## Electronic supplementary information

#### for

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

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#### 1. General

<sup>1</sup>H and <sup>13</sup>C NMR spectra were measured by a Bruker (600 MHz for <sup>1</sup>H, 150 MHz for <sup>13</sup>C) spectrometer. Mass spectrum data were obtained from a JEOL JMS-700 instrument or autoflex III Bruker. FT-IR spectra of the synthesized compounds were recorded using a using a JASCO FT/IR-4200 spectrometer. Single crystal Xray analysis. For crystal 1-2D1, diffraction data were collected on a Rigaku R-AXIS RAPID diffractometer with a 2-D area detector using graphite-monochromatized Cu-K $\alpha$  radiation ( $\lambda = 1.54187$  Å). The cell refinements were performed with software equipped in a Rigaku R-AXIS RAPID system. For crystals 1-2D2, 1-2D3, 1-2D4, 1-1D, and 1-2D(IMP), diffraction data were collected on a CCD (Q315, ADSC or MX225HE, Rayonix) with the synchrotron radiation ( $\lambda = 0.8000$  Å) monochromated by the fixed exit Si (111) double crystal. The cell refinements were performed with HKL2000 software.<sup>S1</sup> Direct methods (SHELXD2013<sup>S2</sup>) were used for the structure solution of the crystals. All calculations were performed with the observed reflections  $[I > 2\sigma(I)]$  with the program CrystalStructure crystallographic software packages,<sup>S3</sup> except for refinement which was performed using Shelx12013.<sup>S2</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed in idealized positions and refined as rigid atoms with the relative isotropic displacement parameters. SQUEEZE function equipped in the PLATON program was used to remove disordered solvent molecules in the cavities.<sup>S4,S5</sup> Synchrotron radiation experiments were undertaken at BL38B1 in SPring-8 with approval of JASRI (proposal Nos. 2014B1168 and 2015A1174). Powder diffraction X-ray analysis. PXRD data were collected on a Rigaku RINT-2000 using graphitemonochromatized Cu-K $\alpha$  radiation ( $\lambda = 1.54187$  Å) at room temperature.



Scheme S1. Synthesis of 1

### 2. Synthesis and characterization of 1

**2,3,6,7,10,11-hexakis(4-methoxycarbonylphenyl)triphenylene 2.** 2,3,6,7,10,11-Hexabromotriphenylene (3.69 g, 5.25 mmol), (4-methoxycarbonylphenyl)bronic acid (8.51 g, 47.3 mmol), Na<sub>2</sub>CO<sub>3</sub> (5.01 g, 47.3 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (3.64 g, 3.15 mmol) were placed in a reaction flask under a nitrogen atomosphere. A mixed solvent of toluene (120 mL), 1,4-dioxane (75 mL), and methanol (75 mL) deoxygenated by N<sub>2</sub> bubbling was

added and the resulting mixture was stirred for 46 h under reflux condition. After the solvent was removed in vacuo, the reaction mixture was extracted with  $CHCl_3$ , washed with water and brine, and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed in vacuo, and the resulting solid was rinsed with small amount of  $CHCl_3$ . The effluent was then passed through column of silicagel ( $CHCl_3$ :hexane = 7:3) to give another solid. The solid products were combined and purified by column chromatography (silicagel,  $CHCl_3$ :AcOEt = 19:1) to give **2** (5.26 g, 96%) as a pale yellow solid.

**2:** mp. 311 °C (decomp.), <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) :  $\delta$  8.73 (s, 6H) , 7.98 (d, J = 8.4 Hz, 12H) , 7.38 (d, J = 8.4 Hz, 12H) , 3.93 (s, 18H) ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) :  $\delta$  167.0, 145.7, 139.7, 130.2, 129.8, 129.5, 129.1, 125.9, 52.4 ppm. FT-IR (KBr) : 1717, 1608, 1436, 1281, 1180, 1104, 1019, 964.0, 894.6, 857.2, 821.5, 775.5, 751.9, 713.1 cm<sup>-1</sup>. HR-MS (FAB) calcd. for C<sub>66</sub>H<sub>48</sub>O<sub>12</sub> [M]<sup>+</sup> 1032.3146 ; found 1032.3148.

**2,3,6,7,10,11-hexakis(4-carboxyphenyl)triphenylene 1.** Thiphenylene derivative **2** (3.00, 2.82 mmol) and 10% aqueous solution of KOH (26 mL) in THF (200 mL) was stirred for 50 h at 50 °C. THF was removed in vacuo and the residual aqueous solution was passed through filter paper. The filtrate was acidized with 6M  $HCl_{aq}$  to yield precipitate. The precipitate was filtered, washed with water, and dried in vacuo to give **1** (2.58g, 93%) as a yellow solid.

1: m.p. : 374 °C (decomp.). <sup>1</sup>H NMR (600 MHz, DMSO- $d_6$ ) :  $\delta$  9.00 (s, 6H) , 7.83 (d, J = 8.4 Hz, 12H) , 7.44 (d, J = 8.4 Hz, 12H) ppm. <sup>13</sup>C NMR (150 MHz, DMSO- $d_6$ ) :  $\delta$  167.2, 144.9, 139.2, 130.4, 129.2, 129.1, 128.9, 126.1 ppm. FT-IR (KBr) : 2361, 1734, 1700, 1652, 1607, 1560, 1419, 1290, 1180, 1089, 1016, 856.7, 777.9, 711.8, 647.0, 546.0 cm<sup>-1</sup>. HR-MS(FAB<sup>-</sup>) : m/z calc. for C<sub>60</sub>H<sub>35</sub>O<sub>12</sub> [M]<sup>-</sup> 947.2129 ; found 947.2160.

## 3. Crystallographic analysis

**Recrystallization procedure.** A hot solution of triphenylene derivative **1** (20 mg) dissolved in DMF (1.0 mL) and methyl benzoate (750  $\mu$ L) prepared at 100 °C was left at 25 °C (room temperature), 50 °C, 100 °C, and 10 °C, until crystalline precipitate was formed to yield crystals, whose structures depend on the crystallization temperature as shown in Scheme S2.



Scheme S2. Recrystallization conditions of 1 and the resulting crystalline forms depending on the crystallization temperature.



**Figure S1.** (a) Selected crystal structures of incompletely networked crystal **1-1D** obtained by recrystallization from a DMF/metyl benzoate solution at room temperature. (b) Hydrogen bonds formed by the carboxy groups: **S** (Self-complementary dimerization), **H** (hetero-hydrogen bond with DMF molecule), and **T** (truncated hydrogen bond). DMF molecules are shown in green. Solvent molecules accommodated in the crystals are omitted for clarity.



**Figure S2.** Crystal structures of imperfect HexNet crystal  $1-2D_{(IMP)}$  obtained by recrystallization from a DMF/metyl benzoate solution at 50 °C. (a) Anisotropic displacement ellipsoid plots of the crystallographically independent two molecules I and II. The ellipsoids were drawn in 75% probability to enhance atomic displacements. (b) Truncated hydrogen bonds formed by the carboxy groups. (c) Imperfect 2D-HexNet structure, in which truncated dimer is marked by double asterisk (\*\*). (d) Layered structure of the HexNet, in which three layers are shown for clarify.

	1-1D	1-2D <sub>(IMP)</sub>
Formula	$(C_{60}H_{36}O_{12})\cdot(C_8H_8O_2)\cdot4(C_3H_7NO)$	2(C <sub>60</sub> H <sub>36</sub> O <sub>12</sub> ), 5(C <sub>8</sub> H <sub>8</sub> O <sub>2</sub> ), 2(C <sub>3</sub> H <sub>7</sub> NO)
Mw.	1377.46	2724.81
crystal system	monoclinic	monoclinic
space group	<i>P</i> -1	P-1
<i>a</i> / Å	14.5203(1)	15.3014(3)
<i>b</i> / Å	16.0332(1)	20.3447(5)
<i>c</i> / Å	18.9168(2)	28.1624(6)
α/°	103.2090(4)	101.571(2)
$\beta / \circ$	94.7720(4)	99.3676(17)
γ/°	106.8690(5)	103.5540(8)
$V/\text{\AA}^3$	4049.7906	8144.6(3)
Ζ	2	2
<i>R</i> 1	0.1103	0.1161
wR2	0.3972	0.3746
Т/К	93	213
CCDC no.	1424087	1424088

# Table S1. Crystal data of 1-1D and $1-2D_{(IMP)}$



Figure S3. PXRD patterns simulated from guest-excluded HexNet flameworks of 1-2D1, 1-2D2, 1-2D3, and 1-2D4.



Figure S4. Location and orientation of the guest molecules in void space of (a) 1-2D1, (b) 1-2D2, (c) 1-2D3, and (d) 1-2D4. In the case of 1-2D2, no guest molecules were refined. On the other hand, crystallographically independent one, two, and five guest molecules were refined for 1-2D1, 1-2D3, and 1-2D4, respectively.

#### 4. Determination of Host Guest ratio of the HexNet crystals

PXRD measurements of as-formed bulk crystals of HexNets obtained at 100 °C (**1-2D1**, **1-2D2**, and/or **1-2D3**) by a general diffractometer in laboratory provided only weak and ambiguous PXRD patterns due to the low electron density contrast generated by disordered MeBz molecules within the pores. This made it difficult to identify a crystal form of the bulk sample. Therefore, crystalline bulk used in analyses can consists of either **1-2D1**, **1-2D2**, or **1-2D3** or more than one of them.



Figure S5. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ) spectrum of the HexNets crystalline bulk dissolved in DMSO- $d_6$ .



Figure S6. Thermal gravimetric analysis of the HexNets crystalline bulk.

# 5. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the synthesized compounds







**Figure S8.** <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of triphenylene derivative **2**.





Figure S10. <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>) spectrum of triphenylene derivative 1.

# 6. References

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