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) and 1,3,5-tri(4-pyridyl)-2,4,6-triazine (tpt, Scheme 1) 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. In 1987 Herbstein and coworkers reported the first non-catenated trimesic acid analogue 2TMA·2methanol·2pyrene while the non-planar hexahelicene promotes puckered TMA sheets, TMA sheet, while the non-planar hexahelicene promotes puckered TMA sheets,10 we hypothesized that the flat coronene molecule favors the planar 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 I described here pyrene is included in a novel infinite rod-like structure.‡

Low temperature X-ray diffraction analysis shows that crystals of I 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(5)°; O2···N1a = 2.610(6) Å, O2-H2···N1a = 163.6(6)°; O4···N2 = 2.638(3) Å, O4-H4···N2 = 175(4)°; O5···N3b = 2.559(3) Å, O5–H5···N3b = 163(4)°]. 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 I is larger as reflected by the increased guest inclusion, compared with 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
polymorphism which merits further attention in the study of molecular packing modes.

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Notes and references

1. 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%).

2. The data were collected on a Bruker SMART1000 CCD with MoKα 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 F² using the SHELXL 97 program. Crystal data: Compound I: C₃₂H₅₉N₄O₇·Mr = 926.95, monoclinic, space group C2/c, a = 36.822(3), b = 18.7942(2), c = 12.904(1) Å, β = 90.533(4), U = 8929.8(12) Å³, Z = 8, Dₐ = 1.379 Mg m⁻³, crystal size 0.28 × 0.14 × 0.10 mm, μ(MoKα) = 0.091 mm⁻¹, F(000) = 3856, GoF = 0.922. Among 53391 reflections, 12922 reflections are unique (Rint = 0.2180). The final R1 and wR2 are 0.0765 and 0.1659, respectively, for 852 parameters and 5061 reflections (I > 2σ(I)). CCDC 217394. See http://www.ccdc.cam.ac.uk/structures/csd for crystallographic data in cif or other electronic format.


13. B. Q. Ma and P. Coppens, to be published.

