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Assembly of a Porous Supramolecular Polyknot from Rigid Trigonal Prismatic Building Blocks

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Supporting Information Placeholder

ABSTRACT: Herein we report a hydrogen-bonded three-dimensional porous supramolecular polyknot assembled from a rigid trigonal prismatic triptycene building block with six extended peripheral aryl-carboxyl groups. Within this superstructure, three arrays of undulated 2D rhombic subnets, which display an inclined polycatenation, are interconnected to give an unprecedented uninodal six-connected net with a point symbol of $(3.4^4.6^{10})$. Such an entanglement results in a trefoil knot motif, which, as the basic repeating unit, is fused and interlocked with itself three-dimensionally to afford a supramolecular polyknot. This example highlights the ability of supramolecular systems to form topologically complex architectures using geometrically simple building blocks.

Mechanically interlocked emblems, such as Borromean Rings and Solomon Knots, have captivated humankind for millennia, showing their presence as symbols of art, culture and spiritual life.[1] Catenanes,[2] rotaxanes[3] and molecular knots[4] represent interlocked and entangled species at the molecular level. Research[1] on these mechanically interlocked molecules (MIMs) has been gaining momentum in recent decades because of their aesthetic beauty[1a] and practical applications[1b,c,d] in nanotechnology. Mechanical interlocking also exists in extended two-dimensional (2D) and three-dimensional (3D) networks in the form[5] of interpenetration, polycatenation, polythreading, and self-entanglement. These topologically complex networks, which can be considered as the polymeric equivalent of MIMs, are well represented[5b] in metal-organic frameworks (MOFs) and coordination polymers (CPs), which are composed of metal cations and organic linkers. Such structural diversity of MOFs, enabled by versatile modularity of the building components, makes them attractive candidates[6] for applications in catalysis, electronics, and gas storage and separation.

Self-assembly of discrete organic molecules relying upon noncovalent bonding interactions (hydrogen, halogen, *etc.*) has led to the construction of supramolecular architectures with, not only exotic topologies, but also exceptional material properties.[7] Nevertheless, pure organic 2D and 3D supramolecular frameworks,[8] compared to MOFs, still lack the diversity and complexity in terms of network topology,[9] a deficiency which hinders the understanding of the underlying assembly principles. Thus, uncovering new network topologies, which can be accessed using simple supramolecular synthons, is of great importance since they broaden the scope of supramolecular chemistry and stimulate the rational design of functional supramolecular materials. Herein, we report the assembly of a hydrogen-bonded supramolecular polyknot (**PETHOF-3**) using a simple trigonal prismatic building block **H$_6$PET-1**. This polyknot[10] displays a complicated 3D architecture with periodically fused and interlocked knot moieties, as well as an unprecedented uninodal self-entangled six-connected topology with a point symbol of $(3.4^4.6^{10})$.

Installation of six 4-(4-phenylethynyl)phenylene carboxyl groups on the periphery of the triptycene backbone creates (Figure 1a and Scheme S2) a rigid trigonal prismatic building block **H$_6$PET-1** for the assembly of 3D networks. Slow evaporation of a THF and PhMe solution of **H$_6$PET-1** afforded faint yellow crystalline blocks (**PETHOF-3**) suitable for single-crystal X-ray crystallographic investigation, which revealed a hexagonal lattice with space group *P*-62*c*. **PETHOF-3** exhibits a complex entangled network topology, which, according to ToposPro,[11] is identified with an unprecedented uninodal six-connected net with a point symbol of $(3.4^4.6^{10})$. In the crystal superstructure, each molecule engages four of its six aryl-carboxyl arms in building (Figure 1b,e) a 4^4-net which shows[12] a puckered 2D geometry with large distorted rhombic windows (dimensions of 33 × 39 Å). The remaining two aryl-carboxyl arms, which participate in a hydrogen-bonded triangle motif (Figure 1c), are oriented perpendicular to the 2D layers (Figure 1f).

Overall, there are three independent arrays of the 2D layers stacked in an alternating AB manner along the [210], [120] and [1–10] directions, leading (Figure 1g) to a 2D → 3D inclined polycatenation in which the 2D sheets are interlocked (Figure S9) through the Hopf-links of the rhombic circuits. The polycatenated 2D layers are further interconnected (Figure 1d and Figure S10) into a singular network through the hydrogen bonding of the appended aryl-carboxyl arms. Therefore, **PETHOF-3**, which is topologically categorized as a self-entangled network, represents a rare example of a supramolecular assembly held together solely by hydrogen bonding. It is noteworthy to point out that **PETHOF-3** is constructed from a single molecular component that is rigid and highly symmetrical, properties which distinguish it from self-entangled MOFs that are built[13] of either asymmetric metal nodes or flexible organic bridges. Moreover, it is well documented[14] that trigonal prismatic building blocks tend to form extended structures based on the edge-transitive six-connected **acs** net. We reported[15] previously that an analogous triptycene building block, with peripheral *p*-phenylene carboxyl groups, assembles into **PETHOF-1** and **PETHOF-2** with, respectively, **acs-2c** and **acs-5c** topologies. Here, **PETHOF-3**, a rare exception, broadens the scope of the complex supramolecular architectures that can be accessed using simple molecular building blocks.

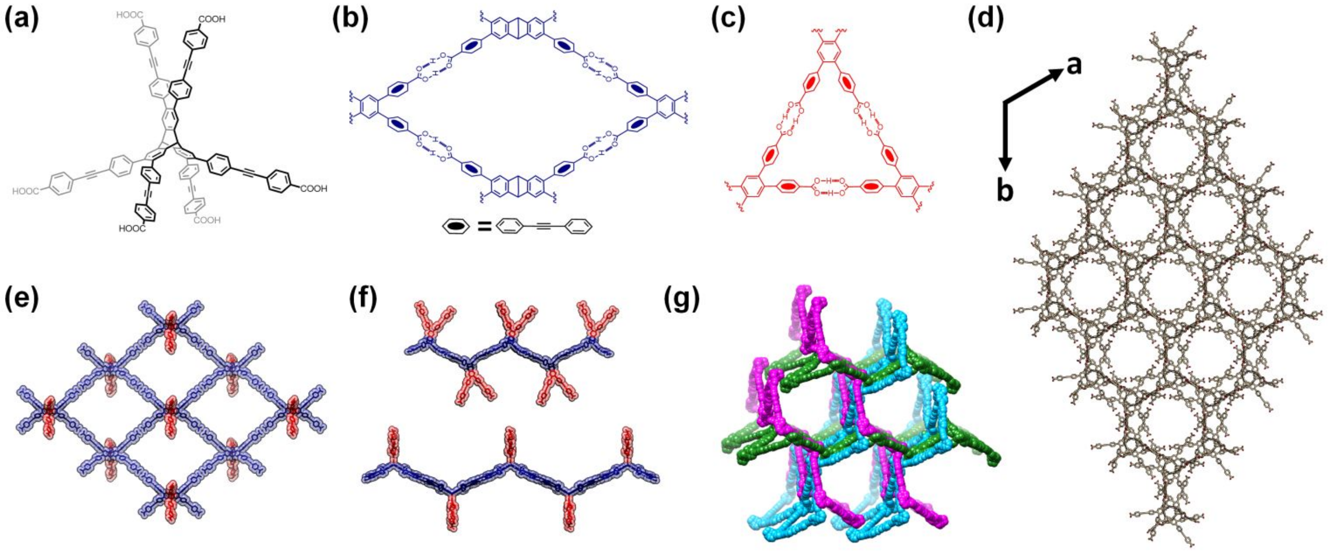

Figure 1. (a) The trigonal prismatic building block **H_6PET-1**. (b) The hydrogen-bonded rhombic circuit motif (depicted in blue). (c) The hydrogen-bonded triangle motif (depicted in red). (d) The extended superstructure of **PETHOF-3** viewed along the *c* axis. (e-f) Views of the rhombic 2D subnet (depicted in blue) with appended carboxyl groups (depicted in red) in different directions. (g) The 2D → 3D inclined polycatenation of three independent arrays of the 2D subnets (depicted in green, magenta and cyan). The appended carboxyl groups are omitted for the sake of clarity.

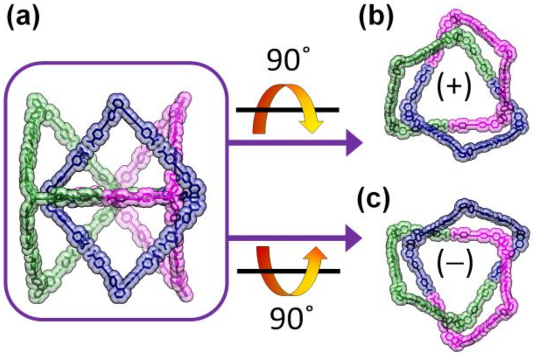

Figure 2. The supramolecular knot (a) in **PETHOF-3** is composed of two enantiomeric trefoil knots with positive (+) (b) and negative (–) (c) crossings. The three rhombic circuits in the supramolecular knot are colored blue, green and magenta. Irrelevant molecular components are omitted for the sake of clarity.

Upon close examination, we identify (Figure 2a) a supramolecular knot, which, as the basic repeating unit, is fused and interlocked periodically with one another three-dimensionally to form the whole network. In this regard, **PETHOF-3** can best be described as a supramolecular polyknot. The knot moiety consists of three rhombic circuits that are connected cyclically at the opposing vertices with the linking bridges threading through each rhombic cavity, creating (Figure 2b,c) a pair of fused trefoil knots with opposite chirality. In this supramolecular knot, 12 molecules of **H_6PET-1** participate as the corners, along with 15 of their hydrogen-bonded carboxyl dimers as the edges. Each **H_6PET-1** molecule is involved in the formation of four supramolecular knots. Along the *c* axis, the supramolecular knots are aligned linearly by sharing three vertices with each neighbor to form (Figure 3a) a 1D columnar superstructure. Two of these 1D columns are entangled in such a way that each supramolecular knot is triply interlocked through the rhombic windows (Figure 3b) with two knots in a different column, which gives (Figure 3d) rise to a 1D channel with a diameter of about 10 Å running parallel to the *c* axis. In the *ab* plane, the supramolecular knots are arranged (Figure 3c) into a 2D triangular tessellation where each knot is interlocked with six neighboring knots with which it shares vertices.

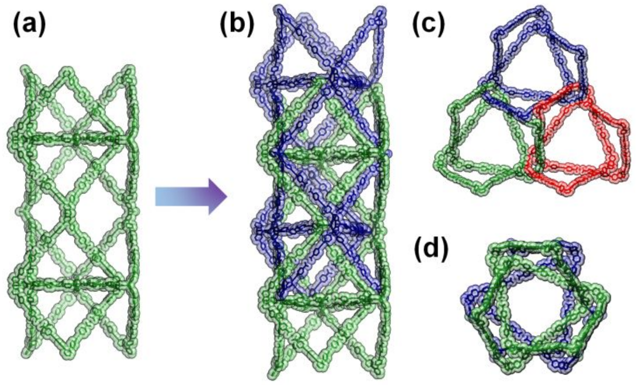

Figure 3. The representations of (a) the 1D supramolecular column (depicted in green) showing two knots with shared vertices, (b) the entangled superstructure containing two 1D columns (depicted in green and blue), (c) the 2D triangular tessellation pattern showing the entanglement of one knot with two of its six neighbors in the *ab* plane (three knots are colored green, red and blue), and (d) the 1D channel viewed along the *c* axis. Irrelevant molecular components are omitted for the sake of clarity.

The supramolecular polyknot is sustained by a combination of intermolecular CH•••π and CH•••O interactions, in addition to the hydrogen bonding of the carboxyl dimers (mean $d_{\mathrm{O\cdots O}}$ = 2.63 Å). These cooperative noncovalent intermolecular forces (*vide infra*), along with the interactions between **H_6PET-1** and solvent molecules, might well be responsible for dictating the formation of the polyknot, instead of the **acs** net, during crystallization. The CH•••π interactions (mean $d_{\mathrm{H\cdots C}}$ = 2.89 Å) occur exclusively in a tris-molecular cluster that exhibits (Figure S11) C_3 symmetry. Each cluster is connected (Figure 4a,b) with 12 neighboring clusters in a cuboctahedral geometry, where six coplanar neighbors in the *ab* plane are linked with the center cluster through a single aryl-carboxyl dimer, and the remaining six neighbors through two paralleled aryl-carboxyl dimers which are also associated (Figure S12) by means of the CH•••O hydrogen bonds with mean $d_{\mathrm{H\cdots O}}$ = 2.50 Å. If we consider this supramolecular cluster as a 12-connected node, the superstructure (Figure 4c) of the polyknot can be simplified[14a] to a 12-connected **hcp** (hexagonal close packing) net with the transitivity of [1232]. This **hcp** net contains two types of tiles, which correlate with the disordered tetrahedral and octahedral cages (Figure 4d,e) of this superstructure, with effectively accessible diameters of 1.6 and 3.0 nm, respectively, taking into account vdW radii. In this sense, the tris-molecular cluster is reminiscent[16] of the multinuclear metal clusters in MOFs, diversifying the network topologies that can be accessed by trigonal prismatic building blocks.

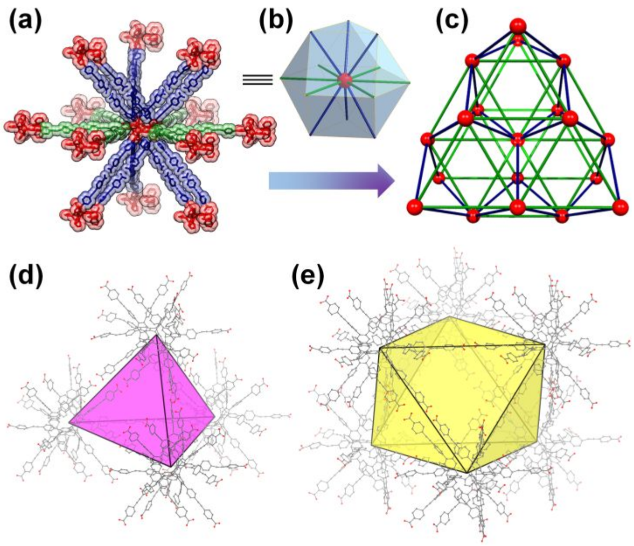

Figure 4. (a-b) The tris-molecular cluster viewed as a 12-connected node in a cuboctahedral geometry. The triptycene cores are shown in red. The connecting bridges composed of a single and two paralleled carboxyl dimers are shown in green and blue, respectively. Irrelevant molecular components are omitted for the sake of clarity. (c) The **hcp** topology (the red spheres, as the vertices, correspond to the tris-triptycene cores; the green and blue sticks, as the edges, correspond to the single and two paralleled carboxyl dimer linkages, respectively). (d-e) Depictions of the tetrahedral (with magenta faces) and the octahedral (with yellow faces) cages with the tris-molecular clusters as the vertices.

PETHOF-3 possesses an extraordinarily large gust-accessible volume[17] of about 85%, which, to the best of our knowledge, is a record for hydrogen-bonded organic frameworks (HOFs). It showcases the ability of the peripherally functionalized triptycenes to assemble into frameworks with large cavities, which are useful for guest encapsulation and low-κ dielectric response.[8g] In fact, density functional theory (DFT) calculations, performed on the optimized single-crystal structure of **PETHOF-3**, predict the static dielectric constant to be as low as 1.29 along the *a* and *b* crystallographic axes. The averaged values are also consistent with the reported[18] trend in the low-κ dielectric response and framework porosity. Thus, **PETHOF-3** represents the lowest predicted value (Table 1) of the static dielectric constant so far reported[15] for framework materials, a status, until now, held by **PETHOF-1**. The voids, however, are filled with highly disordered solvent molecules, which could not be refined by crystallography and hence were omitted from the computational optimization. The experimental dielectric constants would, therefore, be expected to be higher than those predicted on account of the presence of residual solvent molecules. Supercritical CO_2 activation of **PETHOF-3** gave a microporous material with a type-I N_2 isotherm at 77 K (Figure S14a) and an apparent Brunauer-Emmett-Teller (BET) surface area of about 600 m^2/g. The main pore width was estimated (Figure S14b) to be about 1.3 nm, which is slightly smaller than the diameter of the tetrahedral cavities in the crystalline superstructure. We did not observe the mesopores that correspond to the octahedral cavities in the calculated pore distribution, indicating partial collapse of the pore system upon activation. This superstructural change is also evidenced (Figure S13) by the disappearance of the well-resolved peaks in the powder X-ray diffraction patterns (PXRD) of **PETHOF-3** after activation. Overall, these observations suggest that the disordered solvent guests also play a crucial role in supporting the superstructural integrity of **PETHOF-3**.

Table 1. Comparison of the Crystallographic Averaged Electronic and Dielectric Properties of PETHOF-3 with PETHOF-1

Properties	PETHOF-1[15]	PETHOF-3
Polarizability / α (Å^3)	7,334	11,060
Dielectric Tensor / κ	1.33	1.30
Refractive Index / n	1.15	1.14
Electric Susceptibility / χ	0.329	0.304
Guest-Accessible Volume	80%	85%

In summary, **PETHOF-3**, assembled from a rigid trigonal prismatic building block, constitutes a ubiquitous supramolecular polyknot with a complex 3D architecture composed of periodically fused and interlocked supramolecular knots. This polyknot, which also possesses a uninodal self-entangled six-connected framework with a point symbol of $(3.4^4.6^{10})$, represents a new topology, accessible by trigonal prismatic building blocks other than the **acs** net. Most noteworthy of all is that such superstructural complexity is realized using geometrically simple molecular building blocks. We anticipate that this communication will inspire new design strategies for supramolecular materials with tailored architectures for customized applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on ACS Publication website.

Experimental and computational details, including synthesis, NMR, PXRD, gas-sorption studies and density functional theory (DFT) calculations (PDF).

X-ray crystallographic data for **PETHOF-3** (CIF)

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Notes

The authors declare no competing financial interests.

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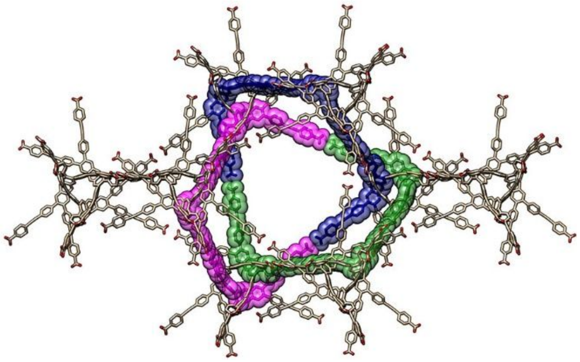

Figure 1. (a) The trigonal prismatic building block H_6PET-1. (b) The hydrogen-bonded rhombic circuit motif (depicted in blue). (c) The hydrogen-bonded triangle motif (depicted in red). (d) The extended superstructure of PETHOF-3 viewed along the c axis. (e-f) Views of the rhombic 2D subnet (depicted in blue) with appended carboxyl groups (depicted in red) in different directions. (g) The 2D → 3D inclined polycatenation of three independent arrays of the 2D subnets (depicted in green, magenta and cyan). The appended carboxyl groups are omitted for the sake of clarity.

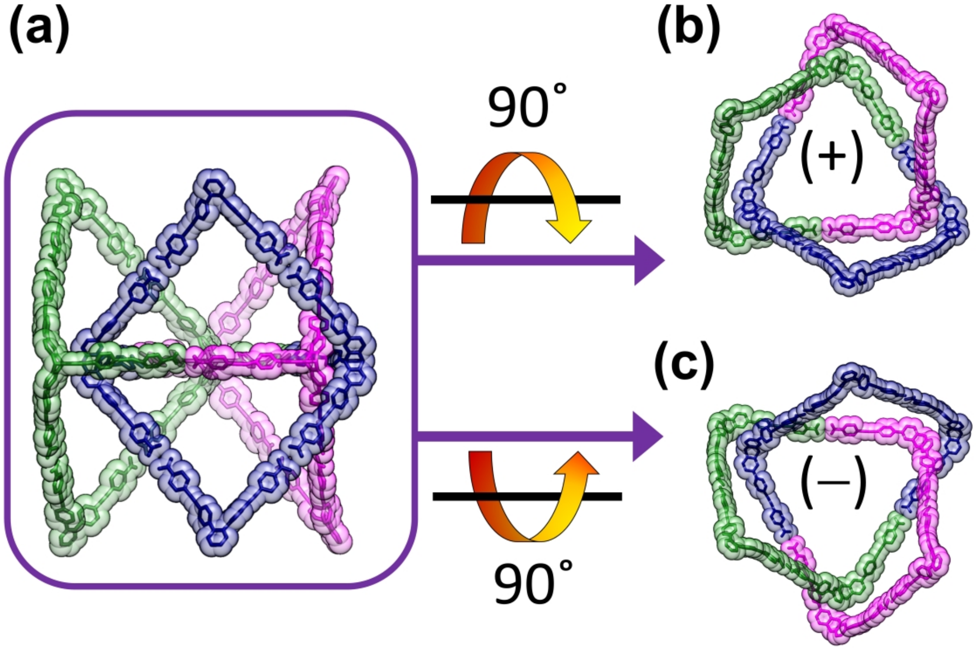

Figure 2. The supramolecular knot (a) in PETHOF-3 is composed of two enantiomeric trefoil knots with positive (+) (b) and negative (-) (c) crossings. The three rhombic circuits in the supramolecular knot are colored blue, green and magenta. Irrelevant molecular components are omitted for the sake of clarity.

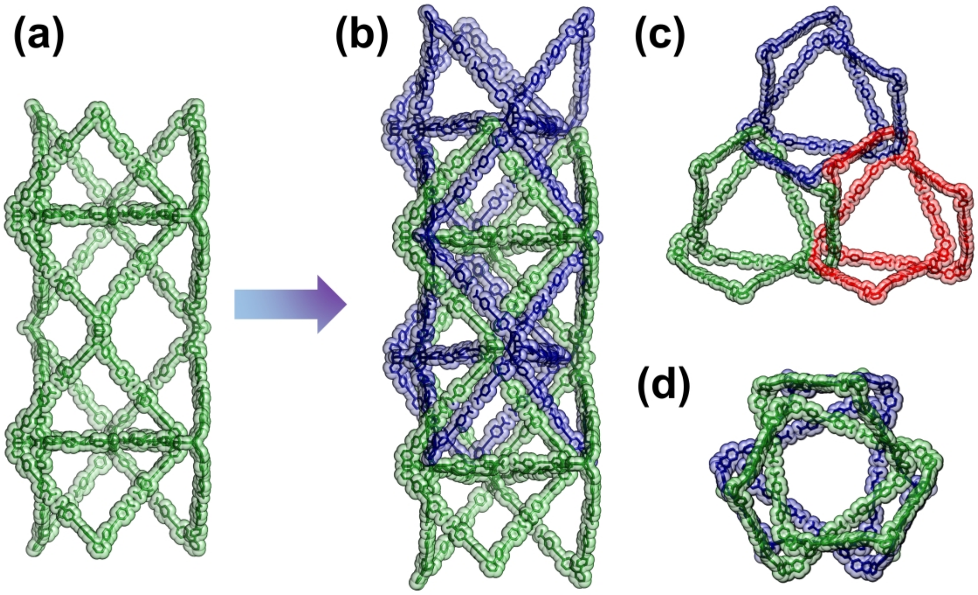

Figure 3. The representations of (a) the 1D supramolecular column (depicted in green) showing two knots with shared ver-tices, (b) the entangled superstructure containing two 1D columns (depicted in green and blue), (c) the 2D triangular tessellation pattern showing the entanglement of one knot with two of its six neighbors in the ab plane (three knots are colored green, red and blue), and (d) the 1D channel viewed along the c axis. Irrelevant molecular components are omitted for the sake of clarity.

Figure 4. (a-b) The tris-molecular cluster viewed as a 12-connected node in a cuboctahedral geometry. The triptycene cores are shown in red. The connecting bridges composed of a single and two paralleled carboxyl dimers are shown in green and blue, respectively. Irrelevant molecular components are omitted for the sake of clarity. (c) The hcp topology (the red spheres, as the vertices, correspond to the tris-triptycene cores; the green and blue sticks, as the edges, correspond to the single and two paralleled carboxyl dimer linkages, respectively). (d-e) Depictions of the tetrahedral (with magenta faces) and the octahedral (with yellow faces) cages with the tris-molecular clusters as the vertices.