DOI: 10.1002/ ((please add manuscript number))

Article type: Research News

Graphene and Carbon Nanotube Nanohybrids Covalently Functionalized by Porphyrins and Phthalocyanines for Optoelectronic Properties

*Aijian Wang, Jun Ye, Mark G. Humphrey, and Chi Zhang**

Dr. A. Wang, Dr. J. Ye, Prof. M.G. Humphrey, Prof. C. Zhang
China-Australia Joint Research Center for Functional Molecular Materials
School of Chemical Science and Engineering, Tongji University
Shanghai 200092, PR China
E-mail: chizhang@tongji.edu.cn

In recent years there has been rapid growth in studies of the optoelectronic properties of graphene, carbon nanotubes (CNTs), and their derivatives. The chemical functionalization of graphene and CNTs is a key requirement for the development of this field, but it remains a significant challenge. This Research News article focuses on recent advances in constructing nanohybrids of graphene or carbon nanotubes covalently linked to porphyrins or phthalocyanines, as well as their application in nonlinear optics. Following a summary of the syntheses of nanohybrids constructed from graphene or CNTs and porphyrins or phthalocyanines, explicit intraconjugate electronic interactions between photoexcited porphyrins/phthalocyanines and graphene/CNTs are introduced classified by energy transfer, electron transfer and charge transfer, and their optoelectronic applications are also highlighted. The article concludes with the major current challenges for the development of covalently-linked nanohybrids of porphyrins or phthalocyanines and carbon nanostructures.

Keywords: Porphyrin and Phthalocyanine; Covalent Functionalization; Graphene and Carbon Nanotube; Synthesis; Photoelectric Effect

1. Introduction

Donor-acceptor hybrids of porphyrinoids (such as porphyrins (Pors) and phthalocyanines (Pcs)) and different allotropes of carbon (such as carbon nanotubes (CNTs) and graphene) are currently an important scientific frontier.^[1-3] The advantages of this combination of components are manifold. Pors and their synthetic analogues, Pcs, are thermally and chemically stable compounds with a rich redox chemistry that can be easily tuned by the careful choice of the metal atom in the macrocyclic cavity and/or by placing appropriate substituents at the peripheral and/or axial positions of the macrocycle.^[4-6] Moreover, these compounds possess an intense optical absorption in the red/near infrared (NIR) region of the solar spectrum, affording near-perfect light-harvesting units that are ideal components for photoelectronic devices.^[5,7] The unique physicochemical properties of Pors and Pcs have prompted the incorporation of these macrocycles into many donor-acceptor systems where their role is (i) to harvest light efficiently, and (ii) to act as an electron donor for an acceptor moiety following photo-excitation.^[1,4,8] Nanohybrids constructed from graphene or CNTs and Pors or Pcs have started a revolution in materials science; the covalent linkages between the components can afford novel behavior, rather than a simple combination of their individual (often excellent) properties.^[8,9]

This research news highlights recent progresses in the preparation of graphene and carbon nanotube nanohybrids covalently functionalized by Pors and Pcs. The diverse synthetic procedures target the basal sp^2 C atoms or the oxygen-containing groups at the edges. A section of this review is also devoted to the photo-induced excited state dynamics of the donor-acceptor ensembles. Selected applications of the donor-acceptor systems in nonlinear optics are highlighted.

2. Design and synthesis

Chemical functionalization can potentially pave the way to the use of graphene and CNTs in real-world applications. In most cases when organic chromophores are covalently attached to graphene/CNTs, their extended aromatic character is perturbed, enabling the control of modulating their optoelectronic properties.^[10-13] In addition, the covalent functionalization affords the opportunity to improve the solubility and processability of graphene/CNTs. In comparison with the non-covalent approach, covalent functionalization may result in conjugation *via* a π -delocalizable linkage that can facilitate their further optoelectronic application. The organic covalent functionalization reactions of graphene/CNTs include two general routes: (a) cycloadditions, free-radical additions, and click reactions applied for the covalent functionalization of CNTs and graphene sp^2 carbon networks and (b) acylations employed at the oxygen-containing groups on graphene and CNTs (Figure 1).

Figure 1. Chemical modification methods for graphene and CNTs: Representative examples including (a) Amidation.^[14] Reproduced with permission. Copyright 2009, American Chemical Society. (b) Nucleophilic substitution.^[15] Reproduced with permission. Copyright 2013, Elsevier. (c) 1,3-Dipolar cycloaddition.^[16] Reproduced with permission. Copyright 2013, Wiley-VCH. (d) Radical addition + Click reaction.^[17] Reproduced with permission.

Copyright 2017, Elsevier. (e) 1,3-Dipolar cycloaddition or radical addition + Nucleophilic substitution.^[18] Reproduced with permission. Copyright 2015, Springer.

2.1. Covalent functionalization of graphene with porphyrins/phthalocyanines

Graphene oxide (GO) has often been employed as the starting material for the preparation of graphene derivatives through acylation reactions, due to the hydroxyl, carboxyl, and epoxy groups providing remarkable hydrophilic character and chemical reactivity.^[15,19-25] The covalent linking of Pors/Pcs to graphene has been achieved by esterification/amidation of hydroxyl/amino-appended Pors/Pcs with GO. Chen et al. reported the first coupling of Pors and GO by condensing an amino-modified tetraphenylporphyrin (TPP) to the carboxylic-functionalized GO, and affording GO-TPP nanohybrids.^[14,26] Similarly, soluble GO covalently functionalized with unsymmetrically substituted zinc phthalocyanine (GO-ZnPc) has been prepared by an amidation reaction,^[27] a common route to GO- and CNT-based functional materials. In most examples, the GO was treated with SOCl_2 to generate $-\text{COCl}$ groups at which covalent anchoring of hydroxyl/amino-functionalized Pors/Pcs was effected *via* an ester/amido bond.

Cycloadditions of azomethine ylides to the π -network of the graphene surface has also been demonstrated,^[28,29] which differ from most other organic reactions in that the electron redistribution involves simultaneous bond cleaving and formation. Torres et al. reported the first covalent graphene-Pc nanohybrid by introducing carboxylic acid groups onto the graphene surface using the Prato protocol;^[28] the grafted carboxylic groups undergo acylation reactions to afford graphene-Pc conjugates. In pioneering the functionalization of reduced graphene oxide (RGO) with Pors using the 1,3-dipolar cycloaddition of azomethine ylides, two possible routes were envisaged by Zhang et al.^[18]: a Prato reaction (i.e. a 1,3-dipolar cycloaddition) with sarcosine and a formyl-containing Por, and a stepwise method involving a 1,3-dipolar cycloaddition to the RGO surface using 4-hydroxybenzaldehyde, followed by nucleophilic substitution with an appropriate Por. The functionalities incorporated by the

1,3-dipolar cycloaddition are dispersed across the RGO surface, with a higher density localized next to the defects. This is in contrast to functionalization *via* ester/amido bond condensation, where these functionalities only exist at the edges. The morphology of the nanohybrids is not affected by the cycloaddition reactions, and the relatively low degree of graphene functionalization allows the retention of the inherent properties of graphene, rendering the samples suitable for optoelectronic applications.

Functionalization of carbon nanomaterials *via* free radical addition has been achieved on graphene; it promotes band gap opening and tweaks the solubility.^[30] Hirsch and coworkers synthesized a novel graphene-Por hybrid material with a direct covalent linkage between the graphene carbon network and the functional porphyrin unit *via* a one-pot reductive diazotization approach. Interestingly, the Por is linked in a perpendicular orientation by a single σ -bond to the graphene lattice, allowing free rotation of the addend with a fixed relative alignment of the π systems of the individual components.^[31] The aryl diazonium salts functionalization has also shown potential as an intermediate step, permitting post-functionalization at the aryl-modified graphene and the introduction of further functional groups.^[32] Hydroxylated groups covalently attached to graphene by diazonium addition may act as initiators for the grafting of Pors/Pcs *via* nucleophilic substitution or a click reaction, thereby affording covalently grafted Pors/Pcs at the graphene surface.^[33-36] The first example of exfoliated graphene covalently linked to electron accepting Pcs was reported by Torres and coworkers; functionalization was accomplished using alkylsulfonyl ZnPcs and alkyne-azide “click” chemistry.^[36]

Direct nucleophilic addition of a primary amine is also possible at carbon nanostructured materials. Reaction of a (2-aminoethoxy)(tri-tert-butyl) zinc phthalocyanine (ZnPc) with exfoliated graphene nanosheets resulted in nucleophilic addition of the ZnPc onto the graphene basal plane, forming a ZnPc-graphene nanohybrid material.^[37]

2.2. Covalent-linked CNT-porphyrin/phthalocyanine systems

Among the large number of possibilities, the acylation of CNTs is probably the most commonly used approach to covalent functionalization.^[9,38-42] The carboxyl groups on CNTs can be readily converted into acid chlorides by treatment with SOCl_2 and the acyl chlorides subsequently coupled with amines or alcohols. Baskaran et al. reported the preparation of meso-substituted-Por-grafted CNTs through esterification, including examples with both multi- and single-walled carbon nanotubes ((Por)_n-MWCNTs/(Por)_n-SWCNTs).^[40] Similarly, Aurisicchio and coworkers reported a porphyrin/double-walled carbon nanotube (DWCNT) hybrid from reaction of COOH-derived DWCNTs and 5,10,15-tris(4-tert-butylphenyl)-20-(4-hydroxybenzyl)porphyrin.^[39]

The direct cycloaddition of photoactive molecules onto the sidewall of CNTs can give rise to photoactive molecule-CNT nanohybrids with more robust and better-defined structures than those resulting from the functionalization *via* acid treatment of carboxylates grafted at the termini and defect sites of the CNTs.^[16,43-46] Research is currently focused on controlling the degree of functionalization and on incorporation of chirality. For example, D'Souza and Ito have recently appended zinc porphyrins to the sidewall of SWCNTs by dipolar cycloaddition of azomethine ylide.^[43] Torres et al. prepared SWCNT-Pc nanohybrids by a two-step approach involving (a) the 1,3-dipolar cycloaddition of azomethine ylides (formed *in situ* by reaction of N-octylglycine and 4-formylbenzoic acid) with pristine SWCNTs, and (b) subsequent esterification of the carboxylic acid-derivatized nanotubes with a hydroxymethyl-substituted ZnPc.^[2]

The main disadvantage of the stepwise synthetic approaches described above is that not all the functional groups grafted onto the CNTs react with the Pors/Pcs molecules, and thus the incorporation of Pors/Pcs units to the surface of CNTs is not maximized. An elegant solution to this problem was proposed by Campidelli and coworkers, who employed Cu(I)-catalyzed click reactions between azide and acetylenes to achieve derivatization of all

reactive groups present on the surface of CNTs with Pcs;^[47] when CNTs are modified by addition of aryl diazonium compounds, further modification *via* subsequent amidation, click, Sonogashira or Suzuki coupling reactions with different electroactive units may offer a broadly applicable route to attaching Pors or Pcs.^[17,48,49] Covalent functionalization of SWCNT conjugates with a dendron bearing one or two zinc porphyrins (ZnPors) or zinc phthalocyanines (ZnPcs) by “click chemistry” has also been demonstrated, with the goal of improving the absorption cross-section of the nanohybrids.^[50,51] The incorporation of one or two ZnPors/ZnPcs improved absorption through the visible region

Functionalization of SWCNTs and DWCNTs with a charge stabilizing zinc porphyrin containing triphenylamine moieties has been accomplished by Sonogashira coupling.^[52] Free radical addition of SWCNTs/DWCNTs with a 4-iodobenzenediazonium salt (generated *in situ* from 4-iodoaniline and isoamyl nitrite) afforded iodophenyl groups on the sidewalls of the CNTs. The modified CNTs were then covalently attached to the alkynyl porphyrin by C-C cross coupling reaction with microwave irradiation.

Photoinduced charge transfer from porphyrins to the CNTs is possible when the organic donors are fixed to the CNT sidewalls by direct aryl addition using aryl diazonium salts.^[53] Tian and Chen et al. prepared the porphyrin-covalently functionalized SWCNTs employing both the direct aryl addition reaction to the sidewalls and the amidation/esterification of carboxylic groups at terminal and defect sites.^[49,54]

Radical polymerization has also been employed to prepare porphyrin-functionalized CNTs;^[55] reaction of an asymmetrically substituted metal-free allyloxyporphyrin with MWCNTs in the presence of azobisisobutyronitrile afforded covalently functionalized MWCNT-TPP nanohybrids.^[55,56] This grafting-from approach minimizes interference with the elaborate molecular framework, and therefore reduces the likelihood of compromising the physical attributes of the nanotubes. Covalent attachment based on the Bingel reaction has

also been used to introduce Pors onto the surface of SWCNTs,^[57] the resulting nanohybrids exhibited improved dispersibility in common organic solvents.

3. Intraconjugate Excited-State Interactions

When targeting diverse optoelectronic uses of nanohybrids such as nonlinear optical applications, solar energy conversion, and photocatalysis, it is important to ascertain their photodynamics due to the decisive role they play in performance. In contrast to C₆₀, whose excited state (¹C₆₀^{*} or ³C₆₀^{*}) can decay by accepting an electron from ground-state Por/Pc to generate charge-separated species,^[58] the exciton formed on the selectively photoexcited CNT or graphene normally undergoes rapid relaxation to the ground state owing to its short lifetime (<10 ps).^[28,58] The excited-state interaction between graphene/CNT and Por/Pc involves initial photoexcitation of the Por/Pc moieties at a visible light wavelength, followed by intraconjugate energy transfer (EN), electron transfer (ET), or charge-transfer (CT), and decay at the graphene/CNT unit (Figure 2). In the following, we summarize representative experimental examples supporting this mechanism.

Figure 2. (a) H₂Por-SWCNT nanohybrids covalently tethered *via* a long (*p*-hydroxyhexyloxyphenyl) tether (I) or a short (*p*-hydroxymethylphenyl) tether (II)^[59] Reproduced with permission. Copyright 2004, Wiley-VCH. Differential absorption spectra (upper: visible; down: near-infrared) of, (b) H₂Por-SWCNT in THF with time delays between 0 and 200 ps.^[60] Reproduced with permission. Copyright 2009, American Chemical Society; (c) a Pc-graphene nanoconjugate in DMF, with time delays between 1.9 and 5.0 ps,^[28] Reproduced with permission. Copyright 2012, Wiley-VCH; (d) an alkylsulfonyl-substituted ZnPc-graphene nanoconjugate in DMF with time delays between 1.3 and 20 ps,^[36] Reproduced with permission. Copyright 2014, American Chemical Society; all spectra were obtained following femtosecond flash photolysis (387 nm) at room temperature. (e) Edge-to-edge separation distance (*R*_{ee}) dependence of the rate constant (*k*) of the exciplex decay in semilogarithmic representation. The line is the linear regression fit, and the slope corresponds to the distance decay parameter (β value). The deviation from the linear fit may stem from variation in the torsion angles between the porphyrin and the CCG planes.^[61] Reproduced with permission. Copyright 2016, American Chemical Society.

3.1 Energy Transfer

Fluorescence quenching can support an initial judgement on whether or not intraconjugate interactions between photoexcited Por/Pc and graphene/CNT occur. Effective intraconjugate interactions normally cause reduction in both the fluorescence intensity and the lifetime of the Por/Pc moieties. The photophysical properties of two SWCNT-based nanohybrids covalently tethered to H₂Por *via* a long (*p*-hydroxyhexyloxyphenyl) tether (I) or a short (*p*-hydroxymethylphenyl) tether (II) were studied (Figure 2a).^[59] In the long-tether case, the fluorescence intensity was quenched to ca. 70% of that of the free H₂Por organic dye, suggestive of the presence of intraconjugate interactions following attachment to SWCNT. However, the fluorescence remained almost unchanged when examined in solvent mixtures of varying polarities. It was deduced that photoinduced ET makes little contribution to the fluorescence quenching because it is sensitive to changes in the polarity of a medium; instead, the quenching is likely to arise from an EN process from the excited-state H₂Por to the SWCNT. In contrast to the long-tether case, no change in either the fluorescence spectral

profile or the fluorescence intensity was observed for the short-tether H₂Por-SWCNT nanoconjugate when compared to the behavior of free H₂Por, the lack of fluorescence quenching indicating ineffective internal excited-state interaction. The differing fluorescence behaviors of the two H₂Por-SWCNT nanohybrids can be explained by considering the possible structural arrangements of the two components in each nanohybrid. The long tether allows the H₂Por ring to be sited sufficiently close to the nanotube surface as to facilitate an ultrafast EN process. However, in the short-tether case, the tether flexibility is greatly diminished, which reduces the likelihood of close proximity of the two components, and thereby the possibility of interaction between the photoexcited H₂Por and the SWCNT. A ZnPor-Py-SWNT nanohybrid in which the short nanotubes have pentyl esters at the tips and pyridyl isoxazolino units along the walls displays very broad emission from the Py-SWCNT moiety, the increase in which correlates with the ZnPor emission decrease (isoemissive points at 580 and 680 nm).^[62] This is consistent with energy transfer from the ZnPor to the Py-SWCNT, which was subsequently confirmed in a laser flash photolysis study by observing the only transient corresponding to the ZnPor triplet excited state (maxima at 470 and 930 nm). The proximal Por and SWCNT moieties in nanoconjugates facilitate intramolecular energy transfer,^[59] and, in some cases, the nanocarbon exhibits enhanced fluorescence due to photoinduced EN.^[62]

3.2 Electron Transfer

Photoinduced ET is fundamental to a range of light-induced applications. Transient absorption (TA) spectra can confirm photoinduced transient species and afford the kinetics of their formation and conversion, and in particular the kinetics of charge separation (CS) and charge recombination (CR) of ET. The photoinduced ET in covalent Por/Pc-graphene/CNT nanohybrids were probed, including an example where H₂Por was linked to the periphery of polyamidoamine dendrimers initially grafted to the SWCNT surface.^[60] Photoexcited H₂Por is known to undergo slow intersystem crossing (τ 10.2 $\pm$ 0.5 ns) to the triplet excited-state, but

time-resolved TA spectroscopy of the nanohybrids revealed a H₂Por singlet excited-state which converted rapidly [rate constant $(1.5 \pm 0.5) \times 10^{10} \text{ s}^{-1}$] into a new product. This transient product possesses absorptions characteristic of one-electron oxidized H₂Por⁺, i.e., broad absorption between 550 and 800 nm, while bleaching of the van Hove singularities of the SWCNTs in the near-infrared region correlates with reductive charging of the SWCNTs (Figure 2b). To explain the spectroscopic observations, an intraconjugate ET process from the H₂Por donor to the SWCNT acceptor was suggested, generating the radical ion pair (RIP) H₂Por⁺-SWCNT⁻ which then decays to the ground state. In subsequent studies, ZnPc was covalently linked to SWCNTs *via* Prato cycloaddition or Huisgen 1,3-dipolar cycloaddition.^[2,47] In a similar fashion, the ZnPc singlet excited-state decay was significantly accelerated (lifetime ~ 20 ps), and simultaneously a new transient species was observed with distinct maxima at 520 and 840 nm, attributed to the one-electron oxidized ZnPc⁺, and with appreciable blue-shifts of the van Hove singularities (i.e., 1000-1400 nm), reflecting the new conduction electrons at the SWCNTs. The first covalently-linked Pc-graphene nanoconjugate was obtained following liquid-phase exfoliation in two steps, an initial modification of the graphene and a subsequent esterification reaction.^[28] In this nanoconjugate, photoinduced ET occurs from the aryloxy-substituted Pc to the graphene; TA analysis identified the characteristic Pc⁺ absorption at 515 and 850 nm, transient decay resulting in a broad maximum at 1100 nm indicating new conduction band electrons in graphene injected from the photoexcited Pc (Figure 2c). Photoinduced ET from few-layer graphene to alkylsulfonyl-substituted ZnPc has been reported, a rare example of inverse ET.^[36] The electron-withdrawing sulfonyl groups results in low-energy HOMO (−5 eV) and LUMO (−3.3 eV) levels for the ZnPc unit, facilitating electron transfer from the Fermi level of graphene/exfoliated graphite (−4.5 eV to −5 eV) to the semioccupied HOMO level of the ZnPc. Following photo-excitation, a new transient species evolves concomitant with decay of the ZnPc singlet excited-state; the new species displays characteristic bands with maxima at

570, 636, and 765 nm that correlate with spectroelectrochemical data following one-electron reduction of the alkylsulfonyl-substituted ZnPc, while a broad maximum ranging from 950 to 1300 nm is attributed to the new valence band holes in graphene (Figure 2d).

Photoinduced CS efficiency depends on the nanotube diameter of H₂Por/ZnPor covalently-functionalized SWCNTs (SWCNT(6,5) and SWCNT(7,6)).^[43] Fluorescence quenching of the H₂Por/ZnPor-SWCNT(7,6) nanohybrid is more efficient than H₂Por/ZnPor-SWCNT(6,5). The k_{CS} values for SWCNT(6,5) and SWCNT(7,6) (9×10^9 and 12×10^9 s⁻¹, respectively) suggest that SWCNT(7,6), with the higher conduction band level, is more favorable for charge separation *via* ZnPor* compared to SWCNT(6,5). TA spectra revealed the 600-700 nm band corresponding to H₂Por⁺/ZnPor⁺ and weak bands in the 900-1300 nm region (with the same decay as that of ZnPor⁺) attributed to SWCNT⁻. The k_{CS}/k_{CR} ratio of ZnPor-SWCNT(n,m) (2000-2100) is larger than that of H₂Por-SWCNT(n,m) (390-550), suggesting higher charge stabilization for ZnPor-SWCNT(n,m). It was concluded that covalent combination of ZnPor and SWCNT(7,6) affords the optimal photoinduced CS system.

The CS state of ZnPor-CNT nanohybrids are stabilized by attaching a secondary donor (triphenylamine, TPA) to the ZnPor meso positions;^[52] femtosecond TA spectra of the hybrids revealed peaks in the 700-740 and 1000-1200 nm ranges where the [(TPA)₄ZnPor]⁺ absorbance was expected, with the charge-separated state persisting for ca. 1 ns.

Photoinduced ET in covalent Por/Pc-graphene/CNT nanoconjugates can be confirmed by TA; characteristic absorptions are seen at ca. 640 nm, 850 nm, and in the NIR for the Por⁺, Pc⁺, and the charged CNT/graphene transient products, respectively.

3.3 Charge Transfer

Another internal electronic interaction is seen between photoexcited Por and graphene/CNT when a covalent bridge of one or several *p*-phenylene units is employed, namely a CT interaction that leads to the formation of an exciplex.^[53,61] This exciplex decays

rapidly to the ground state rather than to the CS state, resulting in no contribution to photocurrent generation. TA studies revealed a rather broad and structureless band due to the partial positive and negative charges localized on the ZnPor and nanocarbon moieties, respectively. ZnPor-graphene nanoconjugates with systematically varied oligo-*p*-phenylene bridges (ZnPor-(1,4-C₆H₄)_n-graphene, *n* = 1-5) were employed to investigate the effect of the D-A interaction between the ZnPor and the graphene units on the photodynamics.^[61] Upon photoexcitation, all samples, irrespective of the bridge length, evolved to an exciplex state which then experienced a rapid decay to the ground state. The exciplex lifetime (ZnPor-(1,4-C₆H₄)-graphene < ZnPor-(1,4-C₆H₄)₃-graphene < ZnPor-(1,4-C₆H₄)₂-graphene < ZnPor-(1,4-C₆H₄)₄-graphene < ZnPor-(1,4-C₆H₄)₅-graphene) is strongly dependent on the distance between the ZnPor and the graphene surface, confirming that the decay to the ground state is dominated by through-space rather than through-bond interactions (Figure 2e). Further study correlating hybrid structures and their internal excited-state interactions is needed.

There are several ways to differentiate the aforementioned interactions: (1) TA spectra show characteristic absorption bands for charged transient products following the photoinduced ET process. In contrast, for EN and CT, the bands for charged species are missing; (2) photoelectrochemical devices using these nanoconjugates as the photo-anode usually show increased photocurrent for EN and ET, but no contribution from CT; (3) in some cases, the nanocarbon may exhibit enhanced fluorescence due to photoinduced EN from the Por/Pc dyes to the nanocarbon.

4. Optoelectronic Applications in Nonlinear Optics

Materials with large third-order optical nonlinearities and fast NLO response are critically important candidates for optoelectronic applications such as optical communication, optical limiting (OL), etc.^[11] Covalent linking of two materials with large optical nonlinearities, in many cases arising from different nonlinear mechanisms, may result in an enhancement of the NLO responses in comparison with the sum of those of the individual

components.^[17,27,42,54,56,63-69] Graphene/CNTs exhibit ultrafast carrier relaxation dynamics and ultra-broadband resonant NLO responses due to their extended π -conjugation and electronic band structure.^[8,70,71] Hybridization with other optically-active materials can resonantly improve their NLO responses by more than an order of magnitude, while retaining ultrafast nonlinear response. With covalent functionalization, a decrease in carrier mobility is often observed, and thereby an increase in the carrier concentration.^[72] The NLO performance of graphene/CNTs can therefore not only be increased but can also be spectrally tailored. A detailed NLO investigation of a GO-TPP nanohybrid revealed that the as-prepared nanohybrid exhibited better OL performance than C₆₀ or a control sample consisting of a physical mixture of GO and the amine-functionalized H₂Por, a result that was attributed to a combination of different photophysical mechanisms, i.e. reverse saturable absorption (RSA), two-photon absorption (TPA), nonlinear scattering (NLS), and photo-induced electron transfer.^[26]

The NLO and OL performances of two GO-based nanohybrids covalently linking axially coordinated dihydroxotin(IV)- and phosphorus-cored TPPs (GO-SnTPP and GO-PTPP) to GO, using both nanosecond (ns) and picosecond (ps) Z-scan measurements at 532 nm,^[15] revealed that GO, SnTPP, PTPP, and both nanohybrids exhibited considerable NLO absorption, with the OL responses of both nanohybrids greater than those of the individual Pors or the pristine GO (Figure 3). The covalently-linked RGO-Por nanohybrids were found to show enhanced NLO performance because of a combination of mechanisms, while significant differences were observed, highlighting the influence on photophysical properties of the degree of functionalization and the synthetic approach employed.^[18,33,34] The effect of morphology on the optoelectronic properties of covalently-linked GO-dihydroxotin(IV) TPP nanohybrids have also been explored.^[22] The structurally similar and biologically important Pcs are also effective optical limiters. The nanohybrid resulting from covalently functionalized GO with unsymmetrically substituted ZnPc is soluble and exhibits improved

NLO extinction coefficients and broadband OL behavior compared to GO at 532 and 1064 nm.^[27]

Figure 3. Open-aperture Z-scan curves of GO, SnTPP, GO-SnTPP, PTPP, and GO-PTPP at 532 nm with (a) 4 ns and (b) 21 ps pulse duration, with ca. 70% linear transmissions; Comparison of the optical limiting performance of (c) GO, SnTPP, and GO-SnTPP, (d) GO, PTPP and GO-PTPP at 532 nm.^[15] Reproduced with permission. Copyright 2013, Elsevier.

CNTs possess significant OL performance over a broad wavelength range from the visible to the near-infrared region, and the combination of Pors with CNTs has also been shown to be an effective means to produce OL materials.^[17,54,56,68] The NLO and OL performance of covalently linked Por-SWCNTs composites were assessed by Z-scan experiments with linearly polarized 5 ns pulses at 532 nm;^[49,54] compared to C₆₀, SWCNTs and Pors, the composite solutions exhibited outstanding OL performances under the same conditions an outcome ascribed to energy transfer between the Pors and SWCNTs, which improved both ESA and NLS. In related studies, two axially coordinated metal-Pors-functionalized MWCNTs nanohybrids constructed through 1,3-dipolar cycloaddition reactions, exhibited improved nonlinear absorption in the ns regime compared

to pristine MWCNTs and the physical mixture of both components.^[45] Allyloxyporphyrin-functionalized MWCNTs prepared by radical polymerization exhibit good NLO properties at 532 nm with 4 ns laser pulses.^[56] Enhanced NLO and OL properties were also observed for two MWCNT-based nanohybrids covalently functionalized by zinc- and free-based TPPs, generated directly from pristine MWCNTs through 1,3-dipolar cycloaddition reactions.^[16] Both cyano (CN) and dimethylamino (DMA) substituents at Por-SWCNT nanohybrids enhance OL performance because of increased RSA of the Por moieties following functionalization; in comparison with CN, the DMA group has a more positive influence on the Por excited-states and thereby the RSA and NLO activity.^[17]

CNTs in covalent combination with Pcs have also been developed as NLO materials. For instance, an unsymmetrically-substituted H₂Pc-functionalized MWCNT hybrid composite exhibits strong NLS at high intensities, which evidently originates from the MWCNT component;^[42] the Pc exhibits RSA, while the nanohybrid shows both RSA and NLS. These two mechanisms are comparable in magnitude and in conflict as far as the global OL performance is concerned, leading to suppression of the NLO behavior of H₂Pc-MWCNTs. The NLO performance of 2(3),9(10),16(17),23(24)-tetrakis-(4-aminophenoxy)-phthalocyaninato indium(III) chloride and its SWCNT nanohybrid was studied in both DMSO and DMF.^[69] The nanohybrid in DMSO solution exhibited long-lived triplet lifetimes with a high triplet quantum yield, and thus displayed the best OL properties of the systems investigated. The NLO response of the as-prepared nanohybrid was lower in DMF solvent compared with that of Pc alone, an outcome attributed to the fact that the nanohybrid in DMF undergoes a resonance stabilization, thus causing the triplet absorption quenching of Pc.

5. Summary and Perspectives

Recent advances in covalently-functionalized Pors/Pcs graphene/CNTs nanohybrids for NLO materials have been summarized. Surface modification of graphene/CNTs using a range of techniques, including cycloadditions, free-radical additions, acylations, click reactions, etc.,

have been performed by various organic chromophores. The synthetic routes and processing methods of these Por/Pc-graphene/CNT nanohybrids may play a significant role in their NLO performance. In most such nanohybrids, the electron/energy transfer from the organic component to graphene or CNTs plays an influential role in enhancing NLO properties. Although promising advances have been made, several challenges require urgent resolution: (1) development of novel covalent-linking chemical methods, to bring in new covalent bridges, or to load organic functional dyes (of different types and/or different amounts) onto the carbon nanostructures with control; (2) control of the intraconjugate excited-state interactions *via* rational structural design; (3) elucidation of possible mechanisms of NLO behavior for the covalent nanohybrids by exploring correlations between the structural parameters and the NLO responses.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (51432006 and 51172100), the Ministry of Education of China for the Changjiang Innovation Research Team (IRT13R24), and the Ministry of Education and the State Administration of Foreign Experts Affairs for the 111 Project (B13025). M.G.H. and C.Z. thank the Australian Research Council for support.

Note:

A.J.W. and J.Y. made equal contributions to this work (co-first authors).

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

References

- [1] G. Bottari, O. Trukhina, M. Ince, T. Torres, *Coord. Chem. Rev.* **2012**, 256, 2453.
- [2] B. Ballestsros, G. Torre, C. Ehli, G. M. A. Rahman, F. A. Agullo-Rueda, D. M. Guldi, T. Torres, *J. Am. Chem. Soc.* **2007**, 129, 5061.
- [3] F. D'Souza, O. Ito, *Chem. Soc. Rev.* **2012**, 41, 96.
- [4] G. Bottari, G. Torre, D. M. Guldi, T. Torres, *Chem. Rev.* **2010**, 110, 6768.
- [5] M. O. Senge, M. Fazekas, E. G. A. Notaras, W. J. Blau, M. Zawadzka, O. B. Locos, E. M. N. Mhuircheartaigh, *Adv. Mater.* **2007**, 19, 2737.
- [6] S. J. Altenburg, M. Lattelais, B. Wang, M. L. Bocquet, R. Berndt, *J. Am. Chem. Soc.* **2015**, 137, 9452.
- [7] M. V. Martínez-Díaz, G. de la Torre, T. Torres, *Chem. Commun.* **2010**, 46, 7090.
- [8] Y. Chen, T. Bai, N. N. Dong, F. Fan, S. F. Zhang, X. D. Zhuang, J. Sun, B. Zhang, X. Y. Zhang, J. Wang, W. J. Blau, *Prog. Mater. Sci.* **2016**, 84, 118.
- [9] G. Bottari, G. de la Torre, T. Torres, *Acc. Chem. Res.* **2015**, 48, 900.
- [10] Y. He, M. Garnica, F. Bischoff, J. Ducke, M. L. Batzill, W. Auwärter, J. V. Barth, *Nat. Chem.* **2017**, 9, 33.
- [11] R. K. Yadav, G. H. Oh, N. Park, A. Kumar, K. Kong, J. Baeg, *J. Am. Chem. Soc.* **2014**, 136, 16728.
- [12] G. Bottari, M. Á. Herranz, L. Wibmer, M. Volland, L. Rodríguez-Pérez, D. M. Guldi, A. Hirsch, N. Martin, F. D'Souza, T. Torres, *Chem. Soc. Rev.* **2017**, 46, 4464.
- [13] G. de la Torre, G. Bottari, T. Torres, *Adv. Energy Mater.* **2017**, 7, 1601700.
- [14] Z. B. Liu, Y. F. Xu, X. Y. Zhang, X. L. Zhang, Y. S. Chen, J. G. Tian, *J. Phys. Chem. B* **2009**, 113, 9681.
- [15] A. J. Wang, L. L. Long, W. Zhao, Y. L. Song, M. G. Humphrey, M. P. Cifuentes, X. Z. Wu, Y. S. Fu, D. D. Zhang, X. F. Li, C. Zhang, *Carbon* **2013**, 53, 327.
- [16] A. J. Wang, Y. Fang, L. L. Long, Y. L. Song, W. Yu, W. Zhao, M. P. Cifuentes, M. G. Humphrey, C. Zhang, *Chem. Eur. J.* **2013**, 19, 14159.
- [17] M. F. Zhang, L. L. Fu, J. Ye, M. G. Humphrey, H. Liu, B. Yan, L. Zhang, J. D. Shao, C. Zhang, *Carbon* **2017**, 124, 618.
- [18] A. J. Wang, Y. Fang, Z. G. Xiao, Y. L. Song, L. L. Long, M. P. Cifuentes, M. G. Humphrey, C. Zhang, *Nano Res.* **2015**, 8, 870.
- [19] S. H. Noh, H. Park, W. Jang, K. H. Koh, M. Yi, J. M. Lee, S. Thirumalairajan, J. Y. Jaung, D. H. Wang, T. H. Han, *Carbon* **2017**, 119, 476.
- [20] R. K. Yadav, J. O. Baeg, G. H. Oh, N. J. Park, K. Kong, J. Kim, D. W. Hwang, S. K.

- Biswas, *J. Am. Chem. Soc.* **2012**, *134*, 11455.
- [21] M. M. Stylianakis, D. Konios, G. Kakavelakis, G. Charalambidis, E. Stratakis, A. G. Coutsolelos, E. Kymakis, S. H. Anastasiadis, *Nanoscale* **2015**, *7*, 17827.
- [22] H. Xu, P. Wu, C. Liao, C. G. Lv, Z. Z. Gu, *Chem. Commun.* **2014**, *50*, 8951.
- [23] S. K. Das, C. B. Kc, K. Ohkubo, Y. Yamada, S. Fukuzumi, F. D'Souza, *Chem. Commun.* **2013**, *49*, 2013.
- [24] K. Garg, R. Shanmugam, P. C. Ramamurthy, *Carbon* **2017**, *122*, 307.
- [25] Q. Li, Q. Zeng, L. Gao, H. Li, Y. F. Guo, W. W. Li, Y. Shi, G. H. Tao, L. W. Liu, *J. Mater. Chem. A* **2017**, *5*, 155.
- [26] Y. F. Xu, Z. B. Liu, X. L. Zhang, Y. Wang, J. G. Tian, Y. Huang, Y. F. Ma, X. Y. Zhang, Y. S. Chen, *Adv. Mater.* **2009**, *21*, 1275.
- [27] J. H. Zhu, Y. X. Li, Y. Chen, J. Wang, B. Zhang, J. J. Zhang, W. J. Blau, *Carbon* **2011**, *49*, 1900.
- [28] M. E. Ragoussi, J. Malig, G. Katsukis, B. Butz, E. Spiecker, G. Torre, T. Torres, D. M. Guldi, *Angew. Chem. Int. Ed.* **2012**, *51*, 6421.
- [29] J. Huang, Y. J. Wu, D. D. Wang, Y. F. Ma, Z. K. Yue, Y. T. Lu, M. X. Zhang, Z. J. Zhang, P. Yang, *ACS Appl. Mater. Interf.* **2015**, *7*, 3732.
- [30] C. K. Chua, M. Pumera, *Chem. Soc. Rev.* **2013**, *42*, 3222.
- [31] D. Dasler, R. A. Schäfer, M. B. Minameyer, J. F. Hitzenberger, F. Hauke, T. Drewello, A. Hirsch, *J. Am. Chem. Soc.* **2017**, *139*, 11760.
- [32] S. P. Economopoulos, N. Tagmatarchis, *Chem. Eur. J.* **2013**, *19*, 12930.
- [33] A. J. Wang, W. Yu, Z. P. Huang, F. Zhou, J. B. Song, Y. L. Song, L. L. Long, M. P. Cifuentes, M. G. Humphrey, L. Zhang, J. D. Shao, C. Zhang, *Sci. Rep.* **2016**, *6*, 23325.
- [34] A. J. Wang, J. B. Song, D. Jia, W. Yu, L. L. Long, Y. L. Song, M. P. Cifuentes, M. G. Humphrey, L. Zhang, J. D. Shao, C. Zhang, *Inorg. Chem. Front.* **2016**, *3*, 296.
- [35] H. X. Wang, K. G. Zhou, Y. L. Xie, J. Zeng, N. N. Chai, J. Li, H. L. Zhang, *Chem. Commun.* **2011**, *47*, 5747.
- [36] M. E. Ragoussi, G. Katsukis, A. Roth, J. Malig, G. de la Torre, D. M. Guldi, T. Torres, *J. Am. Chem. Soc.* **2014**, *136*, 4593.
- [37] N. Karousis, J. Ortiz, K. Ohkubo, T. Hasobe, S. Fukuzumi, Á. Sastre-Santos, N. Tagmatarchis, *J. Phys. Chem. C* **2012**, *116*, 20564.
- [38] H. Wu, Z. M. Chen, J. L. Zhang, F. Wu, C. Y. He, B. Wang, Y. Q. Wu, Z. Y. Ren, *J. Mater. Chem. A* **2016**, *4*, 1096.
- [39] C. Aurisicchio, R. Arega, V. Corvaglia, J. Mohanraj, R. Delamare, D. A. Vlad, C. Kusko,

- C. A. Dutu, A. Minoia, G. Deshares, O. Coulembier, S. Melinte, P. Dubois, R. Lazzaroni, N. Armaroli, D. Bonifazi, *Adv. Funct. Mater.* **2012**, *22*, 3209.
- [40] D. Baskaran, J. W. Mays, X. P. Zhang, M. S. Bratcher, *J. Am. Chem. Soc.* **2005**, *127*, 6916.
- [41] L. M. Arellano, L. Martin-Gomis, H. B. Gobeze, M. Barrejon, D. Molina, M. J. Gomez-Escalonilla, J. L. G. Fierro, M. F. Zhang, M. Yudasaka, S. Iijima, F. D'Souza, F. Langa, Á. Sastre-Santos, *J. Mater. Chem. C* **2015**, *3*, 10215.
- [42] N. He, Y. Chen, J. R. Bai, J. Wang, W. J. Blau, J. H. Zhu, *J. Phys. Chem. C* **2009**, *113*, 13029.
- [43] S. K. Das, A. S. D. Sandanayaka, N. K. Subbaiyan, M. E. Zandler, O. Ito, F. D'Souza, *Chem. Eur. J.* **2012**, *18*, 11388.
- [44] W. Zhang, A. U. Shaikh, E. Y. Tsui, T. M. Swager, *Chem. Mater.* **2009**, *21*, 3234.
- [45] A. J. Wang, J. B. Song, Z. P. Huang, Y. L. Song, W. Yu, H. L. Dong, W. P. Hu, M. P. Cifuentes, M. G. Humphrey, L. Zhang, J. D. Shao, C. Zhang, *Nano Res.* **2016**, *9*, 458.
- [46] A. Maurin, M. Robert, *Chem. Commun.* **2016**, *52*, 12084.
- [47] S. Campidelli, B. Ballesteros, A. Filoramo, D. D. Díaz, G. de la Torre, T. Torre, G. M. A. Rahman, C. Ehli, D. Kiessling, F. Werner, V. Sgobba, D. M. Guldi, C. Cioffi, M. Prato, J. P. Bourgoïn, *J. Am. Chem. Soc.* **2008**, *130*, 11503.
- [48] I. Hijazi, B. Jousselme, P. Jégou, A. Filoramo, S. Campidelli, *J. Mater. Chem.* **2012**, *22*, 20936.
- [49] Z. B. Liu, J. G. Tian, Z. Guo, D. M. Ren, F. Du, J. Y. Zheng, Y. S. Chen, *Adv. Mater.* **2008**, *20*, 511.
- [50] T. Palacin, H. L. Khanh, B. Jousselme, P. Jégou, A. Filoramo, C. Ehli, D. M. Guldi, S. Campidelli, *J. Am. Chem. Soc.* **2009**, *131*, 15394.
- [51] K. H. L. Ho, L. River, B. Jousselme, P. Jégou, A. Filoramo, S. Campidelli, *Chem. Commun.* **2010**, *46*, 8731.
- [52] L. M. Arellano, M. Barrejón, H. B. Gobeze, M. J. Gómez-Escalonilla, J. L. G. Fierro, F. D'Souza, F. Langa, *Nanoscale* **2017**, *9*, 7551.
- [53] T. Umeyama, M. Fujita, N. Tezuka, N. Kadota, Y. Matano, K. Yoshida, S. Isoda, H. Imahori, *J. Phys. Chem. C* **2007**, *111*, 11484.
- [54] Z. Guo, F. Du, D. M. Ren, Y. S. Chen, J. Y. Zheng, Z. B. Liu, J. G. Tian, *J. Mater. Chem.* **2006**, *16*, 3021.
- [55] G. M. A. Rahman, A. Troeger, V. Sgobba, D. M. Guldi, N. Jux, M. N. Tchoul, W. T. Ford, A. Mateo-Alonso, M. Prato, *Chem. Eur. J.* **2008**, *14*, 8837.

- [56] A. J. Wang, Y. Fang, W. Yu, L. L. Long, Y. L. Song, W. Zhao, M. P. Cifuentes, M. G. Humphrey, C. Zhang, *Chem. Asian J.* **2013**, *9*, 639.
- [57] B. Mao, D. G. Calatayud, V. Mirabello, N. Kuganathan, H. Ge, R. M. J. Jacobs, A. M. Shepherd, J. A. R. Martins, J. B. de la Serna, B. J. Hodges, S. W. Botchway, S. I. Pascu, *Chem. Eur. J.* **2017**, *23*, 9772.
- [58] O. Ito, *Chem. Rec.* **2017**, *17*, 326.
- [59] H. Li, R. B. Martin, B. A. Harruff, R. A. Carino, L. F. Allard, Y. P. Sun, *Adv. Mater.* **2004**, *16*, 896.
- [60] S. Campidelli, C. Sooambar, E. L. Diz, D. M. Guldi, M. Prato, *J. Am. Chem. Soc.* **2006**, *128*, 12544.
- [61] T. Umeyama, T. Hanaoka, J. Baek, T. Higashino, F. Abou-Chahine, N. V. Tkachenko, H. Imahori, *J. Phys. Chem. C* **2016**, *120*, 28337.
- [62] M. Alvaro, P. Atienzar, P. de la Cruz, J. L. Delgado, V. Troiani, H. Garcia, F. Langa, A. Palkar, L. Echegoyen, *J. Am. Chem. Soc.* **2006**, *128*, 6626.
- [63] J. Thompson, A. Crossley, P. D. Nellist, V. Nicolosi, *J. Mater. Chem.* **2012**, *22*, 23246.
- [64] D. Dini, M. J. F. Calvete, M. Hanack, *Chem. Rev.* **2016**, *116*, 13043.
- [65] Y. L. Du, N. N. Dong, M. H. Zhang, K. Zhu, R. Q. Na, S. L. Zhang, N. W. Sun, G. B. Wang, J. Wang, *Phys. Chem. Chem. Phys.* **2017**, *19*, 2252.
- [66] W. N. Song, C. Y. He, W. Zhang, Y. C. Gao, Y. X. Yang, Y. Q. Wu, Z. M. Chen, X. C. Li, Y. L. Dong, *Carbon* **2014**, *77*, 1020.
- [67] M. B. M. Krishna, N. Venkatramaiah, R. Venkatesan, D. N. Rao, *J. Mater. Chem.* **2012**, *22*, 3059.
- [68] Z. B. Liu, Z. Guo, X. L. Zhang, J. Y. Zheng, J. G. Tian, *Carbon* **2013**, *51*, 419.
- [69] K. Sanusi, E. K. Amuhaya, T. Nyokong, *J. Phys. Chem. C* **2014**, *118*, 7057.
- [70] J. Wang, Y. Chen, W. J. Blau, *J. Mater. Chem.* **2009**, *19*, 7425.
- [71] J. Wang, Y. Hernandez, M. Lotya, J. Coleman, W. J. Blau, *Adv. Mater.* **2009**, *21*, 2430.
- [72] A. Kaplan, Z. Yuan, J. D. Benck, A. G. Rajan, X. S. Chu, Q. H. Wang, M. S. Strano, *Chem. Soc. Rev.* **2017**, *46*, 4530.

Entry for the Table of Contents