Open pentiptycene networks assembled through charge-assisted hydrogen bonds

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A series of hydrogen bonded networks was prepared incorporating ditopic, tritopic or tetratopic poly-amidinium tectons and linear pentiptycene dicarboxylates. The ditopic amidinium forms a 1D hydrogen bonded chain when combined with the pentiptycene tecton while the tritopic trigonal planar amidinium tecton forms a 2D honeycomb network. A tetratopic amidinium tecton forms a 3D diamondoid network which is 32-fold interpenetrated, the joint-highest degree of interpenetration observed for a hydrogen bonded network. The bulky pentiptycene functionality prohibits the polymers from packing efficiently, leading to voids within each structure. These frameworks were envisaged as potential molecular motors, but unfortunately a lack of stability to solvent removal precluded an investigation of these properties.

Introduction

Hydrogen bonded organic frameworks (HOFs) are supramolecular materials constructed *via* intermolecular hydrogen bonding interactions.¹⁻³ Early HOFs were assembled through hydrogen bonding between neutral self-complementary groups, such as carboxylic acid,⁴⁻⁵ amide,⁶⁻⁷ alcohol,⁸ or diaminotriazine.⁹ Subsequently, HOFs made in this manner have been used to prepare a range of materials including ones that show impressive stability and permanent porosity.^{1-3, 10-14}

Charge-assisted hydrogen bonds have also been employed and in theory this may lead to more robust materials due to the additional electrostatic attraction between the components. HOFs containing charge-assisted hydrogen bonds have been synthesized by pairing positively-charged hydrogen bond donor groups such as guanidinium,¹⁵⁻¹⁶ amidinium,¹⁷⁻²¹ or imidazolium²² with a range of anions.²³

A key advantage of using cationic and anionic components is that a node-and-linker methodology, similar to that used in reticular MOF/COF chemistry can be implemented.²⁴ Ward's group has demonstrated that the guanidinium cation and polysulfonate anions can be used to prepare a range of different architectures.^{15-16, 25-28} Building on this pioneering work, we have used the interaction of amidinium and carboxylate tectons to prepare open three-dimensional frameworks, and have realized a range of diamondoid architectures²⁹⁻³⁰ as well as an open network with PtS topology.³¹ These networks are held together by $R_2^2(8)$ hydrogen bonding geometries³² (Figure 1), although other hydrogen bond geometries have also been observed for amidinium...carboxylate interactions.^{30-31, 33-35}

Pentiptycenes, part of the larger family of iptycenes,^{36,37} are rigid molecules with phenyl rings attached to two [2.2.2]bicyclooctatriene bridgehead systems. The rigidity and geometry of pentiptycenes prevents them from

packing efficiently, and this property has been used to prepare porous organic polymers,³⁸⁻⁴² and metal organic frameworks.⁴³⁻⁴⁷ Additionally, the groups of Yang and Garcia-Garibay have used the pentiptycene group as the stator component in molecular brakes and rotors, where the pentiptycene group remains stationary while another part of the molecule moves.⁴⁸⁻⁵⁴

In this work, we investigate whether the pentiptycene-derived dicarboxylate anion **1**²⁻ can be incorporated into hydrogen-bonded framework materials. We are interested in this for two reasons: first, to test the limits of the amidinium/carboxylate motif for self-assembly. The dianion **1**²⁻ is large (O...O length ~ 21 Å) and sterically-demanding and as such would be expected to be difficult to incorporate into a framework held together by hydrogen bonds.⁵⁵ Second, if such a framework could be prepared, it may be possible that it would act as a molecular rotor where the entire pentiptycene group acted as the rotor (in contrast to previous pentiptycene-based rotors where the pentiptycene acted as the stator).

Figure 1 Structure and approximate dimensions⁵⁶ of **1**²⁻, and diagram showing $R_2^2(8)$ hydrogen bonding geometry often observed in hydrogen bonded amidinium/carboxylate frameworks.

Results and discussion

Synthesis

Synthesis of pentiptycene dicarboxylate

We have optimized the synthesis of the previously-reported dicarboxylic acid **1^{2H}**,⁴⁴ resulting in its synthesis in 44% overall yield from anthracene. An optimized route to gram quantities of this material is provided in the Supporting Information. Addition of *n*-tetrabutylammonium (TBA) hydroxide to the diacid **1^{2H}** gave **TBA₂·1**, which shows good solubility in water and in a range of organic solvents. We also prepared a new extended pentiptycene diacid **S1^{2H}** containing two extra phenyl rings but were unable to isolate any crystalline hydrogen bonded materials from this material, in part due to its low solubility (see Supporting Information).

Synthesis of amidinium tectons

In this work we study the crystallization of **1²⁻** with the linear bisamidinium tecton **2²⁺**, a trigonal planar trisamidinium **3³⁺**, and two tetrahedral tetraamidinium tectons, **4⁴⁺** and **5⁴⁺** (Scheme 1). All amidinium tectons were prepared as their chloride salts: **2·2Cl**,⁵⁷ **4·4Cl**²⁹ and **5·4Cl**³⁰ were prepared following literature procedures, **3·3Cl** was prepared from the trisnitrile **6**⁵⁸ in 89% yield using LiHMDS followed by work-up with ethanolic HCl.

Preparation of frameworks

Frameworks were prepared as single crystals by simply layering solutions of each tecton in water/alcohol mixtures. Frameworks were characterized by single crystal X-ray diffraction (SCXRD) and powder X-ray diffraction (PXRD) studies, as well as NMR and IR spectroscopy, thermogravimetric analysis (TGA) and elemental analysis (see Experimental and Supporting Information).

SCXRD studies

2·1: We first investigated the ability of the pentiptycene dicarboxylate **1²⁻** to form hydrogen bonded networks with the linear bisamidinium **2²⁺**. Layering solutions of **TBA₂·1** with **2·2Cl** gave colourless crystals which SCXRD revealed to be a 1D hydrogen bonded chain, **2·1** (Figure 2). The asymmetric unit contains half a molecule of each tecton and one water molecule as well as a small region of electron density, which appeared to correspond to a disordered solvent molecule. This could not be modelled sensibly and so PLATON-SQUEEZE⁵⁹ was used to include the electron density in the model.

The amidinium and carboxylate groups are involved in $R_2^2(8)$ hydrogen bonding, although there is some distortion from a completely linear H-bond. The water molecule hydrogen bonds to amidinium and carboxylate groups of the 1D H-bonded chain and the pentiptycene motifs interdigitate, presumably to maximize close-packing.

Scheme 1 Structure of amidinium tectons and synthesis of new trisamidinium, **3·3Cl**.

Figure 2 Solid state structure of **2·1**. Water molecules and most hydrogen atoms omitted for clarity, PLATON-SQUEEZE was used.⁵⁹

3₂·1₃: Having demonstrated that **1²⁻** could be used to form 1D H-bonded chains, we next attempted to increase the dimensionality of the network by employing the trigonal amidinium tecton **3³⁺**. The resulting crystals of **3₂·1₃** rapidly lost crystallinity upon removal from solvent, and despite growing very large crystals and employing synchrotron radiation, high quality data could not be obtained. However, sufficient data were obtained to determine the connectivity of the structure (Figure 3).

All of the amidinium and carboxylate groups are involved in $R_2^2(8)$ hydrogen bonding, giving a hexagonal (6,3) sheet structure. The 2D sheets are seven-fold 2D→2D parallel interpenetrated and the interpenetrated 2D sheets are stacked, producing significant void volume between the sheets, accounting for 59% of the unit cell volume (electron density within the voids could not be modelled and so was processed with PLATON-SQUEEZE⁵⁹). It appears that the pentiptycene motif prevents the interpenetrating 2D sheets from stacking close together, and leads to solvent-filled channels in the framework (Figure S29).

4·1₂: We next attempted to prepare 3D frameworks from the tetrahedral amidinium tectons, **4⁴⁺** and **5⁴⁺**. Crystals of **4·1₂** were analysed by SCXRD, revealing that the network crystallized with one tetraamidinium and two dicarboxylate molecules in the asymmetric unit.

Of the four crystallographically-distinct carboxylate and amidinium groups present, three of each are involved in end-to-end $R_2^2(8)$ hydrogen bonding. Two of these interactions link the structure into 1D H-bonded chains (Figure 4). The third $R_2^2(8)$ interaction is between an amidinium group and one end of a dicarboxylate anion; the other end of this anion does not H-bond to an amidinium group. This leaves one amidinium and one carboxylate group “free;” these groups presumably H-bond to solvent molecules, although these could not be located crystallographically, and were accounted for using PLATON-SQUEEZE.⁵⁹ These 1D chains interweave through lateral amidinium⋯carboxylate H-bonds to give a 3D lattice (Figure S30). Despite the low dimensionality of the network the material contains solvent-accessible 1D channels that account for 44% of the unit cell volume.

Figure 3 Views of the solid state structure of **3₂·1₃**: a) a single hexagon, b) two of the seven interpenetrating 2D honeycomb networks. Most hydrogen atoms omitted for clarity, PLATON-SQUEEZE used.⁵⁹

Figure 4 Diagram showing the 1D H-bonded chains in the solid state structure of **4·12**. a) View showing hydrogen bonding arrangement: circled sites indicate that no amidinium...carboxylate hydrogen bonds are present limiting the dimensionality of the network; arrows indicate the direction of the 1D hydrogen bonded chain. b) View of the 1D H-bonded chain (indicated with a dotted blue line). Disorder and most hydrogens omitted for clarity, PLATON-SQUEEZE used.⁵⁹

5·12: The pentiptycene dicarboxylate was also crystallised with the larger tetraamidinium tecton, **5⁴⁺**, forming framework **5·12**. The asymmetric unit contains one half of a tecton of **1²⁻** and one quarter of a tecton of **5⁴⁺**, which participate in $R_2^2(8)$ hydrogen bonding arrangement giving a 3D diamondoid network (Figure 5). Due to the long tectons employed in **5·12** the structure is 32-fold interpenetrated (Figure S33). Despite the interpenetration, the framework still contains solvent channels, accounting for 37% of the unit cell volume.

Discussion of SCXRD structures

In this work, we have prepared 1D, 2D and 3D hydrogen-bonded networks from **1²⁻**. Interestingly, the only structure that does not form the desired self-assembled framework is the 3D material **4·12**. This is in contrast to previous results where a porphyrin-containing tetracarboxylate did not form 2D networks but did form 3D networks, which was attributed to the lower solubility of the 3D material driving crystallization.³¹ In the current case, it is not clear why **4·12** does not form a network but is presumably related to the product having a lower solubility and/or forming more readily than the desired diamondoid network.

The structure of **5·12** contains 32 interpenetrating nets, and yet remarkably still contains significant channels (37% of the unit cell volume is void space, accounted for using PLATON-SQUEEZE⁵⁹). To the best of our knowledge, this is the equal-most interpenetrated H-bonded network reported to date. The other 32-fold interpenetrated H-bonded network also contains **5⁴⁺** as the cation, with these cations linked by 4,4'-biphenyldicarboxylate anions.³⁰ Interestingly, the anion in **5·12** is significantly longer than biphenyldicarboxylate yet it leads to the same degree of

interpenetration, possibly due to the steric demands of the pentiptycene group.

Generally the structures all contain significant amounts of void space, which we attribute to the difficulty in pentiptycene molecules packing efficiently. The 1D hydrogen bonded chain, **2·1**, contains the least solvent, and it appears that pentiptycene units can pack relatively efficiently when they are all facing in the same direction (as they do in this structure). However, when non-linear tectons such as **3³⁺**, **4⁴⁺** or **5⁴⁺** use amidinium...carboxylate interactions to force the pentiptycenes out of alignment, poor packing efficiency results.

Evacuation of frameworks

In order to see whether the networks exhibited molecular rotor properties, we attempted to prepare evacuated samples of **4·12** and **5·12** to allow a solid state NMR (SS-NMR) study of any molecular rotation. We first activated the frameworks by solvent exchange with ethanol and then used super-critical CO₂ drying to remove any solvent. Using this procedure we saw that the frameworks retained some degree of crystallinity upon activation and drying (see Figures S13 and S14). However, given there was a substantial loss of crystallinity, it was felt that SS-NMR experiments of dynamics would not give useful data owing to a variety of environments in the crystalline and amorphous components. Gas adsorption measurements indicated that both **4·12** and **5·12** were non-porous, which we attribute to the collapse of the framework.

Figure 5 Views of the solid state structure of **5·12**: a) view of the hydrogen bonding arrangement; b) view of packing. Most hydrogen atoms omitted for clarity, PLATON-SQUEEZE used.⁵⁹

Conclusions

In order to test the limits of amidinium···carboxylate supramolecular framework formation, we incorporated the large pentiptycene dicarboxylate **1**²⁻ into hydrogen bonded networks. Despite the large and bulky nature of this anion, we were able to prepare 1D, 2D and 3D frameworks. Products included an interpenetrated honeycomb network and a 32-fold interpenetrated 3D diamondoid network, which we believe is tied for the highest degree of interpenetration observed in a hydrogen-bonded material. Generally, even low dimensional materials we prepared were found to contain significant solvent-filled voids, which appears to result from pentiptycene's poor packing efficiency. While the 3D networks were partially stable to evacuation, they did not show any nitrogen absorption. Work directed at preparing more robust materials supramolecular materials is underway.

Experimental

Synthesis

General remarks: The pentiptycene diacid **1**^{2H} was prepared from diethynylpentiptycene^{39,60} by modification of the previously-reported procedure;⁴⁴ an optimized route to this compound is provided in the Supporting Information. The amidinium tectons **2·2Cl**,⁵⁷ **4·4Cl**²⁹ and **5·4Cl**,³⁰ and the trisnitrile **6**⁵⁸ were prepared as previously described. Yields of frameworks (mmol and %) were calculated accounting for the % solvent indicated by TGA. In all cases where NMR spectroscopy was conducted in d₆-DMSO containing DCl_(aq), the integration of the amidinium N–H proton resonances was lower than expected due to H/D exchange – the idealized integration values are provided in the listing of NMR data.

Details of instrumentation and characterization are provided in the Supporting Information.

TBA₂·1: **1**^{2H} (0.431 g, 0.600 mmol) was suspended in ethanol (10 mL), and TBA·OH in methanol (1.0 M, 1.2 mL, 1.2 mmol) was added, causing the solid to dissolve. The solvent was removed under vacuum to give the product as an off-white powder. Yield: 0.720 g (0.60 mmol, 100%).

¹H NMR (d₆-DMSO): 8.01 (d, *J* = 7.8 Hz, 4H), 7.88 (d, *J* = 7.8 Hz, 4H), 7.52 (d, *J* = 8.6 Hz, 8H), 6.98 (d, *J* = 8.6 Hz, 8H), 6.00 (s, 4H), 3.04–3.21 (m, 16H), 1.50–1.65 (m, 16H), 1.25–1.38 (m, 16H), 0.93 (t, *J* = 7.3 Hz, 24H) ppm. ¹³C NMR (d₆-DMSO): 167.6, 144.9, 144.3, 143.7, 131.4, 129.7, 125.8, 124.4, 121.8, 114.5, 98.9, 84.1, 58.0, 51.8, 23.5, 19.7, 14.0 ppm. ESI-MS (neg): 358.2., calc. for [C₅₂H₂₈O₄]²⁻ = 358.1 Da. ESI-MS (pos): 242.3, calc. for [C₁₆H₃₆N]⁺ = 242.3 Da. ATR-IR (*inter alia*): 1602, 1545 cm⁻¹ (C=O stretches). M. Pt.: > 260 °C.

3·3Cl: A solution of **6** (0.191 g, 0.500 mmol) in THF (2 mL) was cooled to 0 °C under a nitrogen atmosphere, and a solution of LiHMDS in THF (1.0 M 3.0 mL, 3.0 mmol) was added dropwise. The solution was allowed to warm to room temperature and stirred overnight. The solution was cooled to 0 °C and ethanolic HCl (prepared by the cautious addition of 0.5 mL of acetyl chloride to 4.5 mL of ethanol at 0 °C) was added dropwise, causing the formation of a pale precipitate. The precipitate was isolated by filtration and washed with ethanol (2 × 5 mL) and THF (2 × 3 mL). It was suspended in ethanol (20 mL), sonicated for 1 hour and the resulting pale solid isolated by filtration, washed with ethanol (2 × 3 mL) and THF (2 × 3 mL). Drying *in vacuo* gave **3·3Cl** as a white powder. Yield: 0.241 g (0.444 mmol, 89%).

¹H NMR (d₆-DMSO): 9.57 (br. s., 6H), 9.34 (br. s., 6H), 8.24 (d, *J* = 8.2 Hz, 6H), 8.19 (s, 3H), 8.05 (d, *J* = 8.2 Hz, 6H) ppm. ¹³C NMR (d₆-DMSO): 165.1, 144.6, 140.2, 128.7, 127.8, 127.2, 126.1 ppm. HRESI-MS: 433.2126, calc. for [C₂₇H₂₅N₆]⁺ (i.e. loss of 2H⁺ and 3Cl⁻): 433.2135 Da. ATR-IR (*inter alia*): 1694, 1670, 1541 cm⁻¹ (C=N, C=O stretches). M. Pt.: > 260 °C.

2·1: The bisamidinium **2·2Cl** (3.5 mg, 15 μmol) was dissolved in water (5 mL) and the clear solution frozen. The frozen solution was carefully layered with ethanol (2 mL) and then a solution of the **TBA₂·1** (18 mg, 15 μmol) in ethanol (3 mL). This was allowed to stand at room temperature over the weekend resulting in the formation of a white crystalline solid. This was isolated by filtration, washed with ethanol (3 × 1 mL) and dried thoroughly. Yield: 7.5 mg (8.5 μmol, 57%).

¹H NMR [d₆-DMSO containing a drop of conc. DCl_(aq)]: 9.75 (br. s, 4H), 9.44 (br. s, 4H), 8.10–8.15 (m, 8H), 8.03 (s, 4H), 7.47–7.51 (m, 8H), 6.94–6.97 (m, 8H), 5.99 (s, 4H) ppm. IR (ATR) (*inter alia*): 1689, 1597, 1532 cm⁻¹ (C=N, C=O stretches). EA: C 78.4, H 4.7, N 5.9; calc. for **2·1**·2H₂O (C₆₀H₄₄N₄O₆): C 78.6, H 4.8, N 6.1%.

3₂·1₃: The trisamidinium **3·3Cl** (3.0 mg, 5.0 μmol) was dissolved in water (3 mL) and carefully layered with a buffer layer of ethanol (10 mL) then methanol (2 mL), followed by a solution of **TBA₂·1** (10 mg, 8.3 μmol) in methanol (1 mL). The solution was left to stand for 7 days, during which time long colourless needle crystals were formed. These crystals were recovered by filtration and air-dried to give **3₂·1₃**. Yield 4.4 mg (1.3 μmol, 52%).

¹H NMR [d₆-DMSO containing 1 drop DCl_(aq)]: 9.63 (br. s., 12H), 9.35 (br. s., 12H), 8.20 (d, *J* = 8.2 Hz, 12H), 8.08–8.17 (m, 30H), 8.03 (d, *J* = 8.2 Hz, 12H), 7.48–7.52 (m, 24H), 6.94–6.99 (m, 24H), 6.00 (s, 12H) ppm. ATR-IR (*inter alia*): 1673, 1580, 1533 cm⁻¹ (C=N, C=O stretches). EA: C 76.1, H 4.6, N 5.1; calc. for **3₂·1₃**·16H₂O (C₂₁₀H₁₇₀N₁₂O₂₈): C 76.2, H 5.2, N 5.1%.

4·1₂: The tetraamidinium **4·4Cl** (10 mg, 6.2 μmol) was dissolved in water (1 mL) and carefully layered with a buffer layer of methanol (9 mL) then ethanol (1 mL), followed by a solution of **TBA₂·1** (10 mg, 12 μmol) in a 1:1 mixture of *i*-propanol/ethanol (1 mL). The solution was left to stand for 12 days, during which time long colourless needle crystals were formed. These crystals were recovered by filtration and air-dried to give **4·1₂**. Yield 7.0 mg (3.1 μmol, 50%).

¹H NMR [d₆-DMSO containing 1 drop DCl_(aq)]: 9.59 (s. br., 8H), 9.32 (s. br., 8H), 8.11–8.17 (m, 16H), 7.92 (d, *J* = 8.3 Hz, 8H), 7.47–7.55 (m, 24 H), 6.95–6.99 (m, 16H), 6.03 (s, 8H) ppm. ATR-IR (*inter alia*): 1666, 1601, 1582 cm⁻¹ (C=N, C=O stretches). EA: C 73.9, H 4.1, N 4.6; calc. for **4·1₂**·13H₂O (C₁₃₃H₁₁₄N₈O₂₁): C 73.9, H 5.3, N 5.2%.

5·1₂: The tetraamidinium **5·4Cl** (7.5 mg, 16 μmol) was dissolved in water (2 mL) and carefully layered with a buffer

layer of methanol (5 mL) then *i*-propanol (2 mL), followed by a solution of **TBA₂·1** (10 mg, 8.0 μmol) in *i*-propanol (2 mL). The solution was left to stand for 7 days, during which time colourless needle crystals were formed. These crystals were recovered by filtration and air-dried to give **5·1₂**. Yield 4.7 mg (1.9 μmol, 11 %).

¹H NMR [d₆-DMSO containing 1 drop DCl_(aq)]: 9.48 (br. s., 8H), 9.22 (br. s., 8H), 8.13–8.19 (m, 16H), 7.96 (s, 16H), 7.84 (d, *J* = 8.7 Hz, 8H), 7.47–7.56 (m, 24H), 6.98–7.02 (m, 16H), 6.03(s, 8H) ppm. ATR-IR (*inter alia*): 1673, 1602, 1579, 1537 cm⁻¹ (C=N, C=O stretches). EA: C 75.9, H 4.4, N 4.3; calc. for **5·1₂**·14H₂O (C₁₅₇H₁₃₂N₈O₂₂): C 76.0, H 5.4, N 4.5%.

We repeated the synthesis of **5·1₂** several times but were never able to obtain large quantities of crystalline material. Mixing the solutions of **5·4Cl** and **TBA₂·1** more rapidly gave larger yields of product, but this was non-crystalline.

X-ray crystallography

Crystals of **3₂·1₃**, **4·1₂** and **5·1₂** were either very small or lost solvent rapidly. The crystallography for these structures was difficult and required the use of synchrotron radiation. Data for these compounds are of relatively low quality, but the overall connectivity can be determined unambiguously. A brief description of the crystallography is given below, with further details provided in the Supporting Information.

Data for **2·1** were collected mirror-monochromated Cu Kα radiation on an Agilent SuperNova diffractometer. Crystals were cooled to 150 K using a Cryostream N2 open-flow cooling device. Raw data (including data reduction, interframe scaling, unit cell refinement and corrections) were processed using CrysAlisPro.⁶¹ Data for **3₂·1₃**, **4·1₂** and **5·1₂** were collected on the MX1 beamline at the Australian Synchrotron.⁶² Crystals were cooled to 100 K using a Cryostream N2 open-flow cooling device. Data indexing and integration was conducted using the XDS package.⁶³

The structures of **2·1** and **5·1₂** were solved with SUPERFLIP⁶⁴ and refined using full-matrix least-squares on *F*² within the CRYSTALS suite.⁶⁵ The structures of **3₂·1₃** and **4·1₂** were solved by direct methods using SHELXS and refined using least-squares methods with SHELXL within OLEX2.⁶⁶

Associated content

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.xxxxxxx.

Characterization details, NMR spectra of new compounds, optimized synthetic procedure for **1^{2H}**, synthesis of extended pentyptylene diacid **S1^{2H}**, crystallographic details and additional crystallographic figures.

Accession Codes

CCDC 1917068–1917071 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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