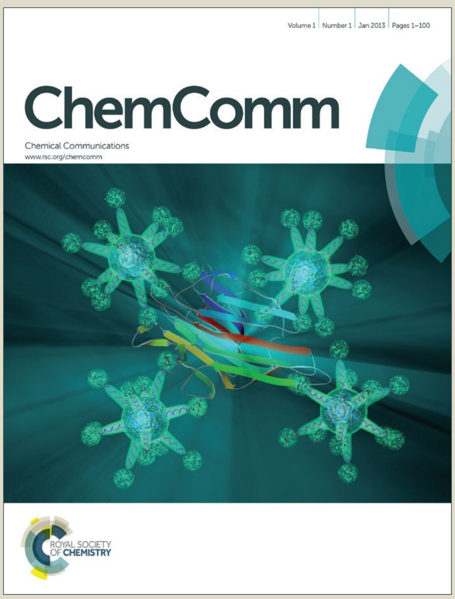
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Polymorphs of Layered Assemblies of Hydrogen-Bonded Hexagonal Networks Caused by Conformational Frustration

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Generation of four polymorphs of 2D-nCOF crystals that are formed through stacking of a hydrogen-bonded, hexagonally-networked framework is first revealed. The structural diversity is caused not from topology or stacking manner of the framework but from subtle structural factors such as rotational conformation and location of geometrical frustration within the framework.

Functional porous material is one of the central targets in the field of modern chemistry.[1] Particularly, porous materials formed by stacking of two-dimensionally (2D) networked π-conjugated organic components have attracted much attention from view points of not only selective gas adsorbents and catalysts but also photoelectronic materials. One of the promising systems is a covalent organic framework (COF), whose facial synthesis was first demonstrated by Yaghi and co-workers,[2] and subsequently, a number of excellent COFs were prepared with various π-conjugated organic building blocks.[3]

Structural characterization of 2D-COFs is often conducted by powder X-ray diffraction (PXRD) analysis combined with other spectroscopic methods to reveal whether porous 2D sheet stacked in a staggered or eclipsed manner.[4] However, it still remains difficult to obtain more precise structural information such as subtle slipping of the stacked layers and conformational changes of the flexible components.[5] 2D non-covalent organic framework (2D-nCOF), on the other hand, is a convenient model system because a single crystal suitable for X-ray crystallographic analysis can be readily prepared by routine recrystallization from a solution, enabling more detailed structural characterization. To date, precise structures and properties of a number of 2D-nCOFs have been reported.[6] We also demonstrated that C_3-symmetric π-conjugated macrocycle, dodecadehydrotribenzo[18]annulene ([18]DBA) possessing six carboxy phenyl groups crystallized into 2D-nCOF,[7] in which a multi-porous hexagonal network (HexNet) is formed through the triangular supramolecular synton,[8] so called phenylene triangle (PhT) motif.[9]

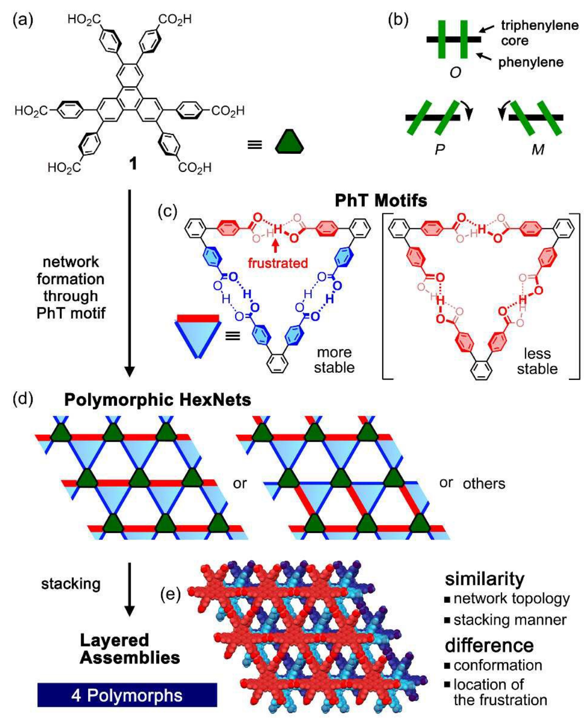

Fig. 1 Hierarchical interpretation for generation of polymorph in 2D non-covalent organic framework (2D-nCOF) crystals with hexagonal network (HexNet) of **1**. (a) Molecular structure of **1**. (b) *P* and *M* conformations of the peripheral phenylene moieties. (c) Hydrogen-bonded phenylene triangle (PhT) motifs. (d) Polymorph of HexNets caused by location of the frustrated hydrogen bond. (e) Formation of polymorphic crystals via stacking of the HexNets. Among the obtained four polymorphic crystals, stacking manner of the HexNets is nearly the same while conformation of the peripheral groups, location of the frustration, and arrangements of guest molecules in void space are different.

In this manuscript, we describe four polymorphs of 2D-nCOF composed of layered HexNets of triphenylene derivative **1** (Fig. 1). The remarkable feature of the present polymorphic system

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Electronic Supplementary Information (ESI) available: [Synthesis, detailed crystal structures, thermal analysis, and NMR spectra]. See DOI: 10.1039/x0xx00000x is that HexNet sheets in the polymorphic crystals have the same topology and are laminated with nearly the same stacking manner, while rotational conformation of the carboxy phenyl groups and location of the geometrical frustration of the PhT motifs are completely different among the four crystals. To our knowledge, this is the first example for 2D-nCOF crystals to disclose as many as four polymorphic structures caused by subtle but clear structural differences such as rotational conformations.

The adjacent two peripheral phenylene groups in **1** incline in the same direction (*P* or *M*) to avoid steric repulsion between them (Fig. 1b). Therefore, the PhT motif includes at least one conformationally-frustrated hydrogen bonded carboxyl dimer (Fig. 1c), except for the case that the all phenylene groups are in the orthogonal conformation (*O*) (Fig. 1b). To date, we have not observed PhT motif with three frustrated dimers because of its instability, while low symmetric PhT motif with one frustrated dimer has been frequently observed.[7] Therefore, It is easy to image that the low symmetric PhT brings versatile location of the frustrated dimer within the HexNet sheet (Fig. 1d), and that stacking of the HexNet sheets yields polymorphs (Fig. 1e). Indeed, we obtained four polymorphs as follows.

1 was synthesized according with Scheme S1. 2,3,6,7,10,11-Hexabromotriphenylene and 4-(methoxycarbonyl)-phenylboronic acid were reacted under a Suzuki-Miyaura coupling condition, affording hexasubstituted triphenylene

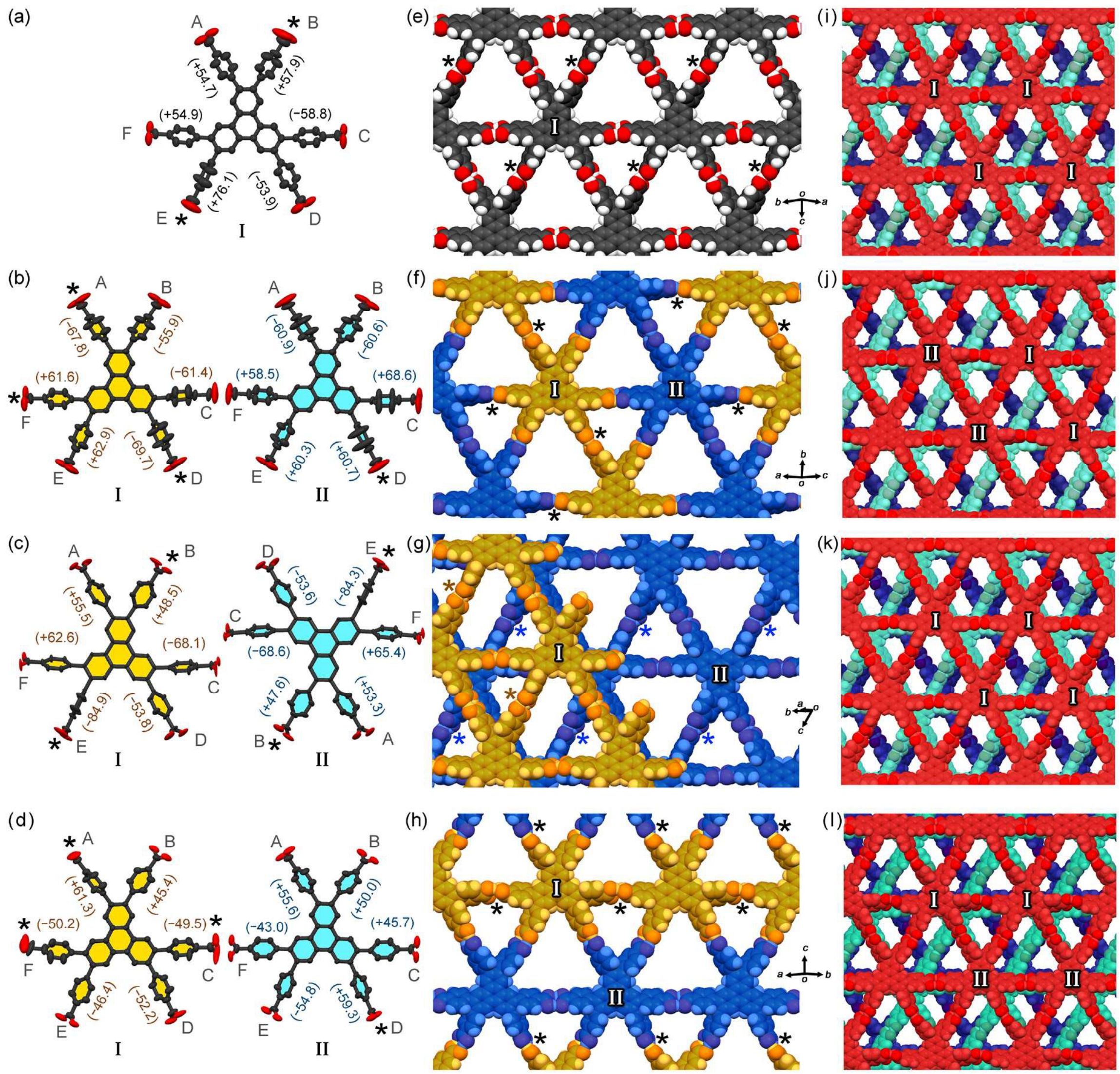

Fig. 2 Crystal structures of (a,e,i) **1-2D1**, (b,f,j) **1-2D2**, (c,g,k) **1-2D3**, and (d,h,l) **1-2D4**. Anisotropic displacement ellipsoid plot of (a) **1-2D1**, (b) **1-2D2**, (c) **1-2D3**, and (d) **1-2D4**. The ellipsoids were drawn in 75% probability to enhance atomic displacements. 2D-HexNet structures of (e) **1-2D1**, (f) **1-2D2**, (g) **1-2D3** and (h) **1-2D4**. Stacked three layers of (i) **1-2D1**, (j) **1-2D2**, (k) **1-2D3** and (l) **1-2D4**. Crystallographically independent two molecules of **1** are labelled by **I** and **II** in **1-2D2**, **1-2D3**, and **1-2D4**. Dihedral angles of the phenylene groups against the triphenylene core are presented in parentheses. An Asterisk (*) points a pair of the carboxy groups possessing conformational frustration. Since the molecule **II** in **1-2D3** corresponds to **I**(*A*) in **1-2D1**, where the symmetry code for *A*: −x, −y, −z, the sign of the dihedral angle value of **II** in **1-2D3** was inverted for easy compassion with others.

derivative **2** in 96% yield. Hydrolysis of **2** with KOH gave **1** in 93% yield. Recrystallization of **1** was performed by slow evaporation of a DMF and methyl benzoate solution under various temperatures. As a result, we acquired totally four kinds of perfectly-networked 2D HexNet crystals (**1-2D1**, **1-2D2**, **1-2D3**, and **1-2D4**), as well as other non-hexagonally-networked crystals (see, ESI). Crystals **1-2D1**, **1-2D2** and **1-2D3** were obtained by recrytallization at 100 °C. Crystals **1-2D1** and **1-2D2** were mainly formed concomitantly or sometime individually depending on crystallization batches. **1-2D3**, on the other hand, was merely obtained, and therefore, its crystal data has not been enough yet. At this moment, we have not found a condition that yields each polymorph selectively. Crystal **1-2D4** was obtained by rapid cooling from 100 °C to 10 °C and leaving at the temperature for a few days.

X-ray crystal structures of the fully-networked HexNet crystals (**1-2D1**, **1-2D2**, **1-2D3**, and **1-2D4**) are shown in Fig. 2.[‡] In their structures, all carboxy groups of **1** form self-complementary hydrogen bonded dimer and subsequently form the PhT motif to achieve porous HexNet structures. The anisotoropic displacement ellipsoids of the carboxy groups are more elongated than those of the triphenylene core because of rotational flexibility of the groups, particularly those of the frustrated ones are significant. The HexNet involves two types of triangle pores: one with diameter of 9.7 Å originated from the PhT motif and the other with wider diameter of 14.2 Å. **1-2D1** includes crystallographically independent one molecule of **1**, while **1-2D2**, **1-2D3** and **1-2D4** do two molecules (**I** and **II**). The HexNet sheet in **1-2D2** and **1-2D4** is composed of alternately aligned **I** and **II** molecules (Figs. 2f,h), while in the case of **1-2D3**, molecules **I** and **II** individually form the corresponding HexNet sheets (Fig 2g). These four crystals are composed of conformers of **1** with different rotational angles of the phenylene and carboxy groups: *PMP* for **1-2D1**, *MMP* and *MPP* for **1-2D2**, *PMP* and *PMP* for **1-2D3**, and *PMM* and *PPM* for **1-2D4** (Figs. 2a-d and Table 1). The diverse conformation, in addition to the number of the crystallographically independent molecule (Z'= 1 or 2), results in the versatile location of conformational frustration of the hydrogen-bonded dimer in a HexNet sheet. The frustrated dimer is marked with asterisk in Figs. 2e-h. The NexNet sheet was slip-stacked without interpenetration to give a 3D framework. Layers are laminated with a AB manner for **1-2D1**, **1-2D2**, and **1-2D4**, while a AA'BB' manner for **1-2D3**. Figs. 2i-l show selected three layers of the HexNet viewed from directly above.

To our surprise, stacking manner of the HexNets in these four crystals is nearly identical, despite of their versatile conformation: Averaged inter layer distances of **1-2D1**, **1-2D2**, **1-2D3**, and **1-2D4** are 4.72 Å,4.76 Å, 4.72 Å, and 4.41 Å, respectively, and distances between centroids of the adjacent two triphenylene cores in the crystals are 8.07-8.13 Å, 7.20-8.05 Å, 7.88-8.89 Å, and 7.26-7.37 Å, respectively. XRD patterns simulated from the guest-excluded HexNet frameworks of **1-2D1**, **1-2D2**, **1-2D3**, and **1-2D4** also indicate that they have quite similar periodic profiles (Fig. S2). More detailed stacking way of the HexNets is shown in Fig. 3a, taking

Table 1 Dihedral angle between the phenylene ring and triphenylene skeleton.[a]

	1-2D1	1-2D2	1-2D3	1-2D4
A(I)	+54.7	−67.8*	+55.5	+61.29*
A(II)		−60.9	+53.3	+55.58
B(I)	+57.9*	−55.9	+48.5*	+45.36
B(II)		−60.6	+47.6*	+49.98
C(I)	−58.8	−61.4	−68.1	−49.45*
C(II)		+68.6*	−68.6	+45.72
D(I)	−53.9	−69.7*	−53.8	−52.21
D(II)		+60.7	−53.6	+59.26*
E(I)	+76.1*	+62.9	−84.9*	−46.36
E(II)		+60.3	−84.3*	−54.79
F(I)	+54.9	+61.6*	+62.6	−50.16*
F(II)		+58.5	+65.4	−42.95
conformer (I)	*PMP*	*MMP*	*PMP*[b]	*PMM*
(II)		*MPP*	*PMP*[b]	*PPM*

[a.] An asterisk (*) denotes that the conformational frustration is located in the corresponding peripheral group. [b.] Phenylene ring at the E position has nearly orthogonal and the sign of dihedral angle is opposite to that at F position. However, the conformation at the E-F bay area can denote as *P*, considered the sign of the dihedral angle at F position.

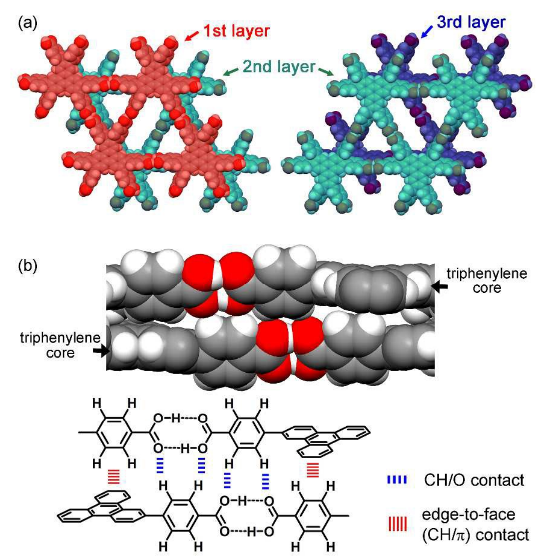

Fig. 3 (a) Stacking manners of the adjacent two rhombic motifs in **1-2D1**. (b) Leading intermolecular interactions observed between the adjacent HexNet sheets of **1-2D1**. CH/O interactions between hydrogen atoms of the phenylene rings and oxygen atoms of the carboxy groups (blue dash line). Edge-to-face contacts (CH/π interactions) between hydrogen bonds of the phenylene rings and π-conjugated plane of the triphenylene ring (red dash line). The other three polymorphs also have the same intermolecular interactions.

1-2D1's structure as a representative example. Rhombic frame, a motif of the HexNet, stacks with another rhombic frame lying on the neighboring sheet in an inverted way so as that these frames contact each other. Intermolecular interactions to make the rhombic frame stacked in the unique manner are self-complementary CH/O contacts between hydrogen atoms of the phenylene groups and oxygen atoms in the carboxy groups, as well as CH/π contacts between the phenylene groups and triphenylene plane (Fig. 3b). π/π Interaction between the triphenylene parts, on the other hand, is not observed because of steric hindrance of the phenylene groups: An averaged interplanar distance is 4.5 Å.

Solvent accessible volume and cavity ratio for the unit cell of the layered HexNet crystals are 2241.0Å^3 (54.4%) for **1-2D1**, 4480.4 Å^3 (54.1%) for **1-2D2**, 4466.8 Å^3 (54.4%) for **1-2D3**, and 3827.8 Å^3 (50.0%) for **1-2D4**.[10] The methyl benzoate molecules accommodated in the void space are highly disordered and many of them were not capable of being refined crystallographically.[†] Because of the guet disorder, the completeness of the crystallogarphic data is relatively low for all crystals. Numbers of the methyl benzoate molecule refined are 1, 0, and 2 for **1-2D1**, **1-2D2**, and **1-2D3**, respectively, while 5 for **1-2D4**. Since the former three crystals were formed at 100 °C, such the high temperature condition enhanced thermal molecular motion, resulting in significant disorder of the guest molecules. However, it is noteworthy that the position and orientation of the refined guest molecules in the void space is different among the polymorphs. (Fig. S3). This implies that, even the stacking manner of the HexNet sheet is nearly the same, the inclusion behavior of the guest molecules is strongly influenced by conformational differences (i.e. dihedral angle and location of the conformational frustration).

In conclusion, we first reported four polymorphs of 2D-nCOF crystals composed of layered HexNets. The structural diversity was brought not from topology or stacking manner of HexNets but from more subtle structural factors such as rotational conformation and location of the conformational frustration in the PhT motifs. This kind of structural diversity has been difficult to be discussed in conventional porous 2D frameworks, such as 2D-COFs. Thus, precise characterization of the present polymorphic HexNet crystals can give a new insight to porous 2D-COFs.

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Notes and references

‡ Crystal data for **1-2D1**: $(C_{60}H_{36}O_{12})\cdot(C_8H_8O_2)$, *Fw* = 1085.09, *a* = 14.5303(5) Å, *b* = 14.9461(6) Å, *c* = 20.2579(8) Å, α = 102.3554(18)°, β = 101.5441(16)°, γ = 99.0611(17)°, *V* = 4117.4(3) Å^3, *T* = 153 K, triclinic, space group *P*-1, *Z* = 2, 46186 collected, 14502 unique (R_{int} = 0.0798) reflections, the final *R*1 and w*R*2 values 0.091 (I > 2.0σ(I)) and 0.326 (all data), respectively. Crystal data for **1-2D2**: $2(C_{60}H_{36}O_{12})$, *Fw* = 1897.87, *a* = 15.4431(3) Å, *b* = 20.9868(4) Å, *c* = 28.0527(6) Å, α = 103.3620(13)°, β = 98.9655(11)°, γ = 105.8050(10)°, *V* = 8275.7(3) Å^3, *T* = 273 K, triclinic, space group *P*-1, *Z* = 2, 87842 collected, 22359 unique (R_{int} = 0.103) reflections, the final *R*1 and w*R*2 values 0.127 (I > 2.0σ(I)) and 0.389 (all data), respectively. Crystal data for **1-2D3**: $2(C_{60}H_{36}O_{12})\cdot 2(C_8H_8O_2)$, *Fw* = 2170.17, *a* = 19.1278(2) Å, *b* = 22.4030(2) Å, *c* = 22.3984(2) Å, α = 60.0460(6)°, β = 87.4093(5)°, γ = 81.0545(4)°, *V* = 8209.05(14) Å^3, *T* = 93 K, triclinic, space group *P*-1, *Z* = 2, 44304 collected, 26851 unique (R_{int} = 0.045) reflections, the final *R*1 and w*R*2 values 0.125 (I > 2.0σ(I)) and 0.445 (all data), respectively. Crystal data for **1-2D4**: $2(C_{60}H_{36}O_{12})\cdot 5(C_8H_8O_2)$, *Fw* = 2578.62, *a* = 12.8218(9) Å, *b* = 15.8756(11) Å, *c* = 38.6736(18) Å, α = 93.295(3)°, β = 93.991(3)°, γ = 102.380(3)°, *V* = 7649.3(8) Å^3, *T* = 213 K, triclinic, space group *P*-1, *Z* = 2, 42603 collected, 22464 unique (R_{int} = 0.058) reflections, the final *R*1 and w*R*2 values 0.108 (I > 2.0σ(I)) and 0.360 (all data), respectively. CCDC numbers: **1-2D1** (CCDC-1424089), **1-2D2** (CCDC-1424090), **1-2D3** (CCDC-1424091) and **1-2D4** (CCDC-1424086) 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/.

† ^{1}H NMR spectrum of the crystalline bulk containing **1-2D1**, **1-2D2** and **1-2D3** dissolved in DMSO-d_6 indicates that no DMF but methyl benzoate molecules are included in the crystals with a 1:6 molar ratio of **1** and methyl benzoate (Fig. S4). Moreover, thermal gravimetric analysis curve reaches a bottom at 240 °C with weight loss of 47%, which is in good agreement with a theoretical value (46.3%) assuming a 1:6 ratio of **1** and methyl benzoate ratio (Fig. S5). These results are consistent with a size of cavity volume in the crystals.

1 A. G. Skater, A. I. Cooper, *Science*, 2015, **348**, aaa8075.
2 A. P. Côté, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger, O. M. Yaghi, *Science*, 2005, **310**, 1166.
3 (a) X. Feng, X. Ding, D. Jiang, *Chem. Soc. Rev*., 2012, **41**, 6010; (b) S.-Y. Ding, W. Wang, *Chem. Soc. Rev.,* 2013, **42**, 548.
4 Recent examples, see; (a) M. Dogru, M. Handloser, F. Auras, T. Kunz, D. Medina, A. Hartschuh, P. Knochel, T. Bein, *Angew. Chem. Int. Ed.,* 2013, **52**, 2920; (b) H. Yang, Y. Du, S. Wan, G. D. Trahan, Y. Jin, W. Zhang, *Chem. Sic.,* 2015, **6**, 4049; (c) L. A. Baldwin, J. W. Crowe, M. D. Shannon, C. P. Jaroniec, P. J. McGrier, *Chem. Mater.,* 2015 (DOI: 10.1021/acs.chemmater.5b02053).
5 Detailed slipping manner of COF layers was investigated, see: B. Lukose, A. Kuc, T. Heine, *Chem. Eur. J.,* 2011, **17**, 2388.
6 (a) D. J. Duchamp, R. Marsh, *Acta. Crystallogra. B,* **1969**, *25*, 5; (b) F. H. Herbstein, M. Kapon, G. M. Reisner, *J. Inclusion Phenom*., 1987, **5**, 211; (c) R. E. Melendez, C. V. K. Sharma, M. J. Zaworotko, C. Bauer, R. D. Rogers, *Angew. Chem., Int. Ed. Engl.,* 1996, **35**, 2213; (d) A. R. A. Palmans, J. A. J. M. Vekemans, H. Kooijman, A. L. Spek, E. W. Meijer, *Chem. Commun*., 1997, 2247; (e) P. Sozzani, A. Comotti, R. Simonutti, T. Meersmann, J. W. Logan, A. Pines, *Angew. Chem. Int. Ed.,* 2000, **39**, 2695; (f) K. Kobayashi, A. Sato, S. Sakamoto, K. Yamaguchi, *J. Am. Chem*. *Soc.,* 2003, **125**, 3035; (g) P. Sozzani, S. Bracco, A. Comotti, L. Ferretti, R. Simonutti, *Angew. Chem. Int. Ed*., 2005, **44**, 1816; (h) K. E. Maly, E. Gagnon, T. Maris, J. D. Wuest, *J. Am. Chem. Soc*., 2007, **129**, 4306; (i) Y.-B. Men, J. Sun, Z.-T. Huang, Q.-Y. Zheng, *Angew. Chem. Int. Ed.,* 2009, **48**, 2873; (j) X.-Z. Luo, X.-J. Jia, J.-H. Deng, J.-L. Zhong, H.-J. Liu, K.-J. Wang, D.-C. Zhong, *J. Am. Chem. Soc.,* 2013, **135**, 11684; (k) T.-H. Chen, I. Popov, W. Kaveevivitchai, Y.-C. Chuang, Y.-S. Chen, O. Daugulis, A. J. Jacobson, O. Š. Miljanić, *Nature* Commun., 2014, **5**:5131.
7 I. Hisaki, S. Nakagawa, N. Tohnai, M. Miyata, *Angew. Chem. Int. Ed.,* 2015, **54**, 3008.
8 For supramolecular synthon, see; G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.,* 1995, **34**, 2311.
9 The first report of the PhT motif; K. Kobayashi, T. Shirasaka, E. Horn, N. Furukawa, *Tetrahedron Lett.,* 2000, **41**, 89.
10 Calculation was conducted by PLATON software with the following atomic radii: 1.20 Å (H), 1.70 Å (C), 1.52 Å (O). The probe radius was 1.2Å.

