly modulate the bindings of charged excitons in monolayer MoSe₂ via their precise dielectric environment engineering. The results open new avenues for exploring fundamental phenomena and novel optoelectronic applications using atomically thin O–I heterostructures.

building blocks for fabricating 2D vdW heterostructures that possess atomically sharp interfaces, enabling promising optoelectronic applications such as efficient photodetectors, light-emitting diodes, resonant tunneling diodes, and solar cells.^[2–4] Organic molecular semiconductors have also recently been integrated with 2D TMDCs to form vdW heterostructures,^[5–10] which can dramatically engineer the light–matter interactions in the hybrid system and allow for new types of optoelectronic devices. However, those organic counterparts reported were based on bulk organic materials (>20 nm thick). The organic molecular arrangements on those reported O–I interfaces were not well controlled on the atomic scale, although the optoelectronic properties of organic molecular crystals are typically very sensitive to its aggregation and molecular arrangements.^[11–13] Compared to their bulk counterparts, our recently

reported atomically thin high-quality 2D organic molecular crystals possess well-defined molecular arrangements and the interesting layer-dependent carrier transport properties.^[14,15] This will allow us to build atomically thin O–I interfaces with well-controlled molecular arrangements on the interface and explore how the molecular aggregations would affect the light–matter interactions in the hybrid system. Furthermore,

reported atomically thin high-quality 2D organic molecular crystals possess well-defined molecular arrangements and the interesting layer-dependent carrier transport properties.^[14,15] This will allow us to build atomically thin O–I interfaces with well-controlled molecular arrangements on the interface and explore how the molecular aggregations would affect the light–matter interactions in the hybrid system. Furthermore,

Dr. L. Zhang, Dr. Y. Zhang, Dr. Y. Cao, Prof. Y. Shi, Prof. X. Wang
National Laboratory of Solid State Microstructures
Collaborative Innovation Center of Advanced Microstructures
School of Electronic Science and Engineering
Nanjing University
Nanjing 210093, P. R. China
E-mail: xrwang@nju.edu.cn

Dr. L. Zhang, Dr. A. Sharma, Dr. Y. Zhu, Dr. B. Wang, Dr. M. Dong,
Dr. H. T. Nguyen, Dr. B. Wen, Dr. B. Liu, Dr. X. Sun, Dr. J. Yang,
Dr. A. Kar, Prof. D. Macdonald, Prof. Y. Lu
Research School of Engineering
College of Engineering and Computer Science
The Australian National University
Canberra, Australian Capital Territory 2601, Australia
E-mail: yuerui.lu@anu.edu.au

Dr. Z. Wang, Dr. Z. Yu
Department of Electrical and Computer Engineering
University of Wisconsin
Madison, WI 53706, USA

Dr. Z. Li
Department of Electronic Materials Engineering
Research School of Physics and Engineering
The Australian National University
Canberra 2601, ACT, Australia

Prof. Y. Lu
ARC Centre of Excellence in Future Low-Energy
Electronics Technologies (FLEET)
ANU node
Canberra, Australian Capital Territory 2601, Australia

DOI: 10.1002/adma.201803986

ultrathin organic molecular crystals have a clear interface and high excitonic densities with high binding energies,^[16] which can comprehensively interact with excitonic states in the inorganic 2D materials and can lead to various applications for optical devices such as light-emitting devices.^[17–19]

Here, we demonstrated atomically thin O–I heterostructures, by stacking exfoliated monolayer MoSe₂ onto mono-/few-layer single-crystal pentacene samples that were epitaxially grown over h-BN surfaces. We observed significant photoluminescence (PL) enhancement from the monolayer MoSe₂ and PL quenching in the pentacene layers. Photoluminescence exciton (PLE) measurements were used to prove the type-I band alignments. The atomically thin O–I heterostructures with well-controlled interfacial molecular arrangements and type-I band alignments allow us to study the efficient and layer-dependent exciton pumping across the high-quality O–I interfaces which is in contrast to previously reported O–I heterostructures^[5,6,14,20,21] (with type-II band alignments). The interfacial exciton pumping efficiency from the hybridization of a wetting layer pentacene (0.5 nm thick) was measured to be ≈ 86 times higher than that from the photoexcitation process in MoSe₂, although the pentacene layer has much lower optical absorption than MoSe₂. The highly enhanced pumping efficiency is attributed to the high quantum yield (QY) in pentacene and the ultrafast energy transfer between the O–I interface. The measured interfacial pumping efficiency was sensitive to the layer number of organic 2D materials. Moreover, compared with other substrates, such as SiO₂ and h-BN, the pentacene layer has highly reduced dielectric screening effect on the many-body interactions in MoSe₂, which resulted in the enhanced bindings of the charged excitons in monolayer MoSe₂ depending on the spacing thickness of pentacene layer.^[22] Our findings provide a new way to engineer the light-matter interactions in atomically thin semiconductors and their hybrids, enabling various new optoelectronic devices, such as ultrathin lighting diodes, heterostructure lasers, etc.

Figure 1a shows the schematic configuration of the heterostructure. First, few layers of h-BN were mechanically exfoliated onto a 290 nm Si/SiO₂ substrate. Then the ultrathin 2D pentacene films were subsequently grown on the exfoliated h-BN via the physical vapor deposition (PVD) method in a tube furnace. The growth process is detailed in the author's previous work.^[14] MoSe₂ monolayer was then exfoliated and stacked on the atomically thin pentacene layers to form the heterostructures.^[23] This technique is a better method to avoid contamination and damage of the organic materials during the transfer process, and achieves ultraclean and intact atomic interfaces.^[24] **Figure 1b,c** shows the optical microscopy images of before and after transfer of monolayer MoSe₂ onto the pentacene film, respectively. The interfacial layer of pentacene grown directly over the h-BN is referred to as the wetting layer (WL) and subsequent layers above the WL are referred to as 1L and 2L.^[14] After heterostructure, all individual heterostructures are characterized by Raman spectroscopy after stacking (see **Figure S1**, Supporting Information) to confirm the formation of heterostructure. Atomic force microscopy (AFM) (**Figure 1d** and **Figure S2**, Supporting Information) was further used to deterministically designate each pentacene layer based on the observed thickness. Three different heterostructures based on the thickness

of pentacene layers underneath the monolayer MoSe₂ were fabricated. The optical image after stacking shown in **Figure 1c** shows three distinct heterostructure regions. PL spectroscopy is a sensitive probe to study the dynamic interlayer and intralayer charge transfer excitonic states which can provide evidence of coupling between the individual heterostructure layers.^[2,24,25] The PL spectra of the various heterostructures are shown in **Figure 1e**, an excitonic peak around 788 nm was observed for MoSe₂ (olive curve) and pentacene showed a broad emission in the range of 550–700 nm (red curve). The PL peak intensity of the 1L MoSe₂ + WL PEN heterostructure at ≈ 788 nm clearly indicates ≈ 2.8 times enhancement (**Figure 1e I**) as compared to that of monolayer MoSe₂ on SiO₂/Si substrate, whereas the PL peak from pentacene has been quenched. The enhancement factor η is defined as the ratio of absolute PL intensities of a HS to that of the monolayer MoSe₂ on SiO₂/Si substrate at 788 nm as observed during the experiments (i.e., $\eta = I_{\text{HS}}/I_{\text{MoSe}_2}$). Slightly lower enhancements were observed in the 1L MoSe₂ + 1L PEN ($\eta \approx 2.4$, **Figure 1e II**), 1L MoSe₂ + 2L PEN ($\eta \approx 1.7$, **Figure 1e III**), and 1L MoSe₂ + bulk PEN ($\eta \approx 1.2$, **Figure S3**, Supporting Information) heterostructures. Several devices (>5) were tested and these results were repeatable after numerous measurements. Also, we tested the heterostructures of 1L MoSe₂ on 2D pentacene after one month and the enhancement factor was observed to be stable, as compared with the initial measurements (**Figure S4**, Supporting Information).

In heterostructure design, the relative band alignment is the key factor that determines the type of heterostructure.^[26] **Figure 2a** illustrates the alignment of electronic bands of pentacene and MoSe₂,^[27–29] where the MoSe₂/pentacene forms a type-I heterojunction. Specifically, the highest occupied molecular orbital (HOMO) of pentacene is lower than the valence band maximum (VB) of monolayer MoSe₂ and the lowest unoccupied molecular orbital (LUMO) of pentacene is higher than the conduction band minimum (CB) of monolayer MoSe₂. As shown in **Figure 2a**, photoexcited carriers would transfer from pentacene to MoSe₂ due to large inbuilt potential and combine radiatively, which leads to the enhancement of the PL intensity in the MoSe₂ layer and the quenching of the PL intensity in pentacene layer (**Figure 1e**).

To further confirm the type-I band alignment nature of O–I hybrid heterostructures, photoluminescence excitation (PLE) experiments at room temperature were conducted. As shown in **Figure 1e**, the exciton peak position of 1L MoSe₂ is ≈ 788 nm (1.57 eV), which matches well with previous results.^[30–32] Pentacene has a broad exciton peak shape at 585 nm (2.12 eV).^[6,14] It implies that pentacene's lowest excited energy should be larger than that of monolayer MoSe₂. **Figure 2b,c** shows the PL spectra from 1L MoSe₂ and the 1L MoSe₂ + WL PEN heterostructure with excitation wavelength of 532 nm (2.33 eV) and 750 nm (1.65 eV), respectively. **Figure 2b** shows the PL intensity enhancement factor (η) is still around 2.8 which matches well with PL spectrum of **Figure 1e**. This is due to both the MoSe₂ and pentacene layers of the heterojunction were excited with an excitation energy of 2.33 eV. The photoexcited carriers can only transfer from the pentacene layer to MoSe₂ if the band alignment is type-I. Specifically, both electrons and holes are expected to transfer to MoSe₂ (see **Figure 2a**). In contrast, under an excitation wavelength of 750 nm as shown in **Figure 2c**, the PL intensity from 1L MoSe₂ + WL PEN

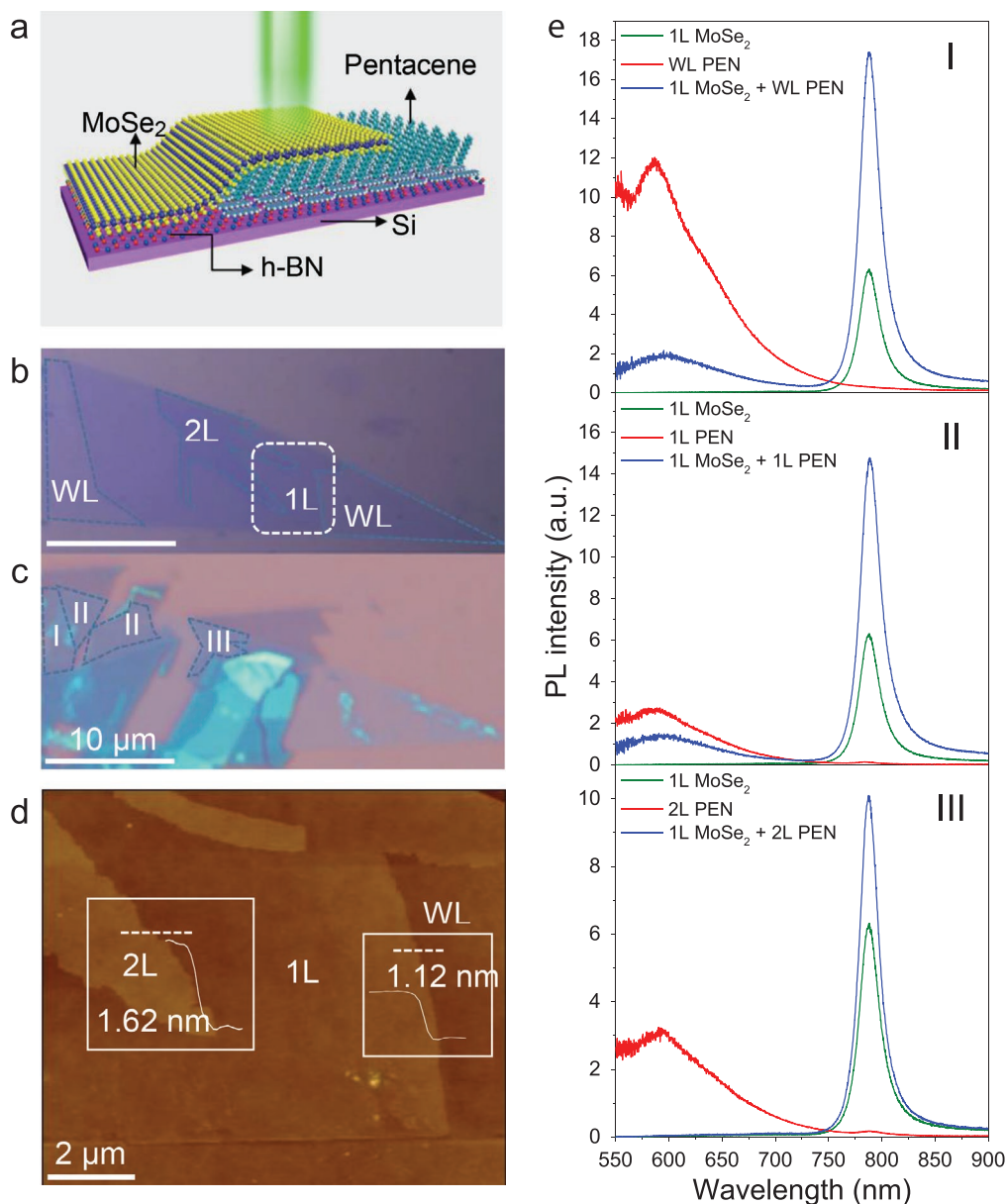


Figure 1. Characterization of layer-dependent heterostructures comprising of monolayer MoSe₂ and 2D pentacene. a) Schematic diagram of heterostructure of monolayer MoSe₂ on 2D pentacene. b) Optical image before heterostructure formation showing wetting layer (WL), one-layer (1L), and two-layer (2L) pentacene regions. Scale bar: 10 μ m. c) Optical image after 1L MoSe₂ transferred on pentacene. Scale bar: 10 μ m. (I) Heterostructure of 1L MoSe₂ on WL pentacene (1L MoSe₂ + WL PEN). (II) Heterostructure of 1L MoSe₂ on 1L pentacene (1L MoSe₂ + 1L PEN). (III) Heterostructure of 1L MoSe₂ on 2L pentacene (1L MoSe₂ + 2L PEN). Scale bar: 10 μ m. d) AFM image of the dotted rectangular area shown in (b). Inset: height measurements along the dashed line showing atomic layer thickness. e) (I) PL spectra of 1L MoSe₂ + WL PEN heterostructure, 1L MoSe₂, and WL PEN. (II) PL spectra from 1L MoSe₂ + 1L PEN heterostructure, 1L MoSe₂, and 1L PEN. (III) PL spectra from 1L MoSe₂ + 2L PEN heterostructure, 1L MoSe₂, and 2L PEN.

heterostructure is comparable to that of monolayer MoSe₂ on SiO₂/Si substrate. In this case with 750 nm excitation, only the MoSe₂ layer was excited since the lowest excitonic energy of pentacene is ≈ 1.83 eV (Figure 1e).^[33] The PL intensity from the heterostructure was slightly higher (≈ 1.19 times) than that from the 1L MoSe₂ sample on SiO₂/Si substrate (Figure 2c). This small PL enhancement might be due to that the pentacene layer acts as a passive layer decreasing nonradiative decay from the substrate or interface, which can be supported by the slightly increased carrier lifetime for exciton (≈ 788 nm) peak

of heterostructure than that of 1L MoSe₂ sample on SiO₂/Si (Figure S5, Supporting Information).^[34,35] From the PLE measurement (Figure 2d), PL intensity ratio (i.e., η) decreases sharply over excitation wavelengths of 700–750 nm, which corresponds to the lowest excitonic energy band in pentacene.^[33] The PLE data clearly confirm the type-I band alignment in our 1L MoSe₂ + WL PEN heterostructure. Similar PLE measurements were conducted to confirm the type-I band alignments in 1L MoSe₂ + 1L PEN and 1L MoSe₂ + 2L PEN heterostructures as shown in Figure S6 (Supporting Information).

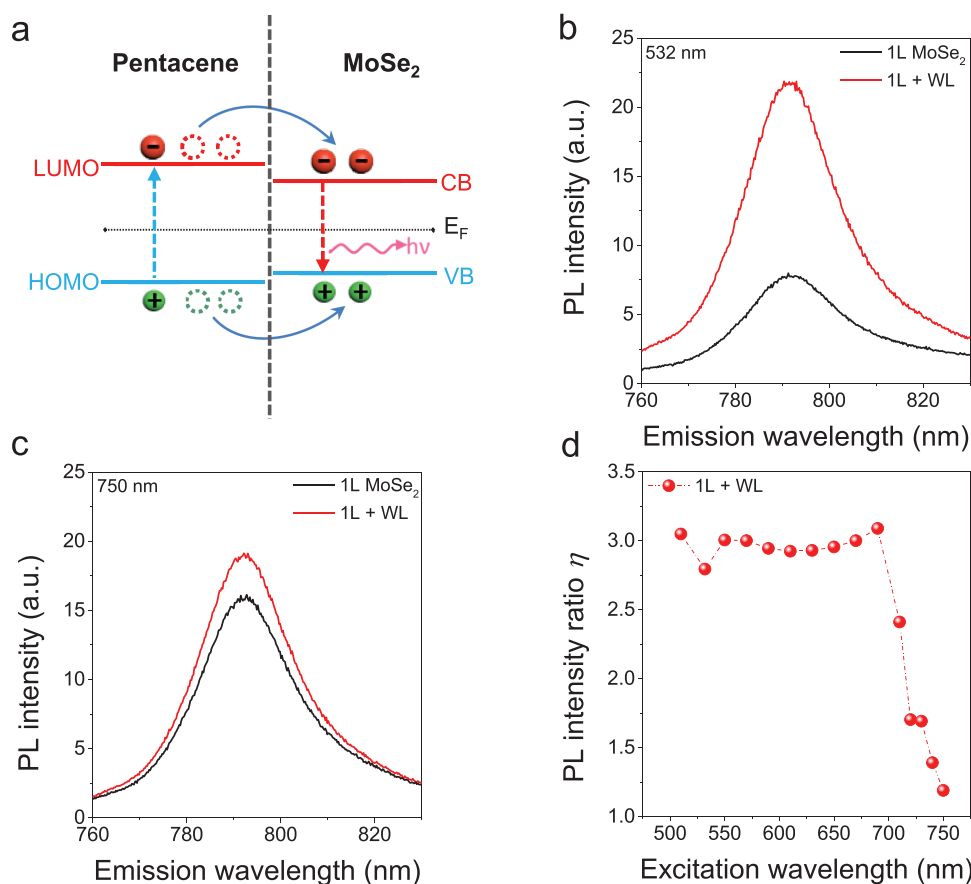


Figure 2. Confirmation of type-I band alignment by photoluminescence excitation (PLE). a) Band alignment diagram of a MoSe₂/pentacene heterostructure, which forms a type I heterostructure. b,c) Measured PL spectra of 1L MoSe₂ from SiO₂/Si substrate and from 1L MoSe₂ + WL PEN heterostructure, with different excitation wavelengths: 532 and 750 nm. d) Measured PL enhancement factor η from 1L MoSe₂ + WL PEN heterostructure as a function of excitation wavelength. The enhancement factor η is defined as the intensity ratio of PL peak at ≈ 788 nm between a heterostructure (HS) and the monolayer MoSe₂ on SiO₂/Si substrate.

The type-I band alignments in our atomically thin O–I heterostructures allow the efficient exciton pumping across the O–I interfaces. The hybridization of a WL pentacene (≈ 0.5 nm) leads to PL enhancement of 2.8 times. Considering that the WL pentacene has much lower measured optical absorption than 1L MoSe₂ (≈ 51 times lower) at the excitation wavelength of 532 nm (see Table S1, Supporting Information, and associated text), the exciton pumping efficiency across the O–I interface should be much higher than that from photoexcitation process in 1L MoSe₂. To further analyze the pumping efficiencies in the different heterostructures, an internal exciton pumping efficiency enhancement factor (β) is defined as

$$\beta = \frac{\text{Exciton pumping efficiency from heterostructure}}{\text{Exciton pumping efficiency from photoexciton in TMD}} = \left(\frac{I_{\text{HS}} - I_{\text{TMD}}}{I_{\text{TMD}}} \right) \left(\frac{A_{\text{TMD}}}{A_{\text{PEN}}} \right) \quad (1)$$

where I_{HS} and I_{TMD} are the measured integrated PL intensity from the HS and 1L MoSe₂ on SiO₂/Si substrate, respectively. A_{TMD} and A_{PEN} represent the measured absorption value from monolayer MoSe₂ and pentacene, respectively (Note S3 and

Table S1, Supporting Information). The measured β values for the 1L MoSe₂ + WL, 1L MoSe₂ + 1L PEN, and 1L MoSe₂ + 2L PEN heterostructures were 86.4, 20.4, and 3.2, respectively, which decrease with increasing thickness of pentacene film (Figure 3a), similar trend with the thickness-normalized PL intensities. The β values are highly related to the QYs (Note S4, Supporting Information) and carrier lifetimes in both layers,^[36] photocarrier relaxation pathways, and energy transfer channels (Figure 3b). In the 1L MoSe₂ + WL PEN heterostructure under 532 nm laser excitation, both the MoSe₂ and pentacene would be excited. The charge transfer process between O–I interfaces is typically ultrafast (6.7 ps, for instance),^[6,37,38] which is much shorter than the measured carrier lifetime in pentacene (1128 ps) and that in monolayer MoSe₂ (448 ps) (Figure 3c).^[35] Therefore, a large fraction of pentacene photoexcited charges (both electrons and holes) could transfer quickly to the MoSe₂ side and relax to some excited states for radiative recombination. Also, because WL pentacene has much higher QY and much lower optical absorption (Note S3 and S4 and Table S1, Supporting Information) than 1L MoSe₂, the interfacial exciton pumping efficiency in our atomically thin heterostructures will be much higher than that from the photoexcitation process in 1L MoSe₂, thus a high β value.

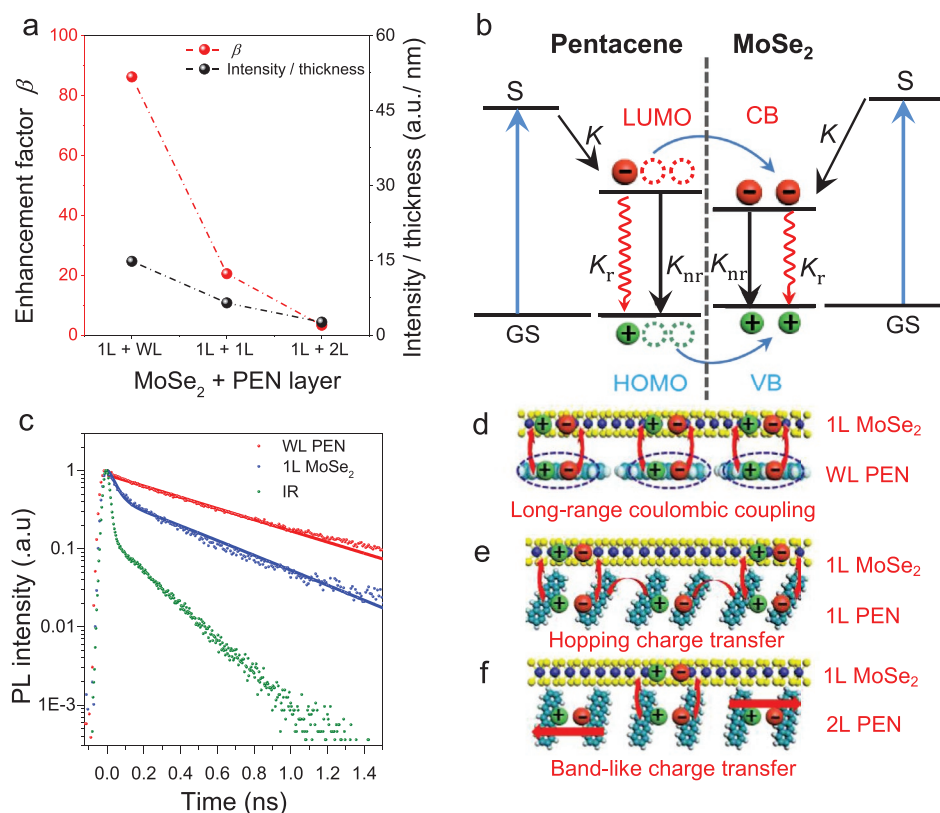


Figure 3. Efficient and layer-dependent interfacial exciton pumping. a) Exciton pumping efficiency enhancement factor β (left), normalized PL intensity (by pentacene layer thickness) of various kinds of heterostructures as compared with 1L MoSe₂ (right). b) Schematic of the exciton relaxation channels in the MoSe₂/pentacene heterostructure for excitation at S state resonance. GS represents ground state and S represents the excitation state. The wavy red (K_r) and straight black arrows (K_{nr}) represent radiative and nonradiative decay process, respectively. K is associated with each transition including intravalley thermalization or intervalley scattering. c) Measured time-resolved PL traces at room temperature for exciton peak ≈ 788 nm from oxide-supported monolayer MoSe₂ and for peak ≈ 590 nm from WL pentacene samples, IR represents instruments response curve. Based on the deconvolution with respect to the instrument response, double exponential equation $I = A \exp(-\frac{t}{\tau_1}) + B \exp(-\frac{t}{\tau_2}) + C$ was used for the fitting. For 1L MoSe₂, τ_1 and τ_2 were extracted to be 36 and 448 ps, respectively, which are considered to be nonradiative and radiative lifetimes, respectively.^[30,34,35] For WL pentacene, the single exponential equation $I = A \exp(-\frac{t}{\tau}) + C$, τ was extracted to be 1128 ps. d) Schematic diagram shows the charge transfer between WL PEN (bottom) and 1L MoSe₂ (top). The dotted ellipse shows long-range intralayer coulombic coupling within WL PEN. e) Schematic diagram shows the charge transfer 1L PEN (bottom) and 1L MoSe₂ (top). The horizontal crooked arrows show the hopping mechanism of charge transfer within 1L PEN. f) Schematic diagram shows the charge transfer between 2L PEN (bottom) and 1L MoSe₂ (top). The horizontal arrows show the band-like mechanism of charge transfer within 2L PEN.

The layer-dependent β values are highly related to the layer-dependent charge transport properties in 2D pentacene.^[14] As described in our previous report,^[14] WL pentacene was not conductive owing to the absence of intralayer π - π stacking. The photoexcited electrons and holes in the WL are coupled through long-range coulombic forces (Figure 3d) and are immobile within the layer.^[14] These localized charges can move more efficiently across the interface of the heterostructure into the MoSe₂. In 1L pentacene, charges are slightly more mobile within the pentacene layer and move through a hopping mechanism and are slightly more diffused along the pentacene layer (Figure 3e).^[14] Some charges diffuse and rest then transfer across the interface into the MoSe₂ layer, this results in fewer exciton pairs recombining and a lower enhancement of PL intensity from the 1L MoSe₂ + 1L PEN heterostructure. Moreover, the lower relative QYs of 1L pentacene as compared to WL pentacene (Note S4, Supporting Information) also

contribute to the smaller β value. In 2L pentacene, the charges are extremely mobile and almost follow a band-like mechanism to move within the pentacene layer (Figure 3f).^[14] Hence, the charges will be more diffused along the pentacene layer rather than crossing over the interface of the junction into the MoSe₂ layer. Furthermore, 2L pentacene has the lowest relative QYs among these pentacene films (Note S4, Supporting Information), in this case, fewer photocarriers transfer to the MoSe₂ and subsequently leads to the small β value and low normalized PL intensity as shown in Figure 3a. In addition, bulk pentacene thin film has the lowest (almost ignorable) PL enhancement factor ($\eta \approx 1.2$, Figure S3, Supporting Information) and thus ultralow interlayer charge transfer efficiency, because bulk pentacene layer possesses the band-like charge transport mechanism (similar to 2L pentacene layer) but more traps and disorders in the thin film.^[14] The comparison clearly shows that the efficient exciton pumping is only prominent at the 2D limit.

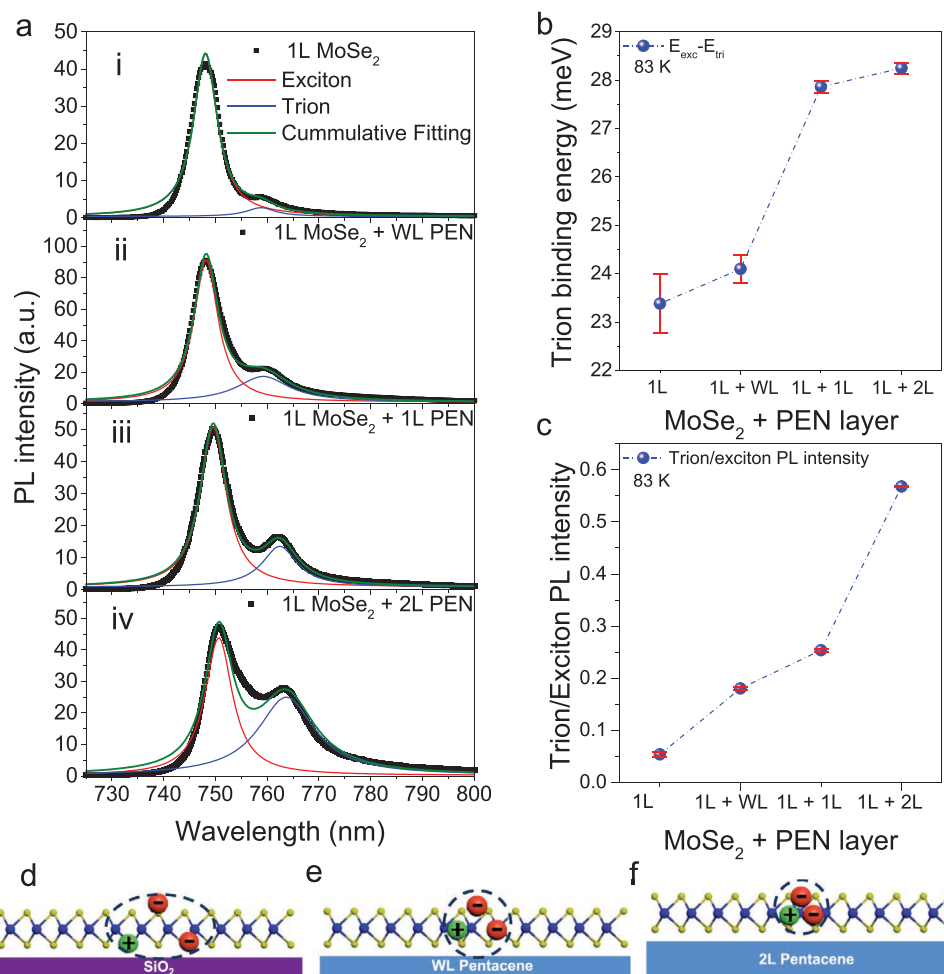


Figure 4. Layer-dependent modulation of the trion binding energy in 1L MoSe₂ via dielectric engineering. a) Measured PL spectra of 1L MoSe₂ from SiO₂/Si substrate, 1L MoSe₂ + WL PEN, 1L MoSe₂ + 1L PEN, and 1L MoSe₂ + 2L PEN heterostructures at 83 K. The PL spectrum was fitted by Lorentz function (black scatter lines are experimental data, red lines are labeled as exciton Peak, blue lines are labeled as trion peak, and olive lines are the cumulative fitting results). b) Measured trion binding energy (energy difference between exciton and trion peaks) of 1L MoSe₂ from SiO₂/Si substrate, 1L MoSe₂ + 1L PEN, and 1L MoSe₂ + 2L PEN heterostructures at 83 K. c) Measured trion/exciton PL peak intensity ratio of 1L MoSe₂ from SiO₂/Si substrate, 1L MoSe₂ + WL PEN, 1L MoSe₂ + 1L PEN, and 1L MoSe₂ + 2L PEN heterostructures at 83 K. d–f) Schematic representation of negatively charged trions in 1L MoSe₂ over different substrates: SiO₂, WL PEN, and 2L PEN. Pentacene has lower dielectric constant than SiO₂ and h-BN. The PEN layer serves as a low-dielectric spacing layer, which provides reduced dielectric screening and leads to enhanced trion binding energy (smaller trion size) in 1L MoSe₂.

The strong many-body interactions in monolayer TMDs lead to the formation of robust quasi-particles, such as excitons, trions (charged excitons), and biexciton which are extremely important for the optoelectronics device applications, such as light-emitting diodes, optical modulators, etc.^[30,39] Besides the efficient interfacial exciton pumping, the hybridization of 2D organic layers in our ultrathin O–I heterostructures would also allow us to precisely modulate the many-body interactions in the monolayer TMD via engineering the dielectric environment (Figure 4).^[32,40] Temperature-dependent (Figure S7, Supporting Information) and gate-dependent PL measurements (Figure S8, Supporting Information) were conducted to explore the detailed modulation of many-body interactions in our heterostructure systems. In the PL spectra measured from the 1L MoSe₂ sample

on SiO₂/Si substrate and in three heterostructures at 83 K, the two PL peaks at ≈ 748 and ≈ 759 nm (Figure 4a) are assigned to be the excitons and trions peaks of 1L MoSe₂, respectively.^[30] Based on the gate-dependent measurements (Figure S8, Note S5, Supporting Information), those trion peaks as shown in Figure 4a are negatively charged. The binding energy of trion in 1L MoSe₂, energy difference between exciton and trion peak position,^[32,41] was clearly enhanced with the hybridization of organic 2D materials and this enhancement increases with increasing pentacene layer number (Figure 4b). For instance, 1L MoSe₂ on SiO₂/Si sample showed a measured trion binding energy of ≈ 23.4 meV, which matches well with the reported value.^[32,42] The trion binding energy of 1L MoSe₂ on 2L PEN is enhanced by 4.9 meV as compared with that of 1L MoSe₂ on SiO₂/Si (Figure 4b). The

PL intensity ratio between trion and exciton peaks was also enhanced with the hybridization of pentacene and this enhancement also increases with increasing pentacene layer number (Figure 4c). It is expected that many-body interactions in low-dimensional materials, such as monolayer TMDs, are sensitive to dielectric environment.^[30] Larger dielectric screening effect can lead to smaller trion binding energy and lower PL intensity ratio between trion and exciton.^[30,43] The dielectric constant of pentacene, h-BN, and SiO₂ has the following ranking: h-BN > SiO₂ > pentacene.^[43,44] Therefore, the pentacene layer with lower dielectric constant will reduce the total screening effect on the 1L MoSe₂ sitting on top, leading to the enhanced trion binding energy of MoSe₂ in the heterostructures compared with that in the 1L MoSe₂ sample on SiO₂/Si (Figure 4d–f). In addition, the thicker pentacene layer can lead to the more reduced dielectric screening, thus higher trion binding energy (Figure 4b) and higher ratio of PL intensity between trions and excitons (Figure 4c). The photoexcitation induced charge transfer within the heterostructures, from the small excitation power used, has a negligible effect on the ratio of PL intensity between trions and excitons (Note S6, Supporting Information). Our results provide a general way to precisely engineer the many-body interactions in atomically thin semiconductors, triggering new applications in ultrathin spintronic and valleytronic devices.

In conclusion, we have demonstrated an O–I 2D vdW heterojunction comprising of ultrathin organic pentacene and monolayer MoSe₂. Our PL and PLE measurements strongly suggest the type-I band alignments in those heterostructures, which provide a powerful platform to explore the efficient and layer-dependent exciton pumping across the O–I interfaces. The interfacial exciton pumping efficiency could be up to ≈86 times higher than the photoexcitation pumping in 1L MoSe₂, considering that the pentacene layer has much lower optical absorption. The high interfacial exciton pumping efficiency is related to ultrafast energy transfer across the O–I interfaces, the high quantum yields of the organic semiconductors, and the relaxation pathways of the photoexcited carriers in the hybrid system. The layer-dependent pumping efficiency is also highly related to the layer-dependent carrier transport in the atomically thin pentacene layers. Moreover, the hybridization of those atomically thin organic 2D materials has significantly modulated the many-body interactions in the monolayer MoSe₂ via precise dielectric engineering. Our demonstrations provide a general and new way to manipulate the exciton pumping and to engineer the many-body interactions in atomically thin semiconductors, enabling various novel and exciting optoelectronic implications in lighting, energy harvesting, spintronic and valleytronic devices, etc.

Experimental Section

Device Fabrication and Characterization: Ultrathin 2D pentacene single-crystal samples were fabricated through the physical vapor deposition method over few-layer h-BN films on a SiO₂/Si substrate (290 nm thermal oxide on p⁺-doped silicon).^[14] The pentacene films were characterized by optical microscopy, AFM, and Raman spectroscopy to identify the number of layers and topological information. Pentacene-layer-dependent heterostructures were fabricated by dry transfer of 1L MoSe₂ flakes on the designated pentacene samples. For the MOS structure, used for back gate-dependent PL measurements, the 100 nm thick gold electrode was transferred to contact part of the MoSe₂ flakes as the probing pad.

Optical Characterization: PL and Raman measurements were conducted using a Horiba LabRAM system equipped with a confocal microscope, a charge-coupled device (CCD) Si detector, and a 532 nm diode-pumped solid-state (DPSS) laser as the excitation source. For temperature-dependent (above 83 K) measurements, the sample was placed into a microscope-compatible chamber with a low-temperature controller (using liquid nitrogen as the coolant). The electrical bias was applied using a Keithley 4200 semiconductor analyzer. The μ -PLE system employed in this study was a Horiba LabRAM system equipped with confocal optics and a CCD array silicon detector. A supercontinuum excitation light source (NKT SuperK Extreme EXR-20) with a tunable wavelength range between 490 and 2000 nm was employed. In this work, excitation wavelengths between 490 and 750 nm were used with a bandwidth of 12 nm for the chosen wavelengths, and the on-sample power was kept constant for all excitation wavelengths. The wavelength selection was achieved using a SuperK VARIA attachment allowing the tuning of both the center wavelength and the bandwidth of the filtered light. The laser light was focused on the sample surface via an objective lens. The diameter of the illuminated spot on the samples is ≈2 μ m. The spectral response of the entire system was determined with a calibrated halogen-tungsten light source. Time-resolved PL (TRPL) measurements were conducted in a setup that incorporates micro-PL spectroscopy with a time-correlated single-photon counting (TCSPC) system. A linearly polarized pulsed laser (frequency doubled to 522 nm, with a 300 fs pulse width and a 20.8 MHz repetition rate) was directed to a high numerical aperture (NA = 0.7) objective (Nikon S Plan 60x). The PL signal was collected by a grating spectrometer, thereby either recording the PL spectrum through the CCD (Princeton Instruments, PIXIS) or detecting the PL intensity decay by a Si single-photon avalanche diode and the TCSPC (PicoHarp 300) system with a resolution of 20 ps. All the PL spectra were corrected for the instrument response. All the optical path length (OPL) characterizations were obtained using a phase-shifting interferometer (Veeco NT9100).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

L.L.Z. and A.S. contributed equally to this work. The authors would like to acknowledge the facility support from Prof. Chennupati Jagadish's group at the ANU, ACT node of the Australian National Fabrication Facility (ANFF). The authors also acknowledge financial support from ANU Ph.D. student scholarship, China Scholarship Council, ANU Major Equipment Committee fund (No. 14MEC34), and Australian Research Council (ARC) Discovery Early Career Researcher Award (DECRA) (DE140100805). ARC Centre of Excellence in Future Low-Energy Electronics Technologies (FLEET), ANU node; this work is also supported by NSFC 61734003, 61521001 and National Key Basic Research Program of China 2015CB921600. Y.R.L. and X.R.W. conceived and supervised the project; L.L.Z., Y.H.Z., Y.J.C., B.L., X.S., and A.K. prepared the samples; H.N. and D.M. contributed to the PLE setup; L.L.Z. and B.W.W. conducted the measurements; L.L.Z. did the PSI measurements. L.L.Z., A.S., and Y.Z. did the PL measurements; B.W.W., M.H.D., B.W., H.N., D.M., Z.Y.L., and Y.S. contributed to data analysis; Z.W. and Z.F.Y. did the absorption simulation; Y.R.L., L.L.Z., and A.S. cowrote the paper; all authors discussed the results and commented on the manuscript.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

2D materials, binding energy, exciton pumping, organic–inorganic, type-I heterostructures

Received: June 23, 2018

Revised: July 19, 2018

Published online: August 30, 2018

- [1] G.-H. Lee, C.-H. Lee, A. M. van der Zande, M. Han, X. Cui, G. Arefe, C. Nuckolls, T. F. Heinz, J. Hone, P. Kim, *APL Mater.* **2014**, 2, 092511.
- [2] Y. C. Lin, R. K. Ghosh, R. Addou, N. Lu, S. M. Eichfeld, H. Zhu, M. Y. Li, X. Peng, M. J. Kim, L. J. Li, R. M. Wallace, S. Datta, J. A. Robinson, *Nat. Commun.* **2015**, 6, 7311.
- [3] C.-H. Lee, G.-H. Lee, A. M. van der Zande, W. Chen, Y. Li, M. Han, X. Cui, G. Arefe, C. Nuckolls, T. F. Heinz, J. Guo, J. Hone, P. Kim, *Nat. Nanotechnol.* **2014**, 9, 676.
- [4] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, M. S. Strano, *Nat. Nanotechnol.* **2012**, 7, 699.
- [5] D. Jariwala, S. L. Howell, K. S. Chen, J. Kang, V. K. Sangwan, S. A. Filippone, R. Turrissi, T. J. Marks, L. J. Lauhon, M. C. Hersam, *Nano Lett.* **2016**, 16, 497.
- [6] S. B. Homan, V. K. Sangwan, I. Balla, H. Bergeron, E. A. Weiss, M. C. Hersam, *Nano Lett.* **2016**, 17, 164.
- [7] E. H. Cho, W. G. Song, C. J. Park, J. Kim, S. Kim, J. Joo, *Nano Res.* **2014**, 8, 790.
- [8] D. Jariwala, T. J. Marks, M. C. Hersam, *Nat. Mater.* **2017**, 16, 170.
- [9] T. Zhu, L. Yuan, Y. Zhao, M. W. Zhou, Y. Wan, J. G. Mei, L. B. Huang, *Sci. Adv.* **2018**, 4, 8.
- [10] X. Liu, J. Gu, K. Ding, D. Fan, X. Hu, Y. W. Tseng, Y. H. Lee, V. Menon, S. R. Forrest, *Nano Lett.* **2017**, 17, 3176.
- [11] F. Zhang, Y. Ma, Y. Chi, H. Yu, Y. Li, T. Jiang, X. Wei, J. Shi, *Sci. Rep.* **2018**, 8, 8208.
- [12] H. Ozaki, *J. Chem. Phys.* **2000**, 113, 6361.
- [13] C. Menozzi, V. Corradini, M. Cavallini, F. Biscarini, M. G. Betti, C. Mariani, *Thin Solid Films* **2003**, 428, 227.
- [14] Y. Zhang, J. Qiao, S. Gao, F. Hu, D. He, B. Wu, Z. Yang, B. Xu, Y. Li, Y. Shi, W. Ji, P. Wang, X. Wang, M. Xiao, H. Xu, J. B. Xu, X. Wang, *Phys. Rev. Lett.* **2016**, 116, 016602.
- [15] D. He, Y. Zhang, Q. Wu, R. Xu, H. Nan, J. Liu, J. Yao, Z. Wang, S. Yuan, Y. Li, Y. Shi, J. Wang, Z. Ni, L. He, F. Miao, F. Song, H. Xu, K. Watanabe, T. Taniguchi, J. B. Xu, X. Wang, *Nat. Commun.* **2014**, 5, 5162.
- [16] I. G. Hill, A. Kahn, Z. G. Soos, R. A. Pascal, *J. Chem. Phys. Lett.* **2000**, 327, 8.
- [17] S. Nakamura, M. Senoh, N. Iwasa, S.-I. Nagahama, *Jpn. J. Appl. Phys.* **1995**, 34, 3.
- [18] C. Hui, K. Jun, S. Hasan, C. Bin, S. Aslihan, W. Kedi, P. Francois, M. Xiuqing, T. Sefaattin, *Nanotechnology* **2016**, 27, 065203.
- [19] M. Z. Bellus, M. Li, S. D. Lane, F. Ceballos, Q. Cui, X. C. Zeng, H. Zhao, *Nanoscale Horiz.* **2017**, 2, 31.
- [20] S. J. Kang, G.-H. Lee, Y.-J. Yu, Y. Zhao, B. Kim, K. Watanabe, T. Taniguchi, J. Hone, P. Kim, C. Nuckolls, *Adv. Funct. Mater.* **2014**, 24, 5157.
- [21] G. H. Lee, Y. J. Yu, X. Cui, N. Petrone, C. H. Lee, M. S. Choi, D. Y. Lee, C. G. Lee, W. J. Yoo, K. J. Watanabe, T. Taniguchi, C. Nuckolls, P. Kim, J. Hone, *ACS Nano* **2013**, 7, 6.
- [22] M. Florian, M. Hartmann, A. Steinhoff, J. Klein, A. W. Holleitner, J. J. Finley, T. O. Wehling, M. Kaniber, C. Gies, *Nano Lett.* **2018**, 18, 2725.
- [23] A. Castellanos-Gomez, M. Buscema, R. Molenaar, V. Singh, L. Janssen, H. S. J. van der Zant, G. A. Steele, *2D Mater.* **2014**, 1, 011002.
- [24] Y. Gong, J. Lin, X. Wang, G. Shi, S. Lei, Z. Lin, X. Zou, G. Ye, R. Vajtai, B. I. Yakobson, H. Terrones, M. Terrones, B. K. Tay, J. Lou, S. T. Pantelides, Z. Liu, W. Zhou, P. M. Ajayan, *Nat. Mater.* **2014**, 13, 1135.
- [25] X. Hong, J. Kim, S. F. Shi, Y. Zhang, C. Jin, Y. Sun, S. Tongay, J. Wu, Y. Zhang, F. Wang, *Nat. Nanotechnol.* **2014**, 9, 682.
- [26] V. O. Özcelik, J. G. Azadani, C. Yang, S. J. Koester, T. Low, *Phys. Rev. B* **2016**, 94, 035125.
- [27] C. Gong, H. Zhang, W. Wang, L. Colombo, R. M. Wallace, K. Cho, *Appl. Phys. Lett.* **2013**, 103, 053513.
- [28] H. Yoshida, K. Yamada, J. Y. Tsutsumi, N. Sato, *Phys. Rev. B* **2015**, 92, 075145.
- [29] M. Shionoiri, M. Kozasa, S. Kera, K. K. Okudaira, N. Ueno, *Jpn. J. Appl. Phys.* **2007**, 46, 1625.
- [30] J. Pei, J. Yang, X. Wang, F. Wang, S. Mookapati, T. Lu, J. C. Zheng, Q. Qin, D. Neshev, H. H. Tan, C. Jagadish, Y. Lu, *ACS Nano* **2017**, 11, 7468.
- [31] P. Tonndorf, R. Schmidt, P. Böttger, X. Zhang, J. Börner, A. Liebig, M. Albrecht, C. Kloc, O. Gordan, D. R. T. Zahn, S. M. Vasconcellos, R. Bratschitsch, *Opt. Express* **2013**, 21, 9.
- [32] J. S. Ross, S. Wu, H. Yu, N. J. Ghimire, A. M. Jones, G. Aivazian, J. Yan, D. G. Mandrus, D. Xiao, W. Yao, X. Xu, *Nat. Commun.* **2013**, 4, 1474.
- [33] A. Rao, M. W. B. Wilson, S. Albert-Seifried, R. Di Pietro, R. H. Friend, *Phys. Rev. B* **2011**, 84, 195411.
- [34] M. Amani, D. H. Lien, D. Kiriya, J. Xiao, A. Azcatl, J. Noh, S. R. Madhupathy, R. Addou, S. KC, M. Dubey, K. Cho, R. M. Wallace, S. Lee, J. He, J. W. Ager III, X. Zhang, E. Y. A. Javey, *Science* **2015**, 350, 4.
- [35] M. Palummo, M. Bernardi, J. C. Grossman, *Nano Lett.* **2015**, 15, 2794.
- [36] D. Kozawa, R. Kumar, A. Carvalho, A. K. Kumar, W. Zhao, S. Wang, M. Toh, R. M. Ribeiro, A. H. C. Neto, K. Matsuda, G. Eda, *Nat. Commun.* **2014**, 5, 4543.
- [37] M. Tabachnyk, B. Ehrler, S. Gelinas, M. L. Böhm, B. J. Walker, K. P. Musselman, N. C. Greenham, R. H. Friend, A. Rao, *Nat. Mater.* **2014**, 13, 1033.
- [38] A. Rao, M. W. B. Wilson, M. H. Justin, A.-S. Sebastian, B. Heinz, R. H. Friend, *J. Am. Chem. Soc.* **2010**, 132, 6.
- [39] A. Sharma, H. Yan, L. Zhang, X. Sun, B. Liu, Y. Lu, *Acc. Chem. Res.* **2018**, 51, 1164.
- [40] M. S. Ugeda, A. J. Bradley, S. F. Shi, F. H. da Jornada, Y. Zhang, D. Y. Qiu, W. Ruan, S. K. Mo, Z. Hussain, Z. X. Shen, F. Wang, S. G. Louie, M. F. Crommie, *Nat. Mater.* **2014**, 13, 1091.
- [41] J. Yang, T. Lu, Y. W. Myint, J. Pei, D. Macdonald, J.-C. Zheng, Y. Lu, *ACS Nano* **2015**, 9, 7.
- [42] I. Kylänpää, H.-P. Komsa, *Phys. Rev. B* **2015**, 92, 205418.
- [43] Y. Lin, X. Ling, L. Yu, S. Huang, A. L. Hsu, Y. H. Lee, J. Kong, M. S. Dresselhaus, T. Palacios, *Nano Lett.* **2014**, 14, 5569.
- [44] C. H. Kim, O. Yaghmazadeh, D. Tondelier, Y. B. Jeong, Y. Bonnasieux, G. Horowitz, *J. Appl. Phys.* **2011**, 109, 083710.

ADVANCED MATERIALS

Supporting Information

for *Adv. Mater.*, DOI: 10.1002/adma.201803986

Efficient and Layer-Dependent Exciton Pumping across
Atomically Thin Organic–Inorganic Type-I Heterostructures

Linglong Zhang, Ankur Sharma, Yi Zhu, Yuhan Zhang, Bowen Wang, Miheng Dong, Hieu T. Nguyen, Zhu Wang, Bo Wen, Yujie Cao, Boqing Liu, Xueqian Sun, Jiong Yang, Ziyuan Li, Arara Kar, Yi Shi, Daniel Macdonald, Zongfu Yu, Xinran Wang, and Yuerui Lu**

DOI: 10.1002/adma.201803986

Article type: Communication

Supporting Information

Efficient and Layer-Dependent Exciton Pumping across Atomically Thin Organic-Inorganic Type-I Heterostructures

Linglong Zhang, Ankur Sharma, Yi Zhu, Yuhan Zhang, Bowen Wang, Miheng Dong, Hieu Nguyen, Zhu Wang, Bo Wen, Yujie Cao, Boqing Liu, Xueqian Sun, Jiong Yang, Ziyuan Li, Arara Kar, Yi Shi, Daniel Macdonald, Zongfu Yu, Xinran Wang, Yuerui Lu**

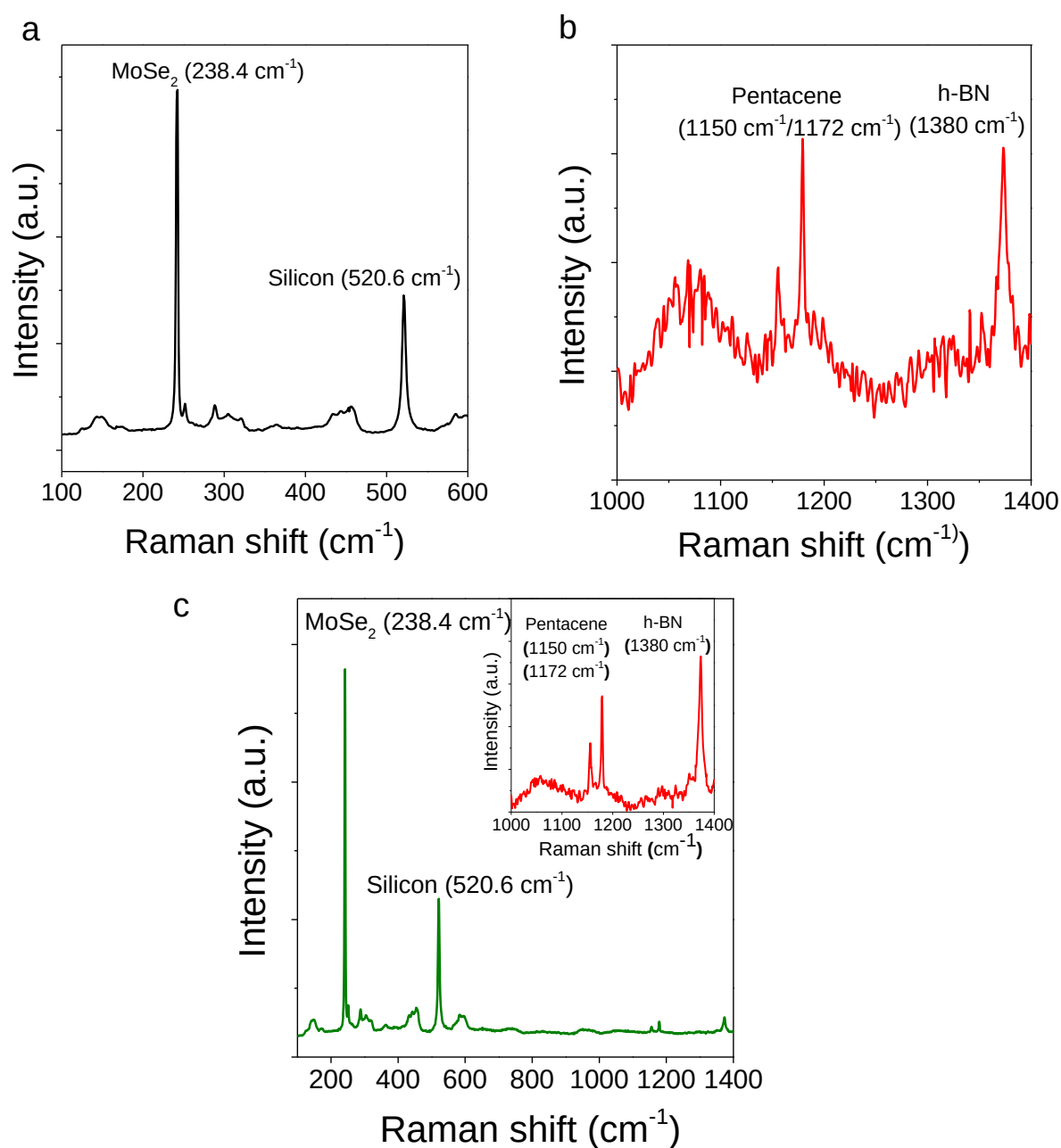


Figure S1 | Characterization of monolayer MoSe_2 , Pentacene and Heterostructure with Raman Spectroscopy. **a**, Measured Raman spectrum from the isolated monolayer MoSe_2 region on SiO_2/Si substrate in the heterostructure. **b**, Measured Raman spectrum of pentacene from the isolated 2L pentacene region on SiO_2/Si substrate. **c**, Measured Raman spectrum from the 1L MoSe_2 + 2L PEN heterostructure region. See Figure 1 (Main text) for microscope images. Inset: Zoom in Raman spectrum of selected areas indicated.

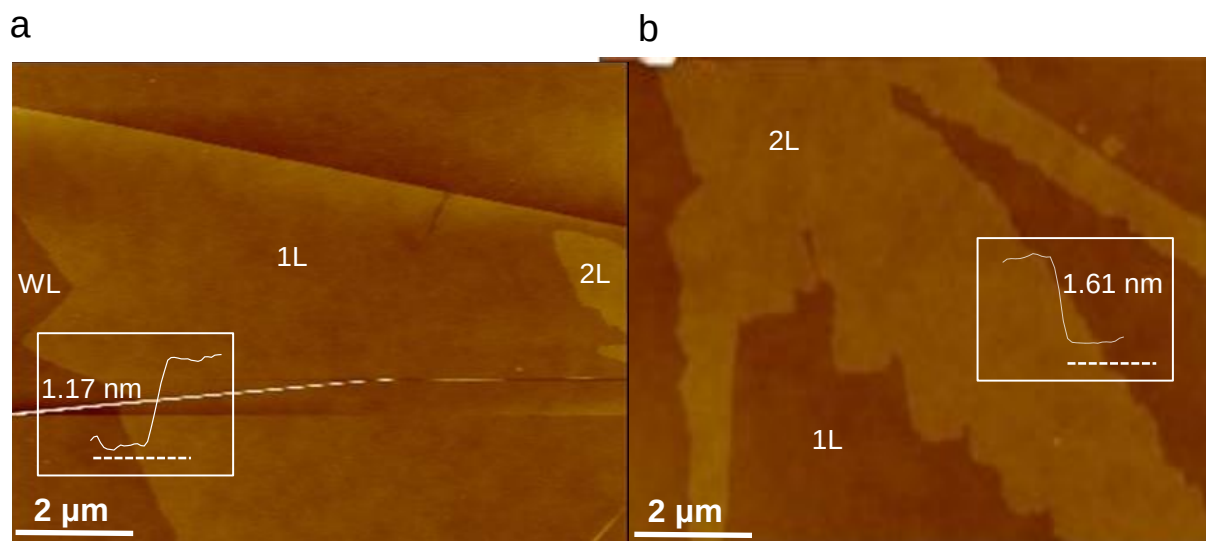


Figure S2 | Layer dependent AFM characterization of pentacene on h-BN. **a**, AFM image of as-grown pentacene layers. (Microscope image shown in main text Figure 1b). WL, 1L and 2L pentacene regions are identified based on the measured thicknesses. (See Supplementary note 2). **b**, Magnified AFM image highlighting the homogenous deposition of 1L and 2L pentacene regions. Inset: height measurements along the dashed lining showing atomic layer thickness of 2L region.

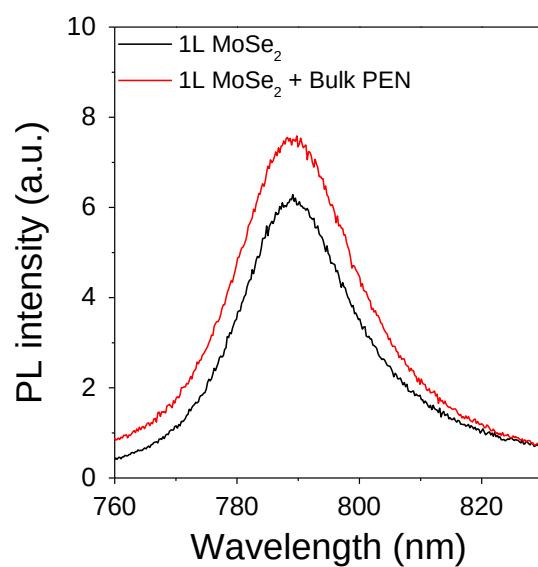


Figure S3 | Characterization of the heterostructure comprising of monolayer MoSe₂ and the bulk pentacene (> 20 nm thick). An enhancement factor η of 1.2 was observed in the 1L MoSe₂ + bulk PEN heterostructures.

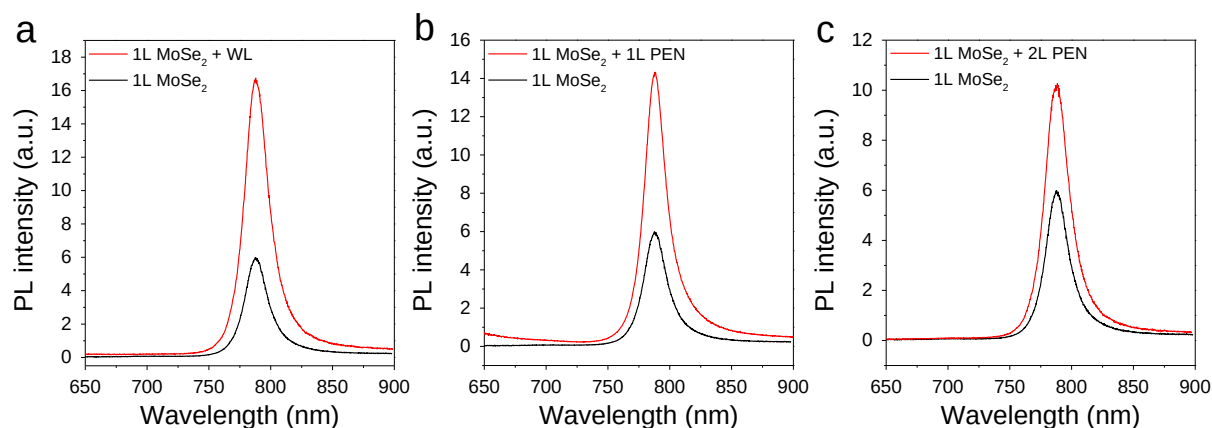


Figure S4 | Long-term PL enhancement stability of heterostructures. **a**, The PL spectra from 1L MoSe₂ + WL PEN heterostructure and 1L MoSe₂. **b**, The PL spectra from 1L MoSe₂ + 1L PEN heterostructure and 1L MoSe₂. **c**, The PL spectra from 1L MoSe₂ + 2L PEN heterostructure and 1L MoSe₂. All PL spectra are measured from the same device, which was stored in nitrogen cabinet for one month after initial measurements. Thus, PL enhancement is quite stable as compared with Figure 1e in the main text. No visible degradation of the sample or the PL intensity was observed.

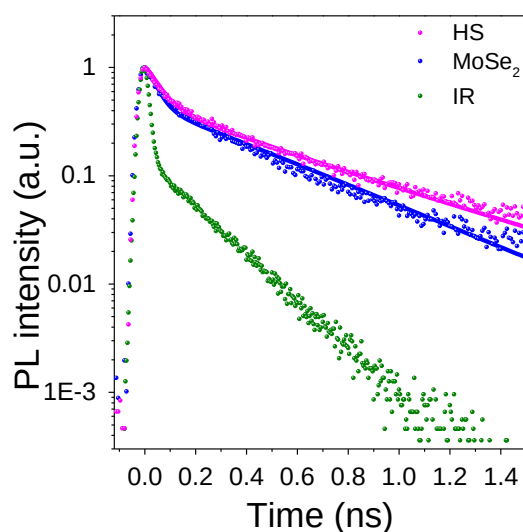


Figure S5 | Time-resolved photoluminescence measurements. Measured time-resolved PL traces for exciton (~ 788 nm) peak at room temperature from SiO_2/Si supported monolayer MoSe_2 (blue curve) and heterostructure of 1L MoSe_2 + WL PEN (magenta curve). IR represents instruments response curve (olive). Deconvolution was done using the system response as reference and using the equation $I = A \exp\left(-\frac{t}{\tau_1}\right) + B \exp\left(-\frac{t}{\tau_2}\right) + C$, the exciton peak fast (slow) decay lifetime τ_1 (τ_2) value from monolayer MoSe_2 on SiO_2/Si and 1L MoSe_2 + WL PEN heterostructure were extracted to be 35.9 (447.8) and 49.0 (612) ps, respectively. τ_2 here implies radiative lifetime.^[1-3]

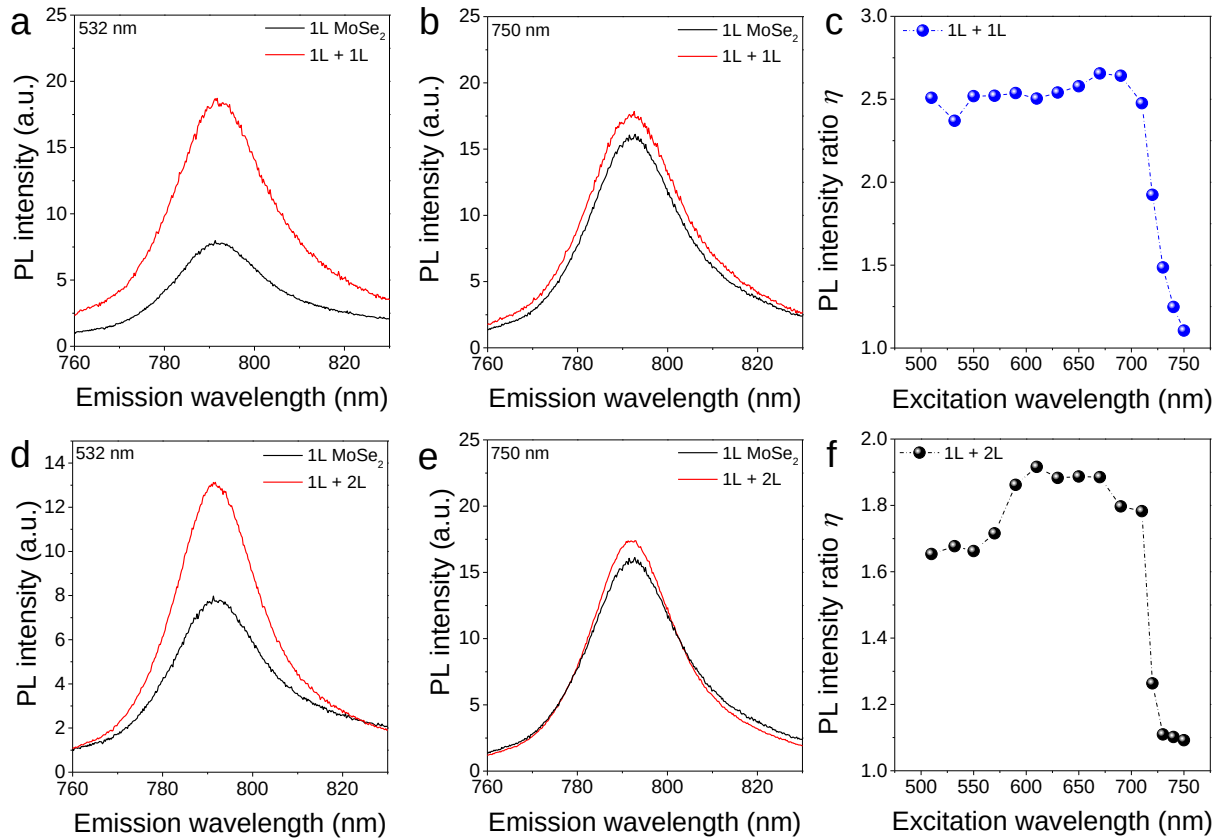


Figure S6 | Confirmation of type-I band alignment by photoluminescence excitation (PLE). **a**, PL spectra from 1L MoSe₂ and heterostructure of 1L MoSe₂ + 1L PEN at 532 nm demonstrating a ' η ' of 2.37. **b**, PL spectra from 1L MoSe₂ and heterostructure of 1L MoSe₂ + 1L PEN at 750 nm with $\eta \sim 1$. **c**, PL intensity ratio of 1L MoSe₂ + 1L PEN to monolayer MoSe₂ as a function of excitation wavelength. **d**, Selected PL spectra of 1L MoSe₂ and 1L MoSe₂ + 2L PEN at 532 nm with $\eta \sim 1.68$. **e**, Selected PL spectra of 1L MoSe₂ and 1L MoSe₂ + 2L PEN at 750 nm and $\eta \sim 1$. **f**, PL intensity ratio of 1L MoSe₂ + 2L PEN heterostructure to monolayer MoSe₂ as a function of excitation wavelength. The enhancement factor shows a similarly sharp drop over 700~750 nm, which confirmed Type-I band alignment in the heterostructure.

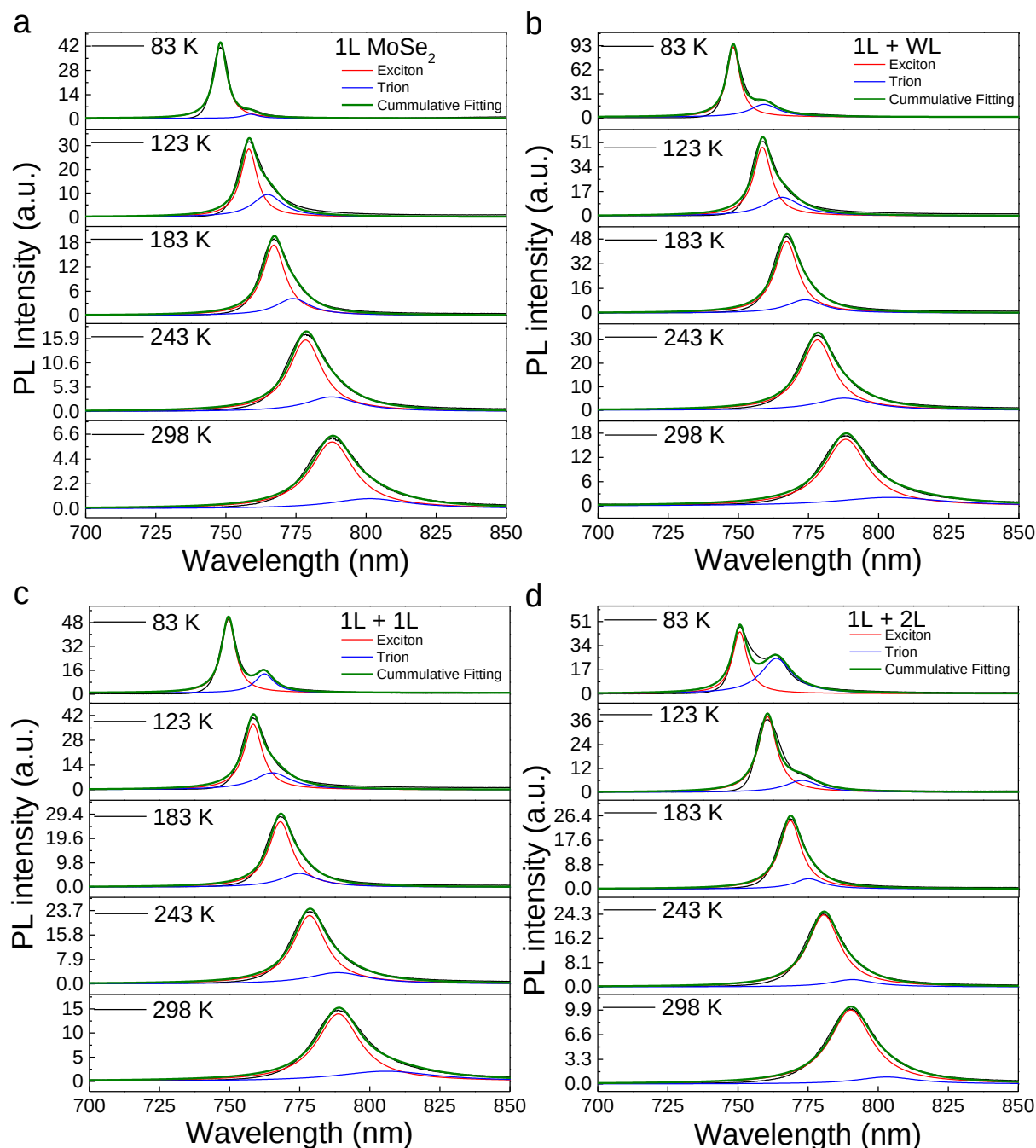


Figure S7 | Deconvoluted temperature-dependent PL Spectra from monolayer MoSe₂ and the heterostructures. a-d, PL spectra as obtained from 1L MoSe₂, 1L MoSe₂ + WL PEN heterojunction, 1L MoSe₂ + 1L PEN heterojunction and 1L MoSe₂ + 2L PEN heterojunction as a function of temperature. The PL spectra are fitted by Lorentz function. (Black lines are experimental data, red lines represent exciton Peak, blue lines show the trion peaks, and olive lines show the cumulative fitting).

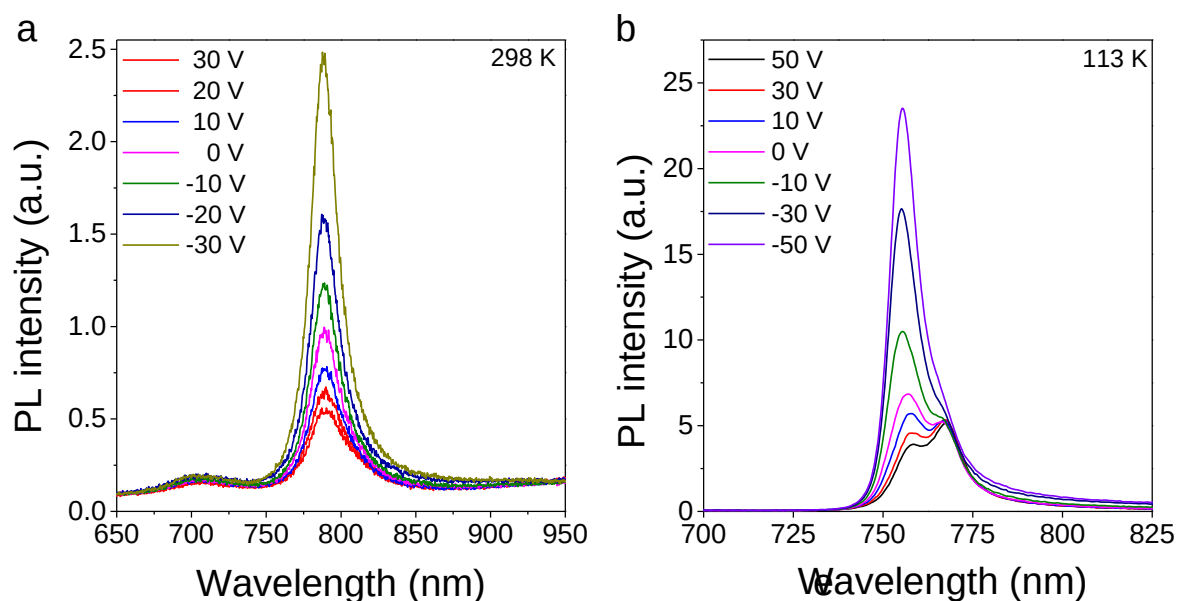


Figure S8 | Trion characterization using back gate tuning PL spectra. **a**, PL intensity as a function of back gate voltage from 1L MoSe₂ region from the heterostructure at room temperature. **b**, The PL spectra from 1L MoSe₂ as a function of gate voltage from monolayer MoSe₂ on SiO₂/Si at 113K. The trion peak shows a clear variation with change in back gate voltage, thus confirming a negative type trion in our sample. (See Supplementary note 5).

Table S1: Absorption of the 2D layers at wavelength of 532 nm.

Name	Absorption at 532 nm
WL pentacene (%)	0.3
1L pentacene (%)	1.1
2L pentacene (%)	2.2
1L MoSe ₂ (%)	15.3

Supplementary Note 1: Raman characterization.

Raman spectra (Figure S1a-b) from 1L MoSe₂ isolated region and pentacene isolated region in the heterostructure confirm monolayer MoSe₂ and pentacene film are obtained. The energy separation between Raman active modes agrees well with previously reported values for monolayer MoSe₂ and high-quality two-dimensional pentacene film.^[4-7] The Raman spectrum of a 1L MoSe₂ + 2L PEN heterostructure comprises of the addition of Raman shift modes from the constituent layers in the heterostructure (in Figure S1c).

Supplementary Note 2: AFM characterization of the pentacene films.

Figure S2 shows typical AFM images of different pentacene area chosen in Fig 1b. The height of 1L and 2L pentacene is observed to be ~1.17 nm and ~1.61 nm, respectively. This thickness matches well with the reported value of the same epitaxially grown pentacene layers.^[6] Referring to the 1L and 2L pentacene region, we could identify the WL pentacene region of the Figure 1b.

Supplementary Note 3: Optical absorption measurements.

Firstly, using a 532 nm CW laser, we measured the differential reflectance $(R-R_0)/R$ from the 2D layers, where R_0 and R represent the measured optical reflectance from the substrate and the individual 2D layer, respectively.^[8] Secondly, we used a phase-shifting interferometry (PSI) system to measure the optical path length (OPL) of the 2D layers.^[9] The OPL is determined from the relation: $OPL_i = -\frac{\lambda}{2\pi}(\phi_i - \phi_{sub})$, where λ is the wavelength of the light source (i.e., 532 nm), and ϕ_i and ϕ_{sub} represent the measured phase shifts of the reflective light from the 2D layers (e.g., pentacene and MoSe₂) and the substrate.^[9] We have recently demonstrated that PSI system, with a high resolution of ~0.1 nm in the z direction, is a powerful tool to image atomically thin materials.^[9] The measured OPL values of WL, 1L, 2L pentacene and 1L MoSe₂ are 1.4, 2.9 and 4.4 and 47 nm, respectively.

Based on the measured differential reflectance and the OPL values from the 2D layers, rigorous coupled wave analysis (RCWA) *via* S4 software,^[10] was used to extract the refractive index values of the 2D layers and thus the optical absorption of the 2D layers. For our samples, the thickness of SiO₂, Si and monolayer MoSe₂ are 290 nm, 500 μ m, and 0.7 nm, respectively. The pentacene layers were on top of 3 nm h-BN, which was measured by AFM. In the analysis, refractive index values of SiO₂, Si, and h-BN are 1.46,^[11] $4.15 + 0.05i$,^[12,13] and 1.65,^[14] respectively. Based on our analysis, the refractive index values of pentacene and 1L MoSe₂ at 532 nm were extracted to be $1.48 + 0.14i$ and $4.24 + 1.67i$, respectively, which are consistent with previously reported values from pentacene thin films and 1L MoSe₂, respectively.^[15-17] From our measurements, we did not see too much difference of the refractive index values for our WL, 1L and 2L pentacene samples. Based on the measured refractive index values, we could determine the optical absorption of the 2D layers, as shown in Table S1. For instance, our measured optical absorption of 1L MoSe₂ on SiO₂/Si substrate at 532 nm was ~15.3% (Table S1), which matches well with reported value.^[4]

Supplementary Note 4: Relative quantum yield (QY) measurements

To quantify the interfacial exciton pumping mechanism, the relative QY is defined by dividing the integrated PL intensity by the absorption value at the excitation energy ($QY = \frac{I}{A}$).^[18] The exciton pumping efficiency enhancement factor β is directly related to the QY. To analyze β in the 1L MoSe₂ + WL PEN heterostructure, a comparison of the relative QY of layer dependent pentacene and 1L MoSe₂ has been performed. Combining PL intensity with the absorption of individual layer of heterostructures (as shown in Figure 1e and Table S1), the relative QY rankings were obtained as follows: WL pentacene > 1L pentacene > 2L pentacene > 1L MoSe₂, which is consistent with the literature.^[2,19,20]

Supplementary Note 5: Gate-dependent PL measurements.

Figure S8a demonstrates room temperature gate tuning data for the 1L MoSe₂. During the measurement, the gold electrode was grounded, and the P⁺ doped Si substrate was used as a back gate providing a uniform electrostatic doping for the MoSe₂ monolayer in this metal-oxide-semiconductor (MOS) structure. The measured PL spectrum was very sensitive to the electrostatic doping and can be significantly modulated by the gate voltage. As we gradually swept the back gate from -30 V to 30 V at room temperature, the intensity of the exciton peak at around 788 nm decreases subsequently. The PL intensity decreases when we inject negative charge into the samples, indicating that the MoSe₂ monolayer has an initial n-type doping, which is consistent with observations in other experiments.^[21] When the MOS device was cooled down to 113 K, gate-dependent PL spectra of trions and exciton was better resolved (Figure S8b). Two clear emission peaks, located at ~755 nm and ~767 nm, respectively, were observed *via* back gate modulation. We ascribe the peak near 767 nm as originating from negative trions.^[22] Comparing PL spectrum of the heterostructures with monolayer MoSe₂ gate tuning data at low temperature, we could identify trions in various heterostructures to be negative trions.^[22]

Supplementary Note 6: Estimation of photo-excitation induced doping.

The PL was measured under an excitation power of 43.8 μ W (532 nm cw laser; laser beam size of 1 μ m). The fast decay lifetime of 1L MoSe₂ was measured to be 35.9 ps (Figure S5). Based on our measured absorption value (*A*) (Table S1), the absorbed photo number is calculated to be $\sim 43.8 \mu\text{W} \times 35.9 \text{ ps} / \text{photon energy} \times A$.^[9] For simplicity, we assume that each of the absorbed photons would create one hole-electron pair and all the photoexcited carriers could be transferred from pentacene to MoSe₂ layer. Then we can estimate photo-excitation induced doping *n* from WL, 1L and 2L pentacene layers to be $\sim 1.3 \times 10^9$, 4.6×10^9 and 9.3×10^9

cm^{-2} , respectively. According to equation $E_F = \hbar^2 \pi n / 2m_e$,^[8] using an electron effective mass $m_e = 0.49 m_0$, where m_0 is electron mass,^[23] we can estimate the photoexcitation induced Fermi energy E_F change of monolayer MoSe₂ to be 0.004, 0.016 and 0.032 meV, respectively. Those Fermi energy change values are much smaller than the change of the trion binding energies (Figure 4b), which suggests that the photoexcitation induced charge transfer from 2D pentacene layers has a negligible impact on the relative spectral weight between the exciton and trion peaks from monolayer MoSe₂ (Figure 4c).

Reference

- [1] Palummo, M., Bernardi, M. & Grossman, J. C., *Nano Lett.* **2015**, *15*, 2794-2800.
- [2] Amani, M., Lien, D. H., Kiriya, D., Xiao, J., Azcatl, A., Noh, J., Madhvapathy, S. R., Addou, R., KC, S., Dubey, M., Cho, K., Wallace, R. M., Lee, S., He, J., Ager III, J. W., Zhang, X. & Ali Javey, E. Y., *Science* **2015**, *350*, 4.
- [3] Pei, J., Yang, J., Wang, X., Wang, F., Mokkaapati, S., Lu, T., Zheng, J. C., Qin, Q., Neshev, D., Tan, H. H., Jagadish, C. & Lu, Y., *Acs Nano* **2017**.
- [4] Tonndorf, P., Schmidt, R., Böttger, P., Zhang, X., Börner, J., Liebig, A., Albrecht, M., Kloc, C., Gordan, O., Zahn, D. R. T., Vasconcellos, S. M. & Bratschitsch, R., *Opt. Express* **2013**, *21*, 9.
- [5] Wang, X. L., Gong, Y. J., Shi, G., Chow, W. L., Keyshar, K., Ye, G. L., R., V., Lou, J., Liu, Z., Ringe, E., Tay, B. K. & M., A. P., *Acs Nano* **2014**, *8*, 7.
- [6] Zhang, Y., Qiao, J., Gao, S., Hu, F., He, D., Wu, B., Yang, Z., Xu, B., Li, Y., Shi, Y., Ji, W., Wang, P., Wang, X., Xiao, M., Xu, H., Xu, J.-B. & Wang, X., *Phys. Rev. Lett.* **2016**, *116*, 016602.
- [7] Horzum, S., Sahin, H., Cahangirov, S., Cudazzo, P., Rubio, A., Serin, T. & Peeters, F. M., *Phys. Rev. B* **2013**, *87*.
- [8] Mak, K. F., He, K., Lee, C., Lee, G. H., Hone, J., Heinz, T. F. & Shan, J., *Nat. Mater.* **2013**, *12*, 207-211.
- [9] Yang, J., Xu, R., Pei, J., Myint, Y. W., Wang, F., Wang, Z., Zhang, S., Yu, Z. & Lu, Y., *Light: Sci. Appl.* **2015**, *4*, e312.
- [10] Liu, V. & Fan, S., *Comput. Phys. Commun.* **2012**, *183*, 2233-2244.
- [11] MALITSON, I. H., *J. Opt. Soc. Am.* 1965, *55*, 5.
- [12] Aspnes, D. E. & Studna, A. A., *Phys. Rev. B* **1983**, *27*, 985-1009.
- [13] Kim, J. H., Ehrman, S. H., Mulholland, G. W. & Germer, T. A., *Appl. Opt.* **2002**, *41*, 8.
- [14] Takahashi, T., ITOH, H. & KURODA, M., *J. Cryst. Growth* **1981**, *53*, 5.
- [15] Faltermeier, D., Gompf, B., Dressel, M., Tripathi, A. K. & Pflaum, J., *Phys. Rev. B* **2006**, *74*.
- [16] Hinderhofer, A., Heinemeyer, U., Gerlach, A., Kowarik, S., Jacobs, R. M., Sakamoto, Y., Suzuki, T. & Schreiber, F., *J. Chem. Phys.* **2007**, *127*, 194705.
- [17] Liu, H.-L., Shen, C.-C., Su, S.-H., Hsu, C.-L., Li, M.-Y. & Li, L.-J., *Appl. Phys. Lett.* **2014**, *105*, 201905.
- [18] Kozawa, D., Kumar, R., Carvalho, A., Kumar Amara, K., Zhao, W., Wang, S., Toh, M., Ribeiro, R. M., Castro Neto, A. H., Matsuda, K. & Eda, G., *Nat. Commun.* **2014**, *5*, 4543.
- [19] Congreve, D. N., Lee, J., Thompson, N. J., Hontz, E., Yost, S. R., Reuswig, P. D., Bahlke, M. E., Reineke, S., Van Voorhis, T. & Baldo, M. A., *Science* **2013**, *340*, 334-337.
- [20] Lee, J., Jadhav, P. & Baldo, M. A., *Appl. Phys. Lett.* **2009**, *95*, 033301.
- [21] Ross, J. S., Wu, S., Yu, H., Ghimire, N. J., Jones, A. M., Aivazian, G., Yan, J., Mandrus, D. G., Xiao, D., Yao, W. & Xu, X., *Nat. Commun.* **2013**, *4*, 1474.
- [22] Jiong Yang, Tieyu Lu, Ye Win Myint, Jiajie Pei, Daniel Macdonald, Jin-Cheng Zheng & Lu, Y., *Acs Nano* **2015**, *9*, 7.
- [23] Rasmussen, F. A. & Thygesen, K. S., *J. Phys. Chem. C* **2015**, *119*, 13169-13183.

CHAPTER 9

Conclusion and Future Work

In summary, this thesis explores the exciton dynamics in organic and inorganic 2D materials, that characteristically determine their optoelectronic properties. The experimental results demonstrated in this thesis establish these materials as strong candidates for their applications in future miniaturized optoelectronic and photonics devices such as photodetectors, sensors, solar cells, LEDs, quantum computing building blocks, candidates for stable Bose-Einstein condensates and nanolasers *etc.* The engineering of excitonic properties opens up avenues in device fabrication using this new class of semiconductor nanomaterials with low dimensionality. Reduced dimensionality

of semiconductor materials entered a new horizon with advent of graphene and similar other 2D materials such as TMDC, phosphorene and other III-V semiconductors. Recently, there has been an emphasis on discovering their interesting opto-electronic and electrical properties and at the same time demonstrating their applications for various device application for next generation electronic devices. The presence of quasi particles such as excitons has been reported in quasi 2D system such as quantum wells. Whereas trions and other similar quasi particles have been reported recently in these 2D materials. But, the physical properties, deeper understanding of their operational/functional properties and more specifically engineering them for device application remains a challenge. This thesis is an attempt to study the intriguing exciton dynamics from a new class of 2D organic semiconductor materials and at the same time engineer the dynamics in inorganic 2D materials to substantiate their application for device making purposes. The thesis also explores the possibility of further reducing the dimensionality of the excitons to 1D space in organic materials by growing 1D nanowires and reporting extraordinary optical properties in the form of quasi-line ZPL spectra from a solid state organic semiconducting system, which was never reported before.

Whereas, in inorganic 2D materials the thesis reports the engineering of dimensions to achieve enhanced excitonic emissions from them by introducing external defect centers. The thesis also reports the use of external voltage to change doping to influence exciton dynamics, which has never been reported before in TMDC materials, resulting in enhanced exciton diffusion in inorganic 2D materials. The thesis finally, combines the organic and inorganic 2D materials to report a first of its kind 2D heterojunction with efficient exciton pumping from the organic to inorganic material in a Type-I heterostructure. The excitonic and optical properties reported from this heterostructure pave the way for its use in specific applications in highly efficient light emitting diodes, photodetectors and tunable wavelength flexible displays.

9.1 Key outcomes

This thesis demonstrates fundamental excitonic properties and dynamics in organic-inorganic semiconductor low dimensional materials for their applications in next generation photonics and optoelectronic devices. The key scientific and research outcomes achieved in this thesis are explained as following:

9.1.1 Superradiance and Supertransport of Frenkel Excitons in an organic 2D material

The use of organic materials for optoelectronic applications has been challenging due to challenges in their growth processes, defect and interfacial sites. But, organic molecular crystals, which are bound by the weak van der Waals cohesive forces between small molecules, are an important class of materials for future electronic, optoelectronic, and photonic devices.^{1, 2, 3} The excitonic nature of organic crystals plays an important role in determining their optoelectronic properties.¹ Chapter 4 demonstrates the intrinsic excitonic emissions in atomically thin organic 2D semiconductors. For the first time, we successfully identified molecular aggregation-sensitive PL emissions in epitaxially grown 2D single-crystal pentacene layers with different types of aggregation (H- and J-type). The identification based on our temperature-dependent PL measurements agreed very well with our DFT simulations. Angle-resolved PL measurements were also used to characterize the in-plane anisotropies of various excitonic transitions in these organic 2D layers, which revealed their Frenkel and/or CT characters. In the 1L pentacene sample, we observed one strongly anisotropic PL peak, which were attributed to the phenomenon of superradiance.^{4, 5, 6, 7} Compared with bulk samples, our 1L pentacene sample showed highly reduced coupling of Frenkel–CT excitons,^{8, 9, 10} which will allow us to probe the intrinsic excitonic nature in organic materials and led us to demonstrate superradiance from a solid state 2D organic material. In addition, we further probed the temporal and spatial dynamics of excitons in 2D organic materials. From the high-quality atomically

thin organic 2D semiconductors, we observed the supertransport of excitons between coherent excitonic states with an ultra-high effective diffusion coefficient of 346.9 cm²/sec at room temperature, which is around one to several orders of magnitude higher than the reported values from other organic quasi-1D and thin film molecular aggregates.^{5, 8, 11} We successfully identified molecular aggregation-sensitive PL emissions in atomically thin single-crystal organic semiconductors with different types of aggregation (H- and J-type)¹² at the 2D quantum limit.

9.1.2 Quasi-line spectra from 1D Organic Nanowires and Shpol' skii spectra

Organic molecules have been established to be strong candidates for cheap miniaturized optoelectronic device applications in chapter 1 and 4. This thesis established that not only in 2D state but in high crystalline 1D state (nanowires) organic molecular crystals with low molecular weight can prove to be perfect candidate for future optical device manufacturing. Earlier organic 1D systems were mostly demonstrate in liquid phase due to challenges with controlling dimensionality in solid state systems. Chapter 5 demonstrates a highly ordered and crystalline 1D organic nanowire grown over hBN surface. We report the first observation of quasi-line spectra at cryogenic temperatures also referred to as Shpol' skii spectra. We observe a quasi-line spectrum with width ~2-3 nm and a very high value of Debye-Waller factor from our 1D wires. We further establish the high crystallinity and higher degree of molecular orientation of the PEN molecules in the 1D nanowire structure using polarization-resolved PL emission spectra and time-resolved PL emission. We also demonstrate a MOS device incorporating the 1D PEN wire to effectively demonstrate an external electric control of the quasi line spectral emission at low temperatures. This has tremendous applications in developing next generation fundamental and connecting blocks of optoelectronic circuits, nanolasers and sensors based on 1D organic nanowires.

9.1.3 Engineering Exciton Dynamics in inorganic 2D materials

The presence of quasi-particles such as excitons, trions and biexcitons has been recently established in inorganic TMDC materials and has critical applications in their feasibility for optoelectronic device making. But, the spatial diffusion of these quasi particles is limited in inorganic materials due to high dielectric constant and high localization of excitons.^{13, 14, 15} Chapter 6 reports a high value of exciton diffusion from monolayer TMDC materials by incorporating the monolayer into a MOS device and modulating the doping of charges enhancing the diffusion coefficient of the excitons. We report a value of 86.53 cm²/sec for excitons from the suspended 1L WS₂ device with back gate voltage modulation, which is much higher than previously reported values of exciton diffusion coefficients in TMDCs and is comparable to other organic systems. These results establish the 2D TMDC materials as robust contenders for various applications in high speed energy transport devices such as excitonic circuits and high quantum yield LEDs utilizing their robustness, high crystallinity, defect free surfaces and visible range band gaps. At low temperatures, we further report the control of dynamic and spatial diffusion of excitons, trions and biexcitons from WS₂.

Similarly, in Chapter 7 utilized defect engineering to introduce external defect sin puckered structure of 3L phosphorene to achieve bright defect excitonic emission in the NIR regime suitable for infrared optoelectronics. These results have promising potential applications in future optoelectronic devices,^{16, 17} such as chip-based optical telecommunication and photodetection devices.

9.1.4 Efficient Exciton pumping across an Organic-Inorganic 2D Heterostructure

Chapters 4-7 have demonstrated key optical properties from both organic and inorganic 2D materials that can be used for potential device applications. Vertical van der Waals heterostructures combining two different thin films or 2D materials have been reported

recently. Chapter 8 demonstrates the epitaxially grown single crystal pentacene (various thickness) over hBN surface stacked under a monolayer MoSe₂ (TMDC) to realize a hetero-epitaxial organic-inorganic type-I vertical vdW heterostructure. Epitaxially grown single crystal pentacene¹⁸ provides a atomically sharp and clean interface with no dangling bonds and impurities over which a TMD MoSe₂ could be deposited to study the fundamental charge transfer mechanisms across the O-I interface.^{19, 20} We report three different heterostructures based on different thickness of pentacene layers used in the heterostructure and observe a three times PL enhancement from the MoSe₂-pentacene as compared to the monolayer MoSe₂ suggesting a type-I band alignment. This MoSe₂-pentacene based heterostructure offers a distinct advantage of PL enhancement (type-I) opposite to the previously demonstrated MoS₂-pentacene heterostructure(type-II)^{21, 22} which showed a quenched PL. The interfacial exciton pumping has much higher efficiency (>86 times) than the photoexcitation process in MoSe₂, although the pentacene layer has much lower optical absorption than MoSe₂. This highly enhanced pumping efficiency is attributed to the high quantum yield in pentacene and the ultra-fast energy transfer between the O-I interface. Furthermore, those organic counterparts significantly modulate the bindings of charged excitons in monolayer MoSe₂ via their precise dielectric environment engineering. These results open new avenues for exploring fundamental phenomena and novel optoelectronic applications using atomically thin O-I heterostructures.

9.2 Future prospects

In this thesis, I have explored excitonic properties from both organic and inorganic 2D semiconductor materials through detailed optical measurements and by engineering prototype devices for excitonic property modulation. However, there are still a few challenges and potential research directions ahead. This section discusses a few possible challenges and future prospects with research in this domain. Chapter 3, section 6 covers some of these potential applications.

9.2.1 Exciton polaritons from organic 2D and 1D materials

As discussed in chapter 4 and 5, the strong sharp narrow emission from 2D and 1D states of organic material is critical for realizing enhanced light-matter interactions also called as exciton-polaritons. Due to low phonon coupling and coherent emissions in the excitonic emission spectra from organic materials, they are ideal candidates to be coupled into cavities to realize stable exciton-polaritons and high Rabi splitting which is critical for various applications including demonstrating room temperature Bose-Einstein (BE) condensates. Microcavities have been demonstrated to combine material eigenstates (or excitons) with optical cavity field modes in inorganic^{23, 24, 25, 26} and organic materials^{27, 28} resulting in the creation of hybrid matter-radiation states known as exciton polaritons. Recent interest in polaritons has largely centred on Bose-Einstein (BE) condensation, which has primarily been observed in inorganic semiconductor microcavities.^{23, 26} Typically, organic molecular crystals and films are more disordered; however, polariton lasing with a reduced threshold compared to ordinary photon lasing has been demonstrated in anthracene microcavities by Kena- Cohen and Forrest.²⁹ Very recently, BE condensation was reported in ladder-type conjugated polymers with narrow, vibronically resolved transitions.^{30, 31} Thus, the vibronically resolved emissions reported

from 1D organic nanowires will be ideal candidates for observing polaritons coupled with a microcavity as shown in Figure 9.1.

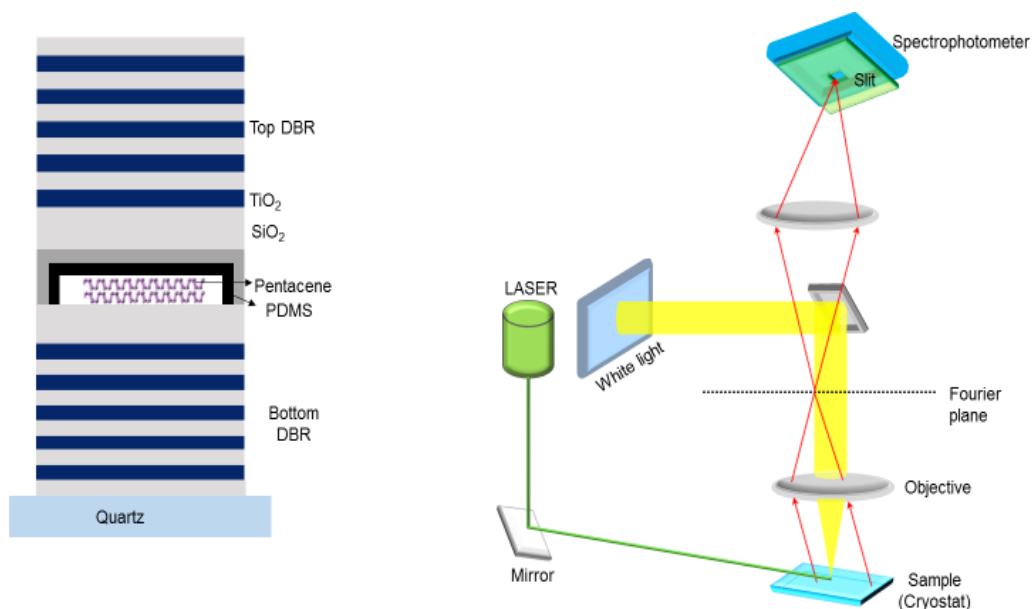


Fig 9.1 Proposed schematic diagram of the optical cavity with monolayer pentacene to achieve exciton polaritons states. The figure on the right shows the far-field emission microscopy setup which can be used to image polariton states.

9.2.2 High speed excitonic circuits and transistors

Chapter 4 and 6 specifically demonstrated the spatial and temporal dynamics of excitons in organic and inorganic 2D materials respectively. The thesis has explored the visualization of excitons by direct imaging technique to quantitatively study the exciton diffusion. The thesis has also established methods to enhance the diffusion coefficient in monolayer materials to higher values, which have never been reported before to substantiate the use of these materials for high speed optoelectronics device applications. Conventional signal processing utilizes electrons. An interconnection between electronic signal processing and optical communication causes a delay, thus slowing down the operation speed in conventional optoelectronic circuits.³² In contrast, excitons form a

medium that can be used for signal processing and also directly combine with optical communication. Thus, the lag between signal processing and optical communication is effectively eliminated in excitonic devices. This can provide a significant advantage in applications where the interconnection speed is important. The switching time combined with the interconnection time for the first proof-of-principle excitonic transistor was ~ 0.2 ns,¹⁷ close to ultrafast photonic modulators. As predicted the major challenges for excitonic devices are finite exciton lifetime and finite exciton binding energy. But, with the demonstration of high binding energies of excitons in this thesis (Chapter 7 and 8) and the control of binding energies of excitons in the organic-inorganic heterostructure, these materials and heterostructures open up new avenues for excitonic device fabrications with ultra-high exciton diffusion speeds complemented by high-quality and defect free growth mechanisms as shown in Figure 9.2.

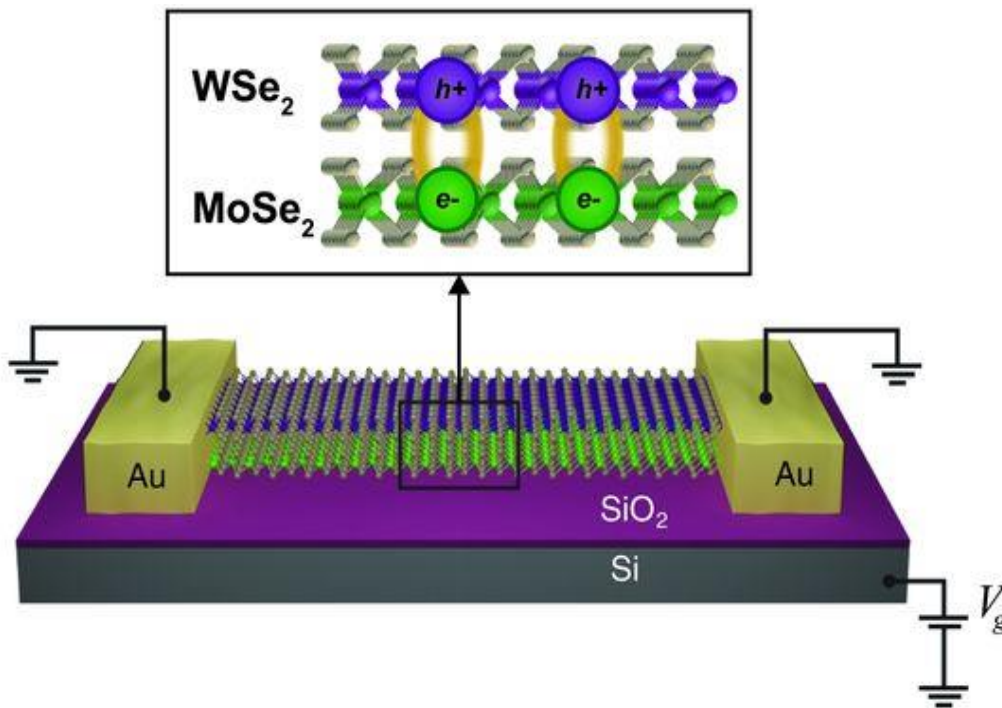


Fig 9.2 Proposed schematic diagram of the excitonic circuits using organic 2D materials.

Adapted with permission from ref.³³

9.2.3 Highly efficient light emitting diodes, lasers and transistors

Low dimensional materials have been established as sources of light emission recently. Because of two-dimensional quantum confinement effect, makes them promising candidates for light emitting applications and especially tuneable wavelength emissions. The emission from organic and inorganic 2D materials can be controlled via exciton properties as demonstrated extensively in this thesis. Earlier research in this field has been focused on inorganic materials, while fewer attempts are made to construct 2D and 1D structured low-molecular-weight compounds. We have now demonstrated that the optical and optoelectronic properties of organic nanomaterials are favourably different from those of their inorganic 2D materials (See chapter 4). Due to their optical tuneability, their high luminescence efficiency, and their property to self-assemble, organic compounds can serve as effective building blocks in future miniaturized optoelectronics that generate and propagate light. This thesis has explored in detail the light emission from low-dimensional organic and inorganic semiconductor materials. We have reported narrow (quasi-line spectra in chapter 5) and ultra-strong emissions (chapter 4) from solid state organic materials. Organic materials especially with highly ordered and crystalline growth as discussed in the earlier chapters can lead to strong and phonon free light emissions in the visible range and can generate and propagate light (chapter 4-5). Thus, they can be used as ideal candidates to demonstrate them as building blocks for nanoscale devices, such as logic gates, photodetectors, chemical sensors and optically driven lasers.³⁴ Fabrication of these organic 2D and 1D nanomaterials on flexible substrate with large mobilities and ultra-fast excitonic diffusion can lead to flexible high-speed transistors and logic gates for quantum computing as predicted with similar other systems.^{32, 35, 36} The MOS device based on 1D organic nanowire demonstrated in chapter 5 substantiates the capability of these materials to be used in OFET devices and flexible circuits.

References

1. Bardeen CJ. Excitonic processes in molecular crystalline materials. *MRS Bulletin* 2013, 38(01): 65-71.
2. Rogers JA. Toward paperlike displays. *Science* 2001, 291(5508): 1502-1503.
3. Sirringhaus H, Tessler N, Friend RH. Integrated Optoelectronic Devices Based on Conjugated Polymers. *Science* 1998, 280(5370): 1741-1744.
4. Bradac C, *et al.* Room-temperature spontaneous superradiance from single diamond nanocrystals. *Nature communications* 2017, 8(1): 1205.
5. Cong K, *et al.* Dicke superradiance in solids. *JOSA B* 2016, 33(7): C80-C101.
6. Gross M, Haroche S. Superradiance: An essay on the theory of collective spontaneous emission. *Physics reports* 1982, 93(5): 301-396.
7. Scheibner M, *et al.* Superradiance of quantum dots. *Nature Physics* 2007, 3(2): 106.
8. Hestand N, *et al.* Polarized Absorption in Crystalline Pentacene: Theory vs Experiment. *The Journal of Physical Chemistry C* 2015, 119(38): 22137-22147.
9. Hestand NJ, *et al.* Polarized Absorption in Crystalline Pentacene: Theory vs Experiment. *The Journal of Physical Chemistry C* 2015, 119(38): 22137-22147.
10. Hoffmann M, *et al.* The lowest energy Frenkel and charge-transfer excitons in quasi-one-dimensional structures: application to MePTCDI and PTCDA crystals. *Chemical Physics* 2000, 258(1): 73-96.
11. Lim S-H, Bjorklund TG, Spano FC, Bardeen CJ. Exciton Delocalization and Superradiance in Tetracene Thin Films and Nanoaggregates. *Physical Review Letters* 2004, 92(10): 107402.
12. Spano FC, Silva C. H-and J-aggregate behavior in polymeric semiconductors. *Annual Review of Physical Chemistry* 2014, 65: 477-500.
13. Ciulin V, *et al.* Radiative behavior of negatively charged excitons in CdTe-based quantum wells: A spectral and temporal analysis. *Physical Review B* 2000, 62(24): R16310.

14. Godde T, *et al.* Exciton and trion dynamics in atomically thin MoSe₂ and WSe₂: Effect of localization. *Physical Review B* 2016, 94(16): 165301.
15. Mikhnenko OV, Blom PW, Nguyen T-Q. Exciton diffusion in organic semiconductors. *Energy & Environmental Science* 2015, 8(7): 1867-1888.
16. High A, *et al.* Exciton optoelectronic transistor. *Optics letters* 2007, 32(17): 2466-2468.
17. High AA, *et al.* Control of exciton fluxes in an excitonic integrated circuit. *Science* 2008, 321(5886): 229-231.
18. Zhang Y, *et al.* Probing Carrier Transport and Structure-Property Relationship of Highly Ordered Organic Semiconductors at the Two-Dimensional Limit. *Physical review letters* 2016, 116(1): 016602.
19. Kang SJ, *et al.* Organic Field Effect Transistors Based on Graphene and Hexagonal Boron Nitride Heterostructures. *Advanced Functional Materials* 2014, 24(32): 5157-5163.
20. Lee G-H, *et al.* Heterostructures based on inorganic and organic van der Waals systems. *APL Materials* 2014, 2(9): 092511.
21. Bettis Homan S, *et al.* Ultrafast Exciton Dissociation and Long-Lived Charge Separation in a Photovoltaic Pentacene–MoS₂ van der Waals Heterojunction. *Nano Letters* 2017, 17(1): 164-169.
22. Jariwala D, *et al.* Hybrid, Gate-Tunable, van der Waals p–n Heterojunctions from Pentacene and MoS₂. *Nano letters* 2016, 16(1): 497-503.
23. Weisbuch C, Nishioka M, Ishikawa A, Arakawa Y. Observation of the coupled exciton-photon mode splitting in a semiconductor quantum microcavity. *Physical review letters* 1992, 69(23): 3314.
24. Kasprzak J, *et al.* Bose–Einstein condensation of exciton polaritons. *Nature* 2006, 443(7110): 409.
25. Deng H, *et al.* Condensation of semiconductor microcavity exciton polaritons. *Science* 2002, 298(5591): 199-202.
26. Skolnick M, Fisher T, Whittaker D. Strong coupling phenomena in quantum microcavity structures. *Semiconductor Science and Technology* 1998, 13(7): 645.

27. Coles DM, *et al.* Vibrationally Assisted Polariton-Relaxation Processes in Strongly Coupled Organic-Semiconductor Microcavities. *Advanced Functional Materials* 2011, 21(19): 3691-3696.
28. Lidzey DG, *et al.* Photon-mediated hybridization of Frenkel excitons in organic semiconductor microcavities. *Science* 2000, 288(5471): 1620-1623.
29. Kéna-Cohen S, Forrest S. Room-temperature polariton lasing in an organic single-crystal microcavity. *Nature Photonics* 2010, 4(6): 371.
30. Daskalakis K, Maier S, Murray R, Kéna-Cohen S. Nonlinear interactions in an organic polariton condensate. *Nature materials* 2014, 13(3): 271.
31. Plumhof JD, *et al.* Room-temperature Bose–Einstein condensation of cavity exciton–polaritons in a polymer. *Nature materials* 2014, 13(3): 247.
32. Grosso G, *et al.* Excitonic switches operating at around 100 K. *Nature Photonics* 2009, 3: 577.
33. Rivera P, *et al.* Valley-polarized exciton dynamics in a 2D semiconductor heterostructure. *Science* 2016, 351(6274): 688-691.
34. 3 - Electronic devices and functional structures based on nanostructured semiconductors. In: Zhuiykov S (ed). *Nanostructured Semiconductor Oxides for the Next Generation of Electronics and Functional Devices*. Woodhead Publishing, 2014, pp 95-138.
35. Scully SR, McGehee MD. Effects of optical interference and energy transfer on exciton diffusion length measurements in organic semiconductors. *Journal of Applied Physics* 2006, 100(3): 034907.
36. Zhu T, *et al.* Highly mobile charge-transfer excitons in two-dimensional WS₂/tetracene heterostructures. *Science Advances* 2018, 4(1): eaao3104.