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Formation of pyrene nano-rods within a supramolecular framework

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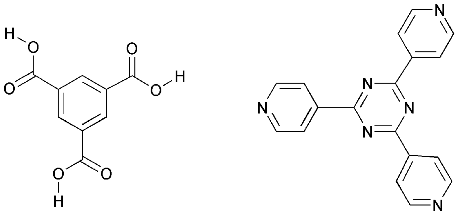
The combination of trimesic acid and the tri-dentate linker 1,3,5-tri(4-pyridyl)-2,4,6-triazine leads to the assembly of a bilayer structure, which contains four pyrene molecules per cavity; adjacent tetrameric aggregates within the channels formed by the superimposed layers combine to yield pyrene nano-rods.

Among the variety of framework-forming building blocks employed in the synthesis of organic supramolecular solids three-armed trimesic acid (TMA)[1] and 1,3,5-tri(4-pyridyl)-2,4,6-triazine (tpt, Scheme 1)[2] are of special interest, as their rigidity and triangular geometry can lead to formation of frameworks enclosing large cavities.

TMA forms a 'chicken-wire' pattern with an approximately 14 Å diameter hole, but has a high tendency for self-inclusion, leading to 4-fold interpenetrating networks, thus filling the cavities and preventing clathrate formation.[3] In 1987 Herbstein and coworkers reported the first non-catenated trimesic acid structures with channels containing disordered alkane molecules.[4] An effective strategy for suppressing interpenetration is to co-crystallize TMA with suitable organic guests in the presence of alcohol or organic amines which are capable of extending the framework.[5] Using this strategy the pyrene inclusion complexes 2TMA·2ethanol·pyrene[6] and 2TMA·2methanol·1.5pyrene[7] were prepared, but an attempt to obtain a stacked pyrene structure led to alternating stacks of TMA and pyrene molecules.[6]

Replacement of the alcohol or amine bridges in the TMA layers with exo-dentate spacers such as 4,4′-bipyridine very much extends the cavity size to give internal dimensions of 35 Å × 26 Å compared to only 14 Å × 14 Å in the pure TMA framework,[8] but the large void is eliminated by the formation of three-fold interpenetrating networks. Similarly, use of the longer spacers bpe and bpmh (bpe = bis(4-pyridyl)ethylene and bpmh = bis(4-pyridylmethylidyne)hydrazine) to prepare pyrene inclusion complexes failed, only compact 3D hydrogen-bonded and five-fold interpenetrating networks respectively were obtained in the two cases.[9] As the mutual interaction between the guest and host conformations is well demonstrated by the finding that the flat coronene molecule favors the planar TMA sheet, while the non-planar hexahelicene promotes formation of puckered TMA sheets,[10] we hypothesized that failure to prepare the TMA inclusion complexes was associated with the puckering of the layer as a result of the flexibility of hydrogen bonds and the ability of the carboxylate group to rotate around the C–C bond. As the three-armed tpt linker molecule symmetry-matches TMA and is strictly planar, it should be possible to combine the two into a honeycomb framework capable of accommodating planar pyrene guests. This is indeed the case. In the supramolecular complex [TMA·tpt]·2pyrene **1** described here pyrene is included in a novel infinite rod-like structure.†



Scheme 1

Low temperature X-ray diffraction analysis shows that crystals of **1** have a layer structure with one TMA, one tpt and two pyrene molecules in the asymmetric unit.‡ Each TMA molecule connects three tpt spacers through O–H···N hydrogen bonds. One of the three carboxylates is disordered over two positions, with a matching disorder occurring in the facing pyridine group, leading to four distinct hydrogen bonds [O1···N1′a = 2.636(9) Å, O1–H1···N1′a = 168(5)°; O2···N1a = 2.610(6) Å, O2–H2···N1a = 163(6)°; O4···N2 = 2.638(3) Å, O4–H4···N2 = 175(4)°; O5···N3b = 2.559(3) Å, O5–H5···N3b = 163(4)°; a $x+\frac{1}{2}, y+\frac{1}{2}, z$; b $x, y+1, z$]. The arrangement gives rise to the anticipated (6,3) honeycomb architecture with large voids (Fig. 1). The sheet is further stabilized by secondary C–H···O interactions between pyridine rings and free carboxylate oxygen atoms. Though three-armed TMA and tpt ligands have been widely explored,[1,2] this is the first example of a supramolecular framework combining both building blocks.

Two adjacent honeycomb layers are eclipsed such that π–π interactions exist between TMA and tpt molecules belonging to different layers (Fig. 2a). There are two different types of interlayer spaces labeled as A and B in Fig. 2b, which alternate along the normal to the layer plane. In each layer one pyrene molecule is coplanar with the mean plane of the layer and anchored to the host by C–H···O interactions, while a second pyrene is inclined and spans the space A (Figs. 2b, 3). The space B is narrower and contains pyrene C–H groups protruding out of the layers. The arrangement is reminiscent of that in the analogue 2TMA·2methanol·1.5pyrene, in which two types of spaces are taken up by pyrene and methyl groups. The cavity size in **1** is larger as reflected by the increased guest inclusion, compared with 2TMA·2ethanol·pyrene and 2TMA·2methanol·1.5pyrene.

Two in-layer pyrenes across the A type space form strong face-to-face π–π interactions (interplanar distance 3.45 Å), while the inclined pyrenes make an angle of 58.4° with in-layer

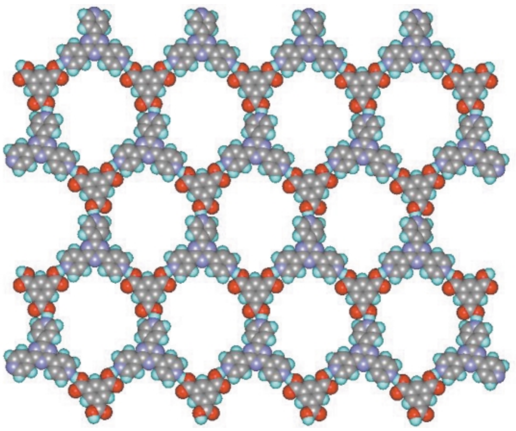


Fig. 1 Honeycomb framework formed by TMA and tpt in **1**.

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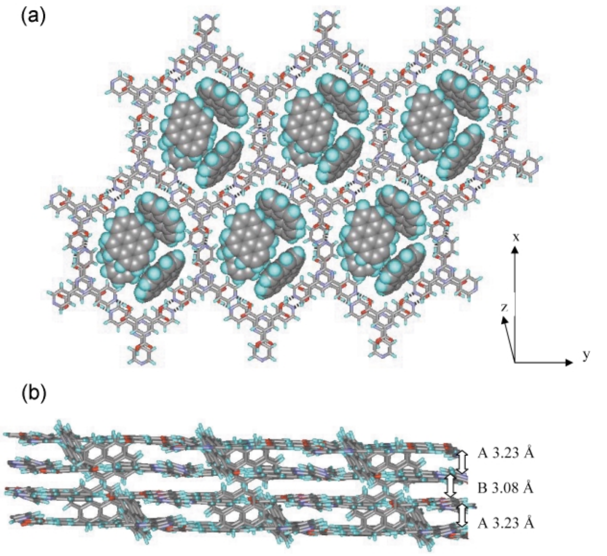

Fig. 2 a) Top view of bilayer structure of **1**, which encapsulates four pyrene molecules per cavity. b) Side view of layer structure of **1**, showing two types of inter-layer spaces.

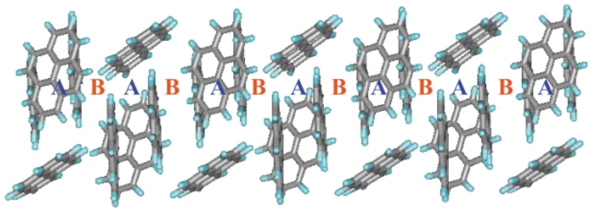

Fig. 3 One-dimensional pyrene aggregate within the channel in **1**.

pyrene molecules and form edge-to-face interactions. The whole structure can be viewed as a bilayer motif, in which a tetrameric pyrene aggregate with a two-fold crystallographic symmetry is accommodated. The neighboring bilayers pack along the *c* axis such as to create continuous channels with a volume corresponding to 50.4% of the crystal space, in which the pyrene guest molecules are located, rather than cavities as observed in other TMA–polycyclic aromatic hydrocarbon host–guest complexes.[6,7,10] The tetrameric pyrene clusters from adjacent bilayers are related by an inversion center such that the inclined pyrenes interact with the in-layer pyrene molecules from an adjacent cluster through edge-to-face C–H$\cdots\pi$ contacts (Fig. 3). This leads to one-dimensional infinite approximately cylindrical pyrene aggregates with a diameter of about 16 Å (1.6 nm), which are well separated by the host matrix.

Pyrene has received considerable attention as a spectroscopic probe of the cavity environment in the supramolecular matrix. Its packing is of special interest because of its relevance to the photochemical properties of pyrene. Pyrene has been successfully included within a number of other supramolecular hosts such as cyclodextrin,[11] GS sheets (G = guanidinium; S = sulfonate moieties),[12] calix[4]resorcinarene–pyridine,[13] and inorganic–organic hybrid frameworks,[14,15] in which pyrene occurs in a variety of forms including the monomer, dimer, trimer and 2D-net structure. The nano-diameter pyrene rods found in **1** have not been observed in any of these matrices and constitute one-dimensionally periodic aggregates within a framework of stacked two-dimensional layers. While nano-sized tube- and rod-like supramolecular structures have been discovered,[16] in the structure described here the rods are formed by the guest molecules rather than by the main structural components.

The great variety of aggregation of pyrene observed in supramolecular crystals[13] is a nano-scale equivalent of crystal polymorphism which merits further attention in the study of molecular packing modes.

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Notes and references

† Good quality crystals of **1** were prepared under hydrothermal conditions. TMA (0.1 mmol), tpt (0.1 mmol), pyrene (0.2 mmol) and 4 ml of water were sealed in a 6 ml Pyrex glass tube. The tube was allowed to remain at 140 °C for 24 hours, followed by cooling to room temperature within 4 days. Yellow prismatic crystals were collected (crystal yield: *ca.* 30%).

‡ The data were collected on a Bruker SMART1000 CCD with Mo$K\alpha$ radiation (λ = 0.71073 Å) at 90(1) K. Reflections were reduced by the SAINT program. The structures were solved by direct methods and refined by a full matrix least squares technique based on F^2 using the SHELXL 97 program. Crystal data: Compound **1**: $C_{59}H_{38}N_6O_6$: Mr = 926.95, monoclinic, space group $C2/c$, a = 36.822(3), b = 18.794(2), c = 12.904(1) Å, β = 90.533(4)°, U = 8929.8(12) Å^3, Z = 8, D_c = 1.379 Mg m^{-3}, crystal size 0.28 × 0.14 × 0.10 mm^3, μ (Mo$K\alpha$) = 0.091 mm^{-1}, F(000) = 3856, GoF = 0.922. Among 53391 reflections, 12922 reflections are unique (R_{int} = 0.1280). The final $R1$ and $wR2$ are 0.0765 and 0.1659, respectively, for 852 parameters and 5061 reflections [$I > 2(\sigma I)$]. CCDC 213794. See http://www.rsc.org/suppdata/cc/b3/b306965f/ for crystallographic data in .cif or other electronic format.

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