Title	A C_3-symmetric macrocycle-based, hydrogen-bonded, multiporous hexagonal network as a motif of porous molecular crystals
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C_3-Symmetric Macrocycle-Based, Hydrogen-Bonded, Multi-Porous Hexagonal Network as Motif of Porous Molecular Crystals

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

Abstract: *C_3 symmetric π-conjugated macrocycle combined with appropriate hydrogen bonding module (phenylene triangle) allowed low density crystalline supramolecular frameworks with cavity volume upto 58%. The frameworks were constructed 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 $cm^3 g^{-1}$ at 195 K under 1 atm.*

Two-dimensional (2D) hexagonal network (HexNet) has attracted much attention not only from a topologically-generated physical properties,[1] but as a structural motif of porous architectures. Namely, construction of a 2D HexNet with large voids and subsequent accumulation of the network without interpenetration can provide materials applicable for storage of certain chemical species[2] or for a platform to build supramolecular or polymeric architectures inside the voids.[3] Particularly, HexNet connected by hydrogen bond (H-HexNet) can provide a reversible dynamic behavior when chemical events undergo. To date, a number of 3D assemblies based on hexagonally networked structures with voids have been constructed from C_3 and C_6 symmetric molecules such as 1,3,5-substituted benzene derivatives,[3,4] aliphatic tricarboxylic acid,[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 well-controlled voids in size, shape, and multiplicity, although many such porous 2D networks are recently achieved on a surface or an interface.[9] The difficulty in 3D systems is caused mainly by the following three factors. (1) Crystallization of a building block molecule with hydrogen bonding groups often needs highly-polar solvents to dissolve it in a homogeneous solution. This, however, frequently results in failure of 2D networking due to trapping of the hydrogen bonding groups by the solvent molecules.[10] (2) Even when a porous 2D networked structure is formed, void spaces in the network are disappeared by interpenetration of the network.[4a] (3) Conventional system such as 1,3,5- and hexa-substituted benzene derivatives[3,4] usually results in a network with uniform-shaped voids (Figure 1a).

In connection with this, we planned to construct a novel assembly of H-HexNet possessing multiple pores with different shape and size, on the basis of a new strategy as follows (Figure 1b). (1) For a core of building block, we applied dodecadehydrotribenzo[18]annulene (18DBA) (Figure 1c),[11] a C_3-symmetric planar macrocycle because (i) its planarity and rigidity have an advantage in forming coplanar 2D assemblies,[12] (ii) it can provides a multi-pores system due to two different length of the sides as well as inherent, shape-persistent void in the molecule itself. (2) In order to arrange a 18DBA core into a porous hexagonally-networked sheet, three 4,4'-carboxy-*o*-terphenyl moieties were introduced into a periphery of the core. This is based on the hypothesis that the group can form triangular porous motifs through hydrogen-bonded dimerization of carboxyl groups[13] as shown in Figure 1d. We named the triangular motif as "phenylene triangle (PhT)".[14] The group is also expected to increase solubility into a solvent and to prevent interpenetrated crystal packing, due to nonplanality and sterical hindrance of the phenylene moieties.

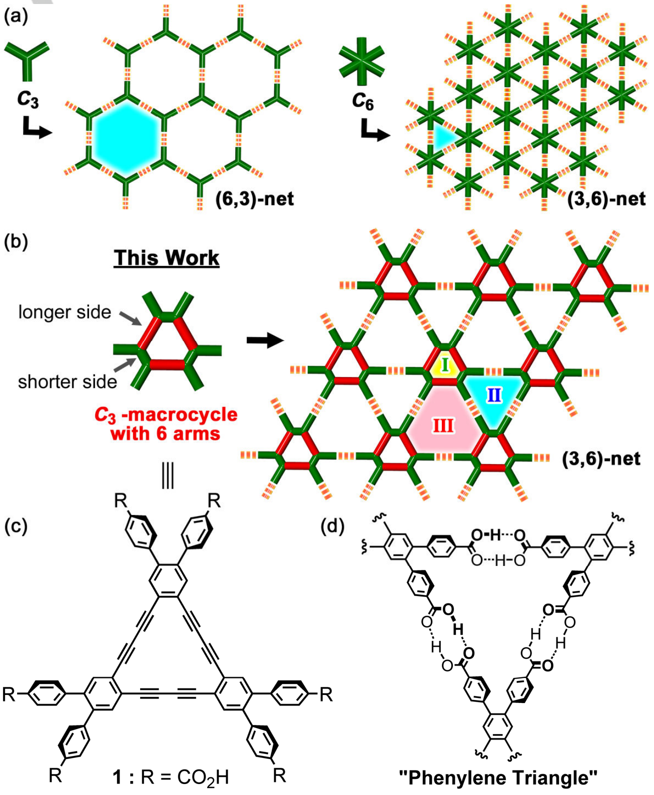

Figure 1. Porous HexNets composed of (a) C_3- and C_6-symmetric radial molecules (conventional systems), and of (b) a C_3-symmetric macrocyclic molecule with alternate short and long sides (the present system), which provides three types of voids I, II, and III in the plane. (c) Chemical structure of macrocyclic 18DBA **1** with six carboxyphenyl groups that can form (d) triangular supramolecular motif named "phenylene triangle (PhT)"

Herein, we describe that 18DBA **1** gave low density H-HexNets possessing three kinds of voids with different sizes and

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shapes and that non-interpenetrated lamination of the H-HexNets can form a porus material. 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 CO_2 gas upto 96 cm^3 g^{-1} at 195 K at 1 atom. The present results would open a door to develop a new class of highly porous functional materials.

Preliminary, to confirm whether PhT is a robust supramolecular motif in a solid state, 1,2-bis(4-carboxyphenyl)benzene (**2a**), the corresponding 4,5-dibromo derivative **2b**, and 1,2,3,4-tetrakis(4-carboxyphenyl)benzene (**3**) (Figure 2a) were crystallized from a mixed solution of DMF, 1,2,4-trichlorobenzene (124TCB) and 1,3,5-trichlorobenzene (135TCB) at 50 °C.[15] X-ray crystallographic analysis of the resulting single crystals revealed that, although **2a** formed an infinite zigzag strand (Figure S1), **2b** achieved the PhT through complementary hydrogen bond of the carboxy groups (Figure 2b). The PhT possesses a triangular void with ca. 12.5 Å on a side and ca. 9.7 Å of diameter, in which 124TCB or 135TCB molecule was accommodated. 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 with inclusion channels (Figure S4). Similarly, **3** formed PhT motifs to give a ladder-type porous network structure (Figure 2d). The porous ladder stacks into coplanar assembly through π/π and CH/π interaction (Figure S5). 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 originated from sterical requirements (see Figure S6).

Subsequently, **1** was synthesized according to Scheme 1a. 1,2-Dibromo-4,5-diidobenzene (**4**),[16] which is obtained by iodization of 1,2,-dibromobenzene, was reacted with 4-methoxycarbonylphenyl boronic acid to give *o*-terphenyl derivative **5**. Cross-coupling of **5** with trimethylsilylacetylene (TMSA), followed by desilylation of **6** by tetrabutylammonium fluoride gave terminal acetylene **7**. Oxidative coupling of **7** in the presence of Cu(II) yielded cyclic trimer **8**,[17] which was then hydrolyzed to give **1** with hexacarboxy groups. 18DBA **1** was then crystallized under various conditions in order to construct a 3D assembly of H-HexNet, yielding three types of crystals (namely, forms **1-1D**, **1-2D1**, and **1-2D2**) as shown in Scheme 1b.

Crystallization of **1** from a DMF solution yielded crystal **1-1D** (Figure S7).[15] In the crystal structure, DMF molecules were hydrogen bonded with four carboxy groups of **1** to prevent expanding 2D hydrogen bonded network, while the other two participate self-complementary hydrogen bonds to allow the one dimensional network structure.

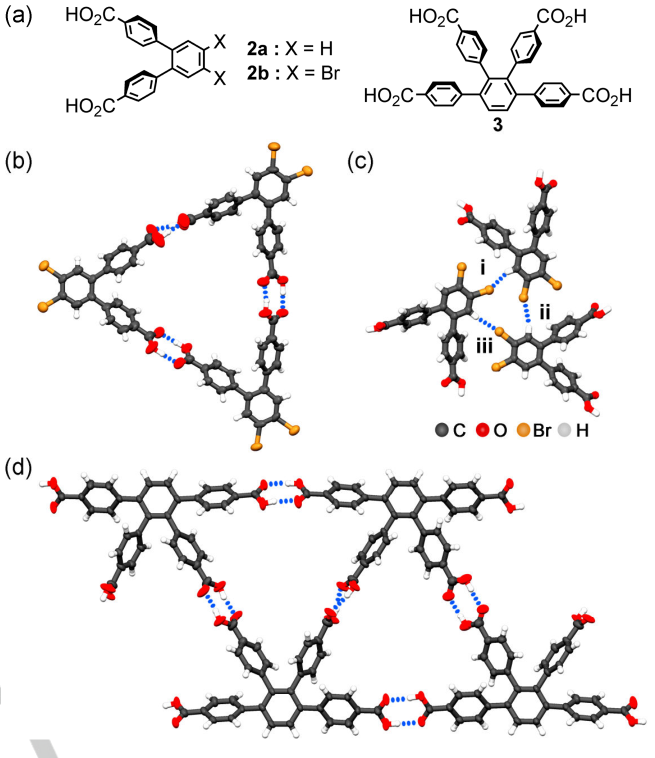
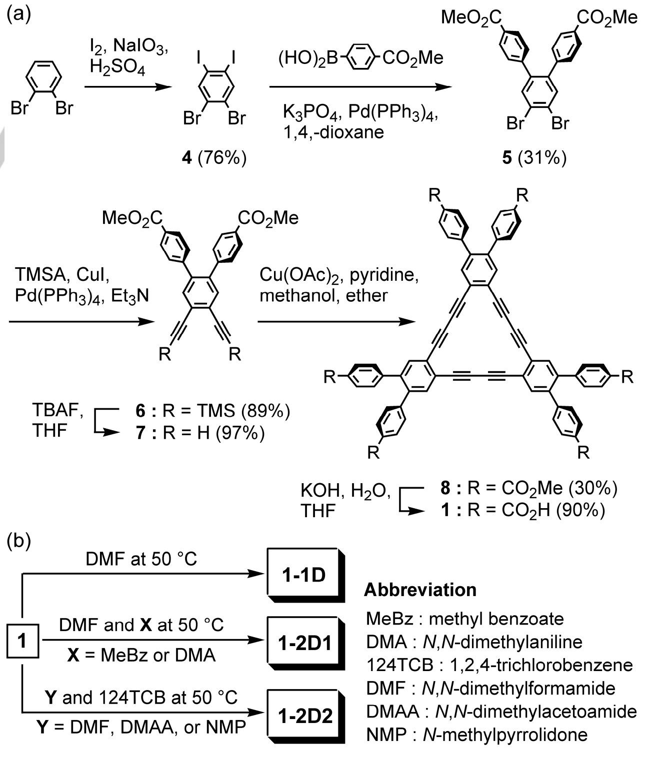


Figure 2. Formation of the phenylene triangles (PhTs) in crystalline state. (a) Chemical structures of reference compounds. (b) PhT structure composed of **2b**. (c) Intermolecular CH/Br interactions. (d) PhT structure composed of **3**. Molecules of 135TCB or 124TCB included in voids are omitted for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



Scheme 1. (a) Synthesis and (b) crystallization conditions of18DBA **1**.

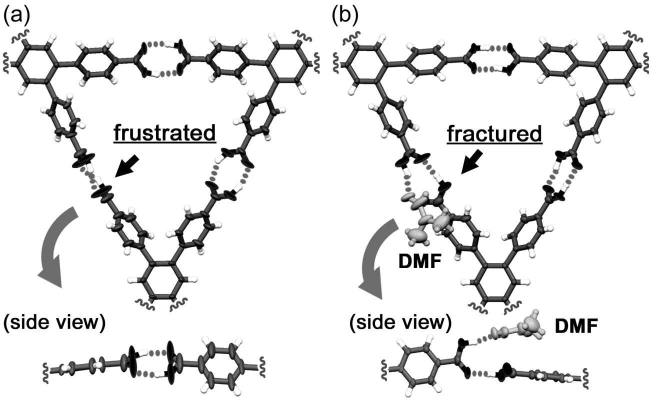


Figure 3. PhT motifs composed of **1** with 75% displacement ellipsoid plots. (a) PhT of **1-2D1**(MeBz), in which one carboxy dimer includes conformational frustration. (b) PhT of **1-2D2**(DMF,124TCB), in which DMF molecule is inserted in the carboxyl dimer to release the distortion.

On the other hand, crystallization of **1** in the presence of aromatic additives gave two-dimensionally spread low density H-HexNets. Crystallization of **1** from a DMF and methyl benzoate (MeBz) solution at 50 °C yielded **1-2D1**(MeBz) crystal,[15] whose structure is shown in Figures 3a and 4a-d. In the crystal structure of **1-2D1**(MeBz), molecules of **1** form the PhT motif as in the case of **2b** (Figure 3a). One pair of the hydrogen bonded carboxy phenyl groups in the PhT has the conformational frustration (Figure 3a). Molecules of **1** were linked in hexagonal manner by the PhT to give 2D networked sheet parallel to the 100 plane as we expected (Figure 4a). The sheet involves three types of voids. The smallest triangular one with ca. 3.5 Å on a side and ca. 3.2 Å of diameter, which is inherent to the cyclic structure of **1**, includes no guest. The PhT's void accommodates one or two molecule(s) of MeBz. The largest non-regular hexagonal void with alternate sides of ca. 4.8 Å and ca. 13.4 Å and diameter of ca. 20.5 Å involves more than two molecules of MeBz. Totally, 36 molecules of MeBz are accommodated in unit cell with host/guest ratio of 1:6 judging from TG analysis and ^{1}H NMR spectroscopy (Figures S8, S16 and S20). The sheet was then stacked without interpenetration to give a HN-HexNet architecture (Figure 4b). The cavity volume of the framework was estimated at 58% by PLATON software.[18] 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 crystal **1-2D2**(DMF,124TCB) whose structure is shown in Figures 3b and 4e-h.[15] Although

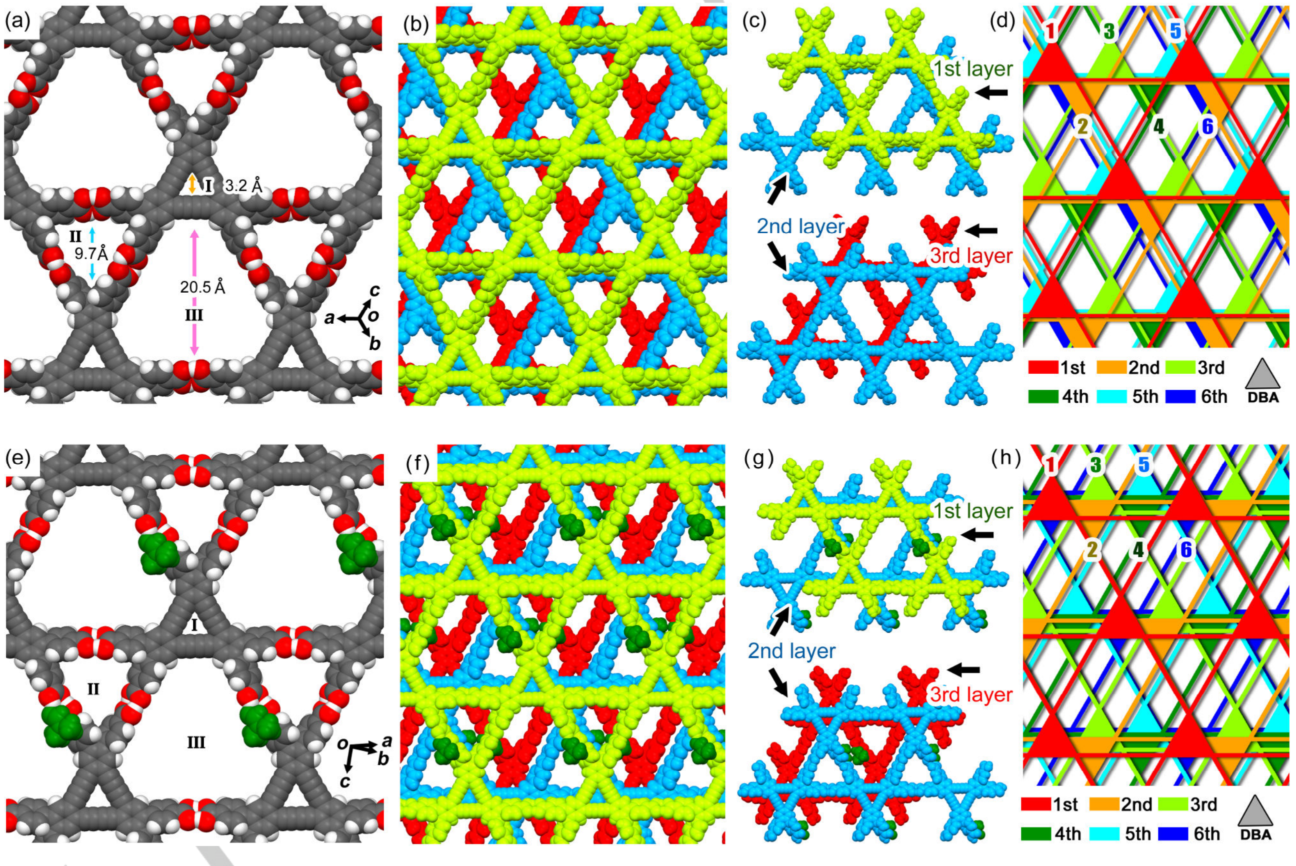


Figure 4. Crystal structures of **1-2D1**(MeBz) (a-d) and **1-2D2**(DMF,124TCB) (e-h). (a,e) Multi-porous HexNets with three types of voids I, II, and III. (b,f) Packing diagrams of three layers colored light green, light blue, and red stacking without interpenetration. (c,g) Stacking manners of the 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 the DBA core in the each layer. DMF molecules hydrogen-bonding with the framework are colored green in (e-g). Included guest molecules (methyl benzoate for**1- 2D1** and 1,2,4-trichlorobenzene for **1-2D2**) within the void spaces are omitted for clarity.

molecules of **1** in **1-2D2**(DMF,124TCB) formed a PhT similar to **1-2D1**(MeBz), a DMF molecule is inserted to the frustrated dimer moiety to form "truncated catemer" type hydrogen bond[10d] to release the distortion (Figure 3b). The resulting H-HexNet parallel to the 1−21 plane involves three types of void spaces similar to that of **1-2D1**(MeBz) (Figure 4e). The PhT's void involves one 124TCB molecule in a parallel fashion and the hexagonal void was estimated to accommodate seven 124TCB molecules (Figures S10, S17 and S21). Molar ratio of **1**, DMF, and 124TCB is 1:1:6. The sheet was stacked without interpenetration (Figure 4f). The cavity volumn of the framework was estimated at 49%.[18] Crystalline form **1-2D2** was also obtained when *N*-methylpyrrolidone (NMP) or *N*,*N*-dimethylacetamide (DMAA) was applied instead of DMF for the crystallization (Table S1 and 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 to yield different shapes of the void spaces. As shown in Figure 4c, a rhombic frame of **1-2D1**(MeBz) crystal stacks with another rhombic frame lying on the neighboring sheet in an inverted way so as that these frames contact each other through π/π and CH/π interactions.[19] **1-2D2**(DMF,124TCB), on the other hand, has two stacking ways of the rhombic frame: one is the similar with that of **1-2D1**(MeBz) (Figure 4g top), while the other has relatively smaller overlap compared with the former (Figure 4g bottom). The latter stacking way is caused by steric repulsion between the DMF molecules bonding to the frame and/or by chemical species included in the void spaces. Schematic stacking diagrams of **1-2D1**(MeBz) and **1-2D2**(DMF,124TCB) (Figures 4d and 4h) show that **1-2D1**(MeBz) has a wider bottle neck of the inclusion space.

To remove the accommodated molecules and activate a H-HexNet assembly, crystalline bulk of **1-2D2**(DMF,124TCB) was soaked into benzene at ambient condition followed by laying under vacuum condition resulted in desolvated crystalline powder (i.e. **1-2D-apo**). A powder X-ray diffraction (PXRD) pattern of the resultant material shows slightly broad but unambiguous peaks as shown in Figure 5a. A peak at 3.74° (d spacing: 23.6 Å) attributed to the 001 face of **1-2D2**(DMF,124TCB) disappeared and that at 4.12° (d spacing: 21.4 Å) newly appeared, combined with those at 4.96° and 6.6° upon the guest desorption. Assuming that porous H-HexNet could remain, the above mentioned changes in the PXRD pattern indicates that the layer was slipped by ca. 3 Å, along a certain direction (see Figures S22 and S23). Moreover, soaking of **1-2D-apo** crystalline bulk into benzene brought about a shift of the PXRD peak at 4.12° to 3.76°. due to adsorption of benzene into the void spaces to form **1-2D**(Ben). The pattern of **1-2D**(Ben) rapidly changed into that of **1-2D-apo**, indicating recover 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 layers can be changed dynamically by absorption/desorption of guest molecules.

To confirm porosity of the **1-2D-apo**, absorption experiment was performed using N_2 and CO_2 at 77K and 195 K, respectively (Figure 5c). **1-2D-apo** absorbed CO_2 up to 95.6 cm^3 g^{-1} at 1 atm. On the other hand, the uptake of N_2 is 11.7 cm^3 g^{-1} at 1 atm. Remarkable uptake of CO_2 compared with N_2 is probably originated in favorable electrostatic interactions between the π-electron-rich surface of the pore and the quadrupolar CO_2 molecules.[20] Adsorption isotherms of CO_2 show the type I adsorption profile,[21] indicating that the material has micro pores. Although many gas adsorbents based on organic molecular have been reported,[4e,4f,22,23] the present system is the first example of DBA-based gas adsorbent.

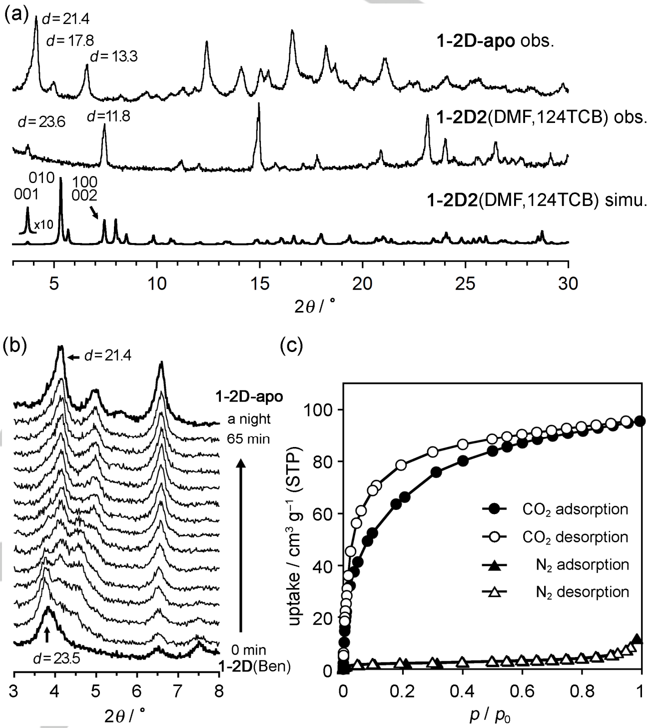


Figure 5. Dynamic behaviour of **1-2D2** upon desorption and adsorption of guest molecule. (a) PXRD patterns of **1-2D2**(DMF,124TCB) before and after guest (DMF and 124TCB) desorption to give guest free **1-2D-apo**. (b) PXRD pattern changes of benzene-soaked **1-2D**(Ben) into **1-2D-apo** upon release of benzene under ambient condition. (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.

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 low density hexagonal network possessing multiple voids with different sizes and shapes, and consequently to construct a non-interpenetrated 3D porous architecture. The activated porous material showed CO_2 gas adsorption. The results promise that the present system would open a door to develop a new class of highly porous functional materials. Furthermore, stacking manner of layers of the H-HexNets can be changed statistically and dynamically upon guest absorption and desorption. Turning of the stacking manner into, for example, the on-top arrangement surely provides certifiable three kinds of channels,[24] which is under investigation in our laboratory.

Acknowledgements

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Keywords: supramolecular chemistry • hydrogen bonds • phenylene triangle • annulenes • gas adsorption

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[14] The PhT motif was first observed in Kobayashi's system, see Ref 6b.

[15] The detailed crystal data are shown in Table S1 in Supporting Information. CCDC numbers: **2a** (CCDC-1035276), **2b** (CCDC-1035277), **3** (CCDC-1035275), **1-1D** (CCDC-1035278), **1-2D1**(MeBz) (CCDC-1035280), **1-2D1**(DMA) (CCDC-1035279), **1-2D2**(DMF,124TCB) (CCDC-1035282), **1-2D2**(DMAA,124TCB) (CCDC-1035281), **1-2D2**(NMP,124TCB) (CCDC-1035283) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/.

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

[19] Crystallographically independent three sheets in **1-2D1**(MeBz) are stacked with corresponding neighbour sheets in the quite similar manner (see Figure S13 in Supporting Information).

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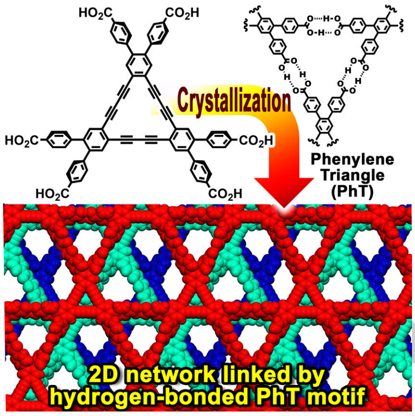
Entry for the Table of Contents

COMMUNICATION

We first describe construction of porous crystalline frameworks formed through non-interpenetrated stacking of a multi-porous hexagonal network possessing three kinds of voids with different sizes and shapes.



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C3-Symmetric Macrocycle-Based, Hydrogen-Bonded, Multi-Porous Hexagonal Network as Motif of Porous Molecular Crystals