

C_3 -Symmetric Macrocyclic-Based, Hydrogen-Bonded, Multiporous Hexagonal Network as Motif of Porous Molecular Crystals**

Ichiro Hisaki,* Shoichi Nakagawa, Norimitsu Tohnai, and Mikiji Miyata*

Abstract: A C_3 -symmetric π -conjugated macrocycle combined with an appropriate hydrogen bonding module (phenylene triangle) allowed the construction of crystalline supramolecular frameworks with a cavity volume of up to 58%. The frameworks were obtained through non-interpenetrated stacking of a hexagonal sheet possessing three kinds of pores with different sizes and shapes. The activated porous material absorbed CO_2 up to $96\text{ cm}^3\text{ g}^{-1}$ at 195 K under 1 atm.

Two-dimensional (2D) hexagonal networks (HexNets) have attracted much attention not only because of their topology-generated physical properties,^[1] but also their porous architectures. Namely, the construction of a 2D HexNet with large voids and subsequent accumulation of the network without interpenetration can yield materials applicable for storage of certain chemical species^[2] or for a platform to build supramolecular architectures.^[3] Particularly, a HexNet connected by hydrogen bonds (H-HexNet) can provide a reversible dynamic behavior when chemical events occur. To date, 3D assemblies based on porous H-HexNets have been constructed from molecules such as 1,3,5-substituted benzene derivatives,^[3,4] aliphatic tricarboxylic acids,^[5] hexasubstituted benzene derivatives,^[6] phosphazene derivatives,^[7] and others.^[8] However, it still remains challenging to construct a 3D assembly of H-HexNet with voids that are well-controlled in size, shape, and multiplicity, although such porous 2D networks were recently achieved on a surface.^[9] The difficulty in 3D systems is caused mainly by the following three factors: 1) Crystallization of a building block with hydrogen bonding groups needs highly polar solvents, which, however, frequently results in failure of 2D networking by trapping of the hydrogen bonding groups by the solvent molecules.^[10] 2) Even when a porous 2D network structure is formed, voids disappear by interpenetration of the net-

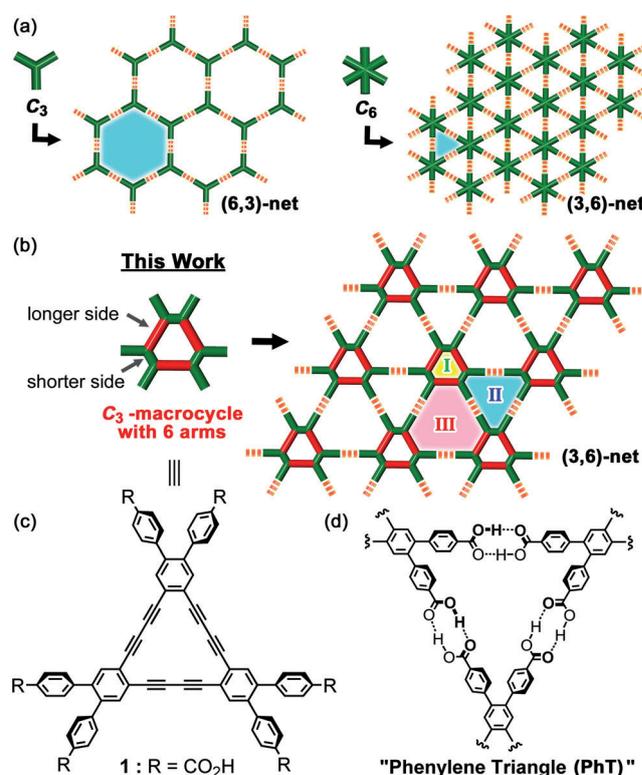


Figure 1. Porous HexNets composed of a) C_3 - and C_6 -symmetric radial molecules (conventional systems), and of b) a C_3 -symmetric macrocyclic molecule with alternate short and long sides (this work), which provides three types of voids I, II, and III. c) Chemical structure of macrocyclic **1** that can form a triangular supramolecular motif named “phenylene triangle (PhT)” (d).

work.^[4a] 3) Conventional systems such as 1,3,5- and hexasubstituted benzene derivatives^[3,4] usually result in a network with uniform-shaped voids (Figure 1 a).

In this regard, we planned to construct a novel 3D assembly of H-HexNet possessing multiple pores with different shape and size, based on a new strategy as follows (Figure 1 b): 1) As a building block core, we used dodecahydrotribenzo[18]annulene (DBA **1**) (Figure 1 c),^[11] a C_3 -symmetric planar macrocycle because a) its planarity and rigidity are advantageous in forming coplanar assemblies,^[12] b) it can provide a multiporous system due to two different lengths of the sides as well as an inherent shape-persistent void in the molecule. 2) To arrange a DBA core into a porous H-HexNet, three 4,4'-carboxy-*o*-terphenyl groups were introduced in the core. This is based on the hypothesis that the group can form triangular porous motifs through hydrogen-bonded dimerization of carboxy groups (Figure 1 d). We

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named the triangular motif as “phenylene triangle (PhT)”.^[13] The group is also expected to increase solubility into a solvent and to prevent interpenetrated crystal packing, due to nonplanarity and sterical hindrance of the phenylene moieties.

Herein, we describe that **1** gave low-density H-HexNets possessing three kinds of voids with different sizes and shapes and that non-interpenetrated lamination of the H-HexNets can provide a new class of porous materials. The stacking manner of the sheets can be varied statistically and dynamically by changing template molecules adsorbed in the voids. Furthermore, the activated porous material can absorb CO₂ gas up to 96 cm³ g⁻¹ at 195 K at 1 atm.

Preliminary, to confirm whether PhT is a robust supra-molecular motif in a solid state, reference compounds **2a**, **2b**, and **3** (Figure 2a) were crystallized from a solution of DMF,

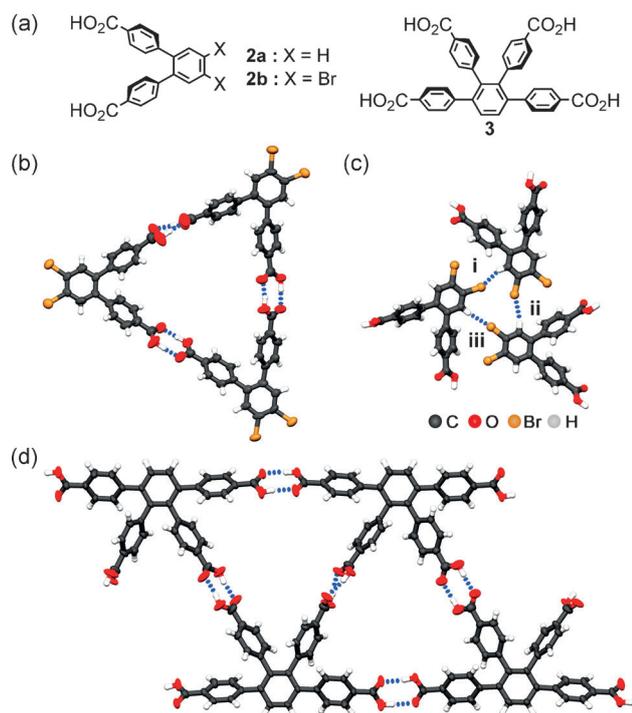
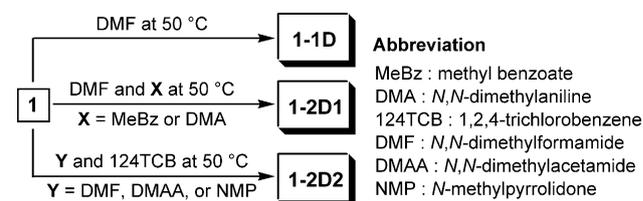


Figure 2. Formation of the phenylene triangles (PhTs) in the crystalline state. a) Chemical structures of reference compounds. b) PhT structure composed of **2b**. c) Intermolecular CH/Br interactions. d) PhT structure composed of **3**. Molecules of 135TCB or 124TCB included in the voids are omitted for clarity.

1,2,4-trichlorobenzene (124TCB), and 1,3,5-trichlorobenzene (135TCB) at 50 °C.^[14] X-ray crystallographic analysis of the obtained single crystals revealed that, although **2a** formed an infinite zigzag strand (Figure S1), **2b** achieved the PhT through hydrogen-bonded dimerization of the carboxy groups (Figure 2b). The PhT possesses a triangular void with 12.5 Å on a side and a diameter of 9.7 Å. The PhT interacts with the neighboring PhT units through threefold C–H⋯Br interactions (H⋯Br distances: 2.79–2.96 Å, C–H–Br angles: 144–167°) (Figure 2c) to form a hexagonally packed coplanar structure (Figure S4). Similarly, **3** formed PhT

motifs to give a ladder-type porous network structure (Figure 2d). These results indicate that, although the 4,4'-carboxy-*o*-terphenyl unit does not always form the PhT motif, geometrically or electrostatically well-preorganized derivatives can form the PhT motif. Another trivial interest is that the PhT includes conformational frustration originating from sterical requirements (see Figure S6).

Subsequently, **1** was crystallized under various conditions (Scheme 1) to construct a 3D assembly of H-HexNet, yielding



Scheme 1. Crystallization conditions of **1**.

three types of crystals (**1-1D**, **1-2D1**, and **1-2D2**). Crystallization from a DMF solution yielded **1-1D** (Figure S7),^[14] in which DMF molecules are bonded through hydrogen bonds with four carboxy groups of **1** to prevent the H-HexNet structure. On the other hand, crystallization of **1** in the presence of aromatic additives gave low-density H-HexNets. DBA **1** dissolved in a mixture of DMF and methyl benzoate (MeBz) at 50 °C yielded **1-2D1**(MeBz) crystals^[14] (Figures 3a

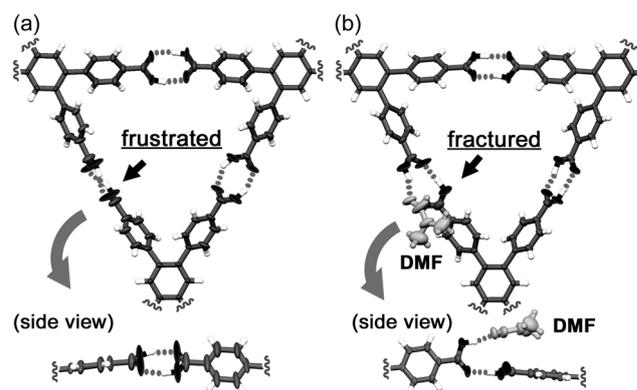


Figure 3. PhT motifs of **1** with 75% displacement ellipsoid plots. a) PhT of **1-2D1**(MeBz), in which one carboxy dimer includes conformational frustration. b) PhT of **1-2D2**(DMF, 124TCB), in which a DMF molecule is inserted in the carboxy dimer.

and 4a–d). The **1-2D1**(MeBz) crystal involves the PhT motif (Figure 3a), in which one pair of the hydrogen-bonded carboxy phenyl groups shows conformational frustration. Molecules of **1** were linked by the PhT to give a H-HexNet (Figure 4a). The H-HexNet contains three types of voids I, II, and III. The smallest triangular one, I with 3.5 Å on a side and a diameter of 3.2 Å, includes no guest. The PhT's void II accommodates one or two molecule(s) of MeBz. The largest nonregular hexagonal void III with alternate sides of 4.8 Å and 13.4 Å and a diameter of ca. 20.5 Å accommodates more than two molecules of MeBz. Overall, 36 molecules of MeBz

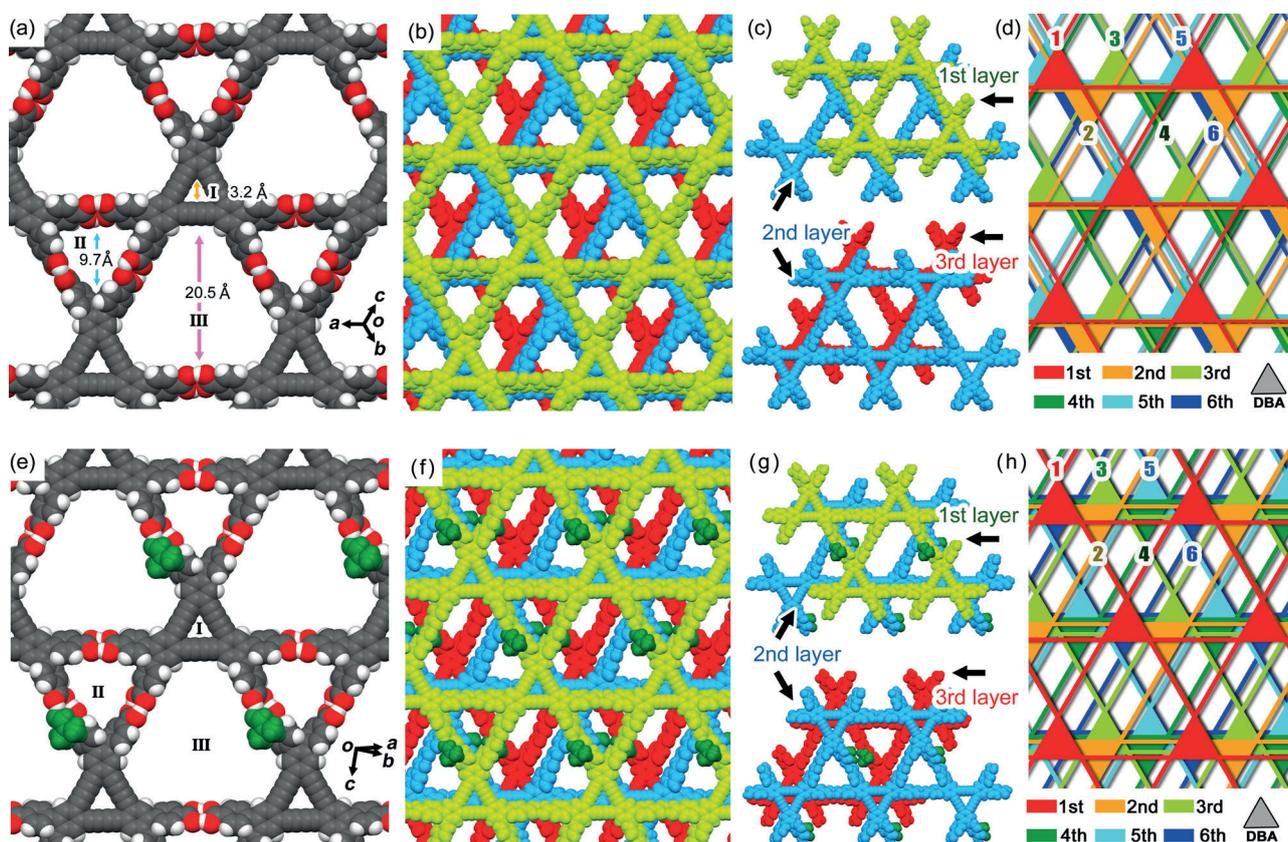


Figure 4. Crystal structures of **1-2D1** (MeBz) (a–d) and **1-2D2** (DMF, 124TCB) (e–h). a,e) Multiporous HexNets with three types of voids I, II, and III. b,f) Packing diagrams of three layers colored light green, light blue, and red stacking without interpenetration. c,g) Stacking manners of the adjacent two rhombic motifs. d,h) Schematic representations for stacking diagrams of six layers (colored of the layers, 1st: red, 2nd: orange, 3rd: light green, 4th: green, 5th: light blue, 6th: blue). Arabic numbers point to the DBA core in the each layer. Hydrogen-bonding of DMF molecules with the framework is colored green in (e–g). Guest molecules included in the voids are omitted for clarity.

are accommodated in the unit cell with a host/guest ratio of 1:6 (Figures S8, S16, and S20). The H-HexNet was stacked without interpenetration to give a 3D framework (Figure 4 b). The cavity volume of the framework was calculated to 58 % by PLATON software.^[15] The form **1-2D1** was also obtained when *N,N*-dimethylaniline (DMA) was applied instead of MeBz (Figure S9).

Similarly, crystallization of **1** from a DMF and 124TCB solution at 50 °C yielded the **1-2D2** (DMF, 124TCB) crystal (Figures 3 b and 4 e–h).^[14] Although **1-2D2** (DMF, 124TCB) has a PhT similar to that of **1-2D1** (MeBz), a DMF molecule is inserted to the frustrated dimer moiety to release the distortion (Figure 3 b). The resulting H-HexNet involves three types of void spaces similar to that of **1-2D1** (MeBz) (Figure 4 e). The PhT's void involves one 124TCB molecule and the hexagonal void was estimated to accommodate seven 124TCB molecules (Figures S10, S17, and S21). The sheet was stacked without interpenetration (Figure 4 f). The cavity volume of the framework was calculated at 49%.^[15] The form **1-2D2** was also obtained when *N*-methylpyrrolidone (NMP) or *N,N*-dimethylacetamide (DMAA) was applied instead of DMF for crystallization (Figures S11 and S12).

Interestingly, although **1-2D1** (MeBz) and **1-2D2** (DMF, 124TCB) exhibits quite similar H-HexNets, the networks accumulate in a different way. As shown in Fig-

ure 4c, a rhombic frame of the **1-2D1** (MeBz) crystal stacks with another rhombic frame lying on the neighboring sheet in an inverted way so that these frames contact each other.^[16] **1-2D2** (DMF, 124TCB), on the other hand, has two stacking ways of the rhombic frame: one is similar with that of **1-2D1** (MeBz) (Figure 4g, top), whereas the second has a smaller overlap compared with the former (Figure 4g, bottom). The latter stacking way is caused by steric repulsion between the DMF molecules and/or by packing of guests in the voids. Schematic stacking diagrams (Figure 4d and h) show that **1-2D1** (MeBz) has a wider bottle neck of the inclusion space than **1-2D2** (DMF, 124TCB).

To remove the accommodated molecules and activate the H-HexNet assembly, the crystalline bulk of **1-2D2** (DMF, 124TCB) was soaked with benzene followed by the application of vacuum, resulting in desolvated crystalline material (i.e., **1-2D-apo**). A powder X-ray diffraction (PXRD) pattern of the material shows slightly broad but unambiguous peaks (Figure 5 a). A peak at 3.74° (d spacing: 23.6 Å) attributed to the 001 face of **1-2D2** (DMF, 124TCB) disappeared and one at 4.12° (d spacing: 21.4 Å) newly appeared, combined with those at 4.96° and 6.58° upon guest desorption. Assuming that the porous H-HexNet could remain, the above-mentioned changes in the PXRD pattern indicate that the layer was slipped by ca. 3 Å along a certain

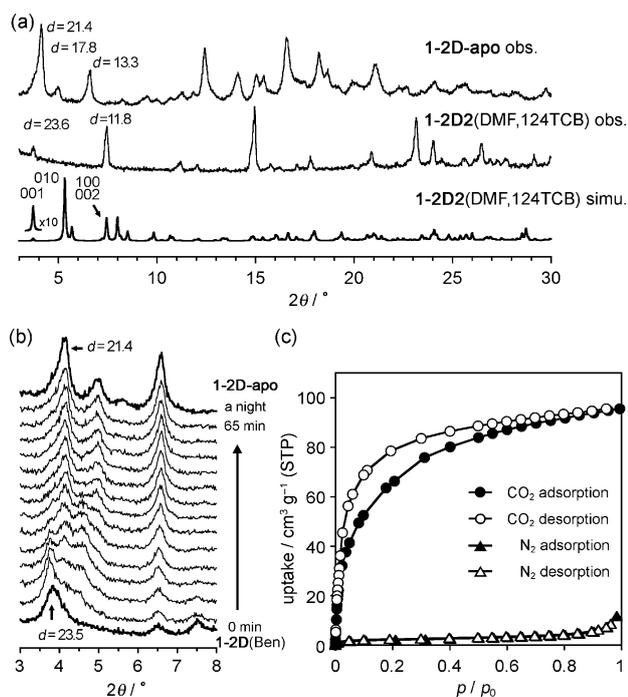


Figure 5. Dynamic behavior of the 3D assembly of H-HexNet upon desorption and adsorption of guest molecules. a) PXRD patterns of 1-2D2(DMF,124TCB) before and after the activation to give guest free 1-2D-**apo**. b) PXRD pattern changes of benzene-soaked 1-2D(Ben) to 1-2D-**apo** upon the release of benzene. c) Adsorption isotherms of 1-2D-**apo** for N_2 and CO_2 . The observed PXRD pattern of 1-2D2(DMF,124TCB) in (a) show much fewer peaks compared with the simulated one because of orientation of bulk crystals.

direction (see Figures S22 and S23). Moreover, soaking of 1-2D-**apo** in benzene brought about a shift of the PXRD peak at 4.12° to 3.76° , due to the adsorption of benzene into the voids to form 1-2D(Ben). The pattern of 1-2D(Ben) rapidly changed to that of 1-2D-**apo**, indicating recovery of 1-2D-**apo** upon releasing benzene (Figure 5b). This process is repeated several times (Figure S24). These results demonstrated that stacking manners of the H-HexNets can be changed dynamically by absorption/desorption of guest molecules.

To confirm the porosity of the 1-2D-**apo**, absorption experiment was performed using N_2 and CO_2 at 77 K and 195 K, respectively (Figure 5c). 1-2D-**apo** absorbed CO_2 and N_2 up to $95.6 \text{ cm}^3 \text{g}^{-1}$ and $11.7 \text{ cm}^3 \text{g}^{-1}$, respectively, at 1 atm. The remarkable uptake of CO_2 is probably originated in favorable electrostatic interactions between the π -electron-rich surface of the pore and the quadrupolar CO_2 molecules.^[17] Adsorption isotherms of CO_2 show the type I adsorption profile,^[18] indicating that the material has micropores. Although many gas adsorbents based on porous molecular crystals have been reported,^[4e,f,19,20] the present system is the first example of a dehydrobenzoannulene-based gas adsorbent.

In conclusion, we demonstrated that a C_3 -symmetric macrocycle possessing alternate sides with different lengths, combined with 4,4'-carboxy-*o*-terphenyl group, is a powerful building block to access a multiporous, hydrogen-bonded, hexagonal network (H-HexNet), and consequently to con-

struct 3D porous molecular architecture. The activated porous material showed CO_2 gas adsorption. The results promise that the present system could open a door to develop a new class of highly porous functional materials. Furthermore, the stacking manner of the H-HexNet can be changed statistically and dynamically depending on the guest molecules. Turning of the stacking manner, for example, to the on-top arrangement surely provides three kinds of channels,^[21] which is under investigation in our laboratory.

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- [15] Atomic radii were adopted as follows: 1.20 Å (H), 1.70 Å (C), 1.52 Å (O). The probe radius was 1.2 Å.
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Communications



Supramolecular Chemistry

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C_3 -Symmetric Macrocyclic-Based,
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Construction of porous crystalline two-dimensional frameworks is achieved through non-interpenetrated stacking of a multiporous hexagonal network possessing three kinds of voids with different sizes and shapes. A cavity volume of up to 58% is obtained.