## Supporting Information for *Chemical Communications*

# Gas-induced Solid State Transformation of an Organic Lattice: From Nonporous to Nanoporous

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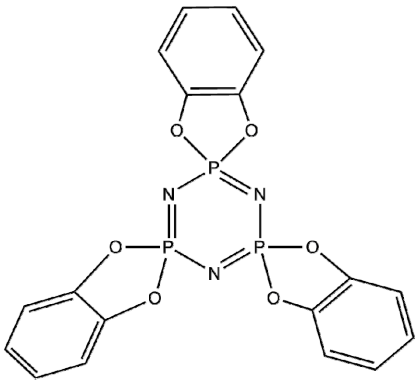
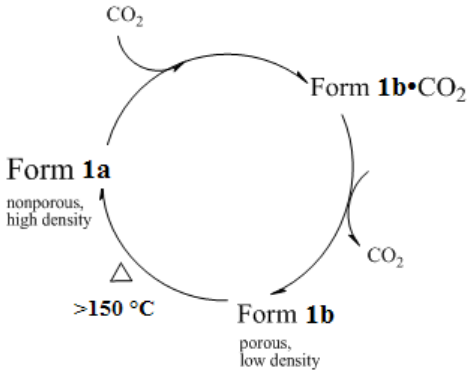
## SUPPLEMENTARY INFORMATION

**Experimental procedures:**

**1. Preparation of the materials:** TPP **1** was synthesized according to the reported procedure. The purity of **1** has been checked by $^1$HNMR. Nonporous **1a** crystals were obtained by triple sublimation of **1** at 175 °C under vacuum. Alternatively, desolvation of TPP benzene inclusion compound at 125 °C under vacuum can also afford pure **1a** crystalline solids. The phase purity of resulting **1a** solids was checked by powder X-ray diffraction (PXRD). It is reported that desolvation of TPP benzene inclusion compoundat 70 °C under vacuum would afford empty-channel **1b** crystals, which were used to calculate powder X-ray diffraction pattern of **1b** solids. **1b** solids can be transformed to thermodynamically stable form **1a** when heated at 150 °C.[1]



**1**



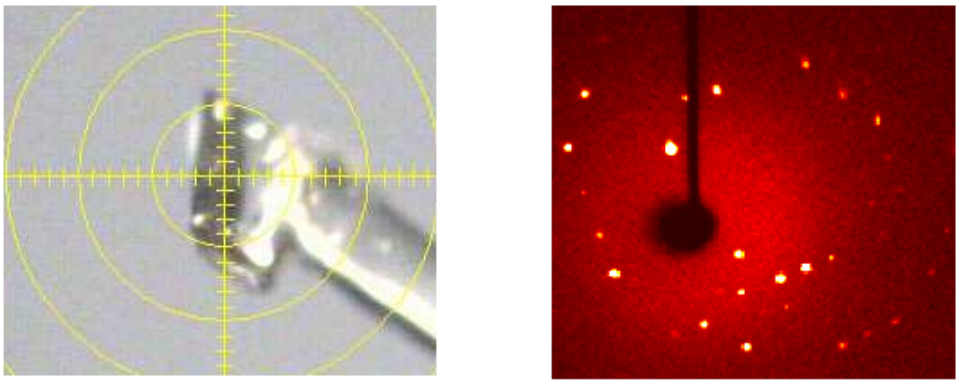

**2. Single crystal X-ray Collection:** Single crystal X-ray data of **1a** crystals was collected under $N_2$ flow at 173 K on a Bruker Apex II diffractometer equipped with a fine-focus sealed-tube X-ray source (Mo-Kα radiation, λ =0.71073 Å).[2]

**Crystal data of 1a**: $C_{36}H_{24}N_6O_{12}P_6$, $M$ = 918.43, Colorless Block, 0.20 x 0.15 x 0.10

mm$^3$, monoclinic, space group $P2_1/n$ (No. 19), $a$ = 24.969(6), $b$ = 5.8268(14), $c$ = 25.895(6) Å, $\beta$ = 96.015(3)°, $V$ =3746.7(15) Å$^3$, $Z$ = 4, 29147 reflections collected, 5430 unique ($R_{int}$ = 0.0514). Final *GooF* = 1.104, $R_1$ = 0.1129, $wR_2$ = 0.3025, $R$ indices based on 4821 reflections with I > 2sigma(I) (refinement on $F^2$).

Unit cell parameters of **1b**: $a = b$ = 11.454 Å, $c$ = 10.16 Å, $\alpha = \beta$ = 90°, $\gamma$ = 120°, $V$ = 1154.35 Å$^3$.

**(A)**



**(B)**

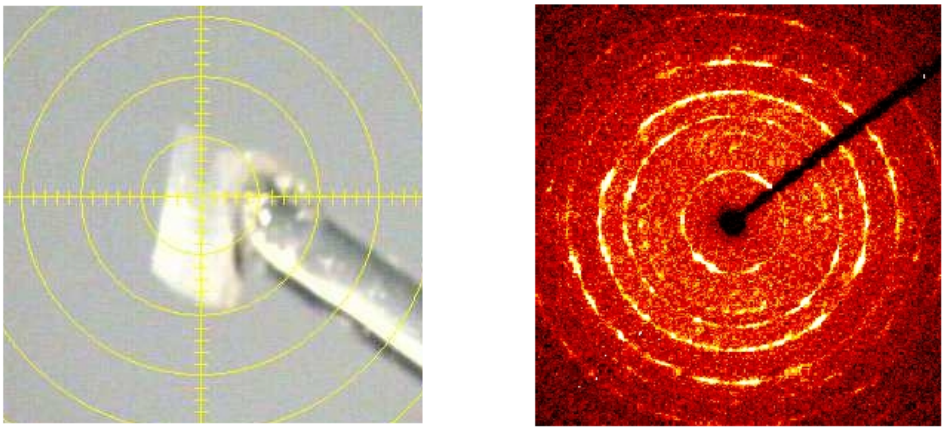


**Figure S1**. (A) A fresh single crystal of **1a** obtained by sublimation of **1** at 175 °C. (B) The same crystal of (A) exposed to $CO_2$ at 350 psi and room temperature for 15 minutes shows a diffused pattern, implying the crystal doesn't retain the single crystallinity.

**3. Powder X-ray diffraction (PXRD)**: Powder X-ray diffraction data were collected at room temperature on an Bruker D8 Advanced Diffraction System equipped with high pressure devices using Cu-Kα radiation (λ= 1.5418 Å). Measurements were made using a step-scanning technique with a fixed time of 0.02$^{o}$ /min 2θ. Data points were obtained from 5 to 30$^{o}$ 2θ. PXRD analyses were performed using fine ground samples. The $CO_2$ gas used to pressurize the solid is purchased from Air liquide USA (Purity: 99.999%).

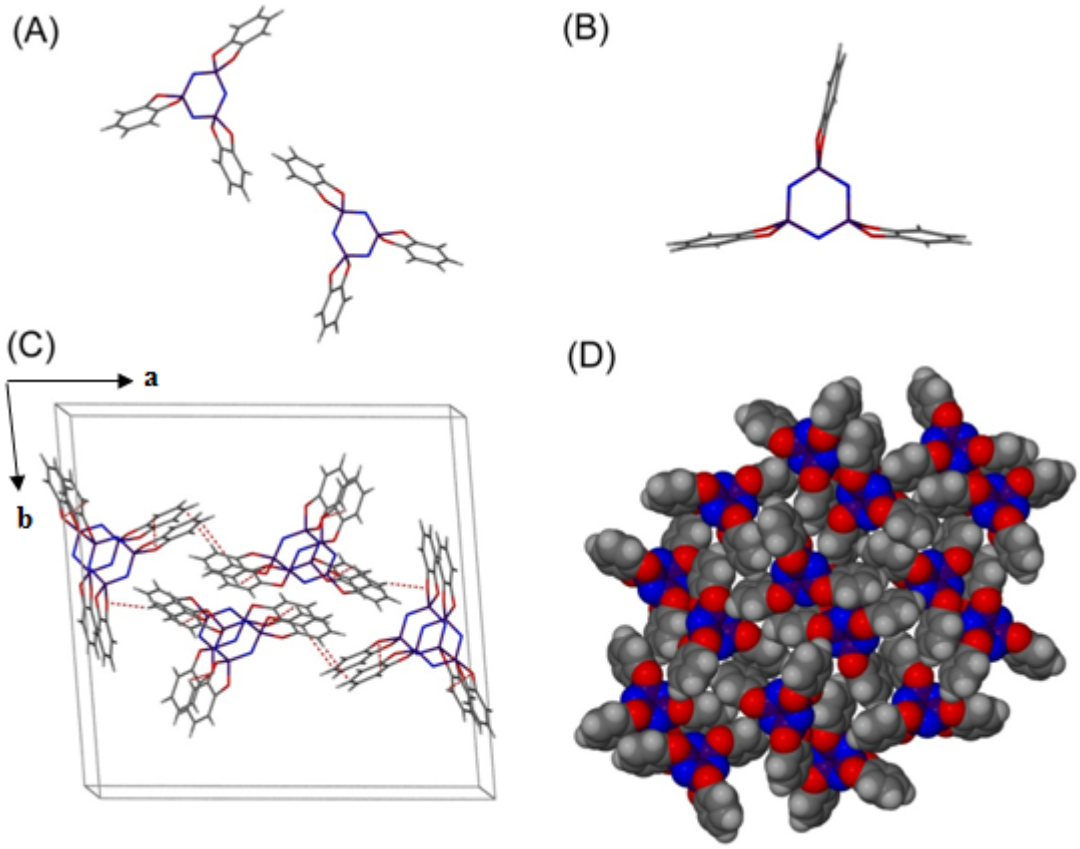



**Figure S2.** (A) Asymmetric unit of **1a** crystals. (B) Conformation of molecules of **1** in **1a** crystals. The dihedral angles between the planes O-P-O and O-phenyl-O are 10.7, 19.3 and 24.6° respectively. (C) Intermolecular hydrogen bonding interactions (shown as dash lines) consolidate the host framework of **1a** (C-H---O = 3.172-3.433 Å). (D) Space filling view of molecular packing revealing the nonporous nature of **1a** solid. View down the *c* axis. (Blue: Nitrogen, Red: Oxygen, Purple: Phosphine, Gray: Carbon. White: Hydrogen)

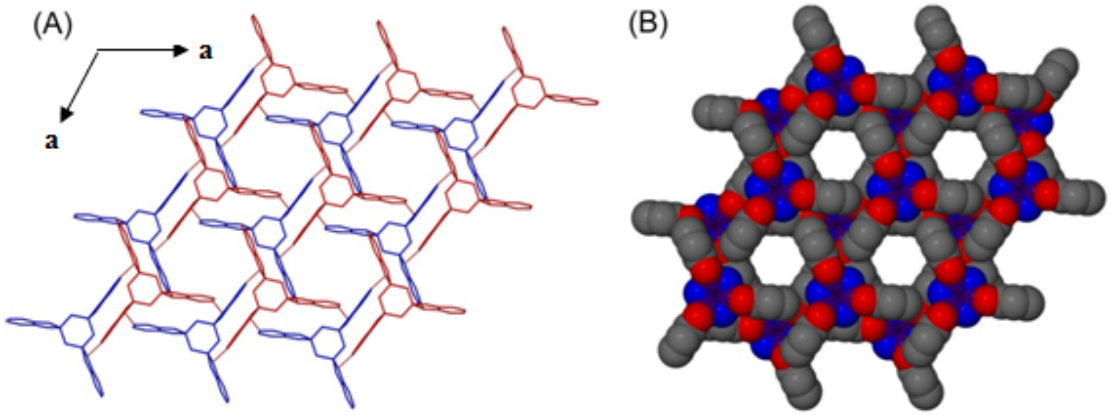



**Figure S3**. (A) Intermolecular hydrogen bonding array links AB layers and consolidates the host framework of **1b** crystals. Hydrogen bonds are shown as dash lines. (B) Crystal structure of **1b** in the nanoporous hexagonal modification viewed along the channel axis.[3] Hydrogen atoms were omitted for clarity (Blue: Nitrogen, Red: Oxygen, Purple: Phosphine, Gray: Carbon.)

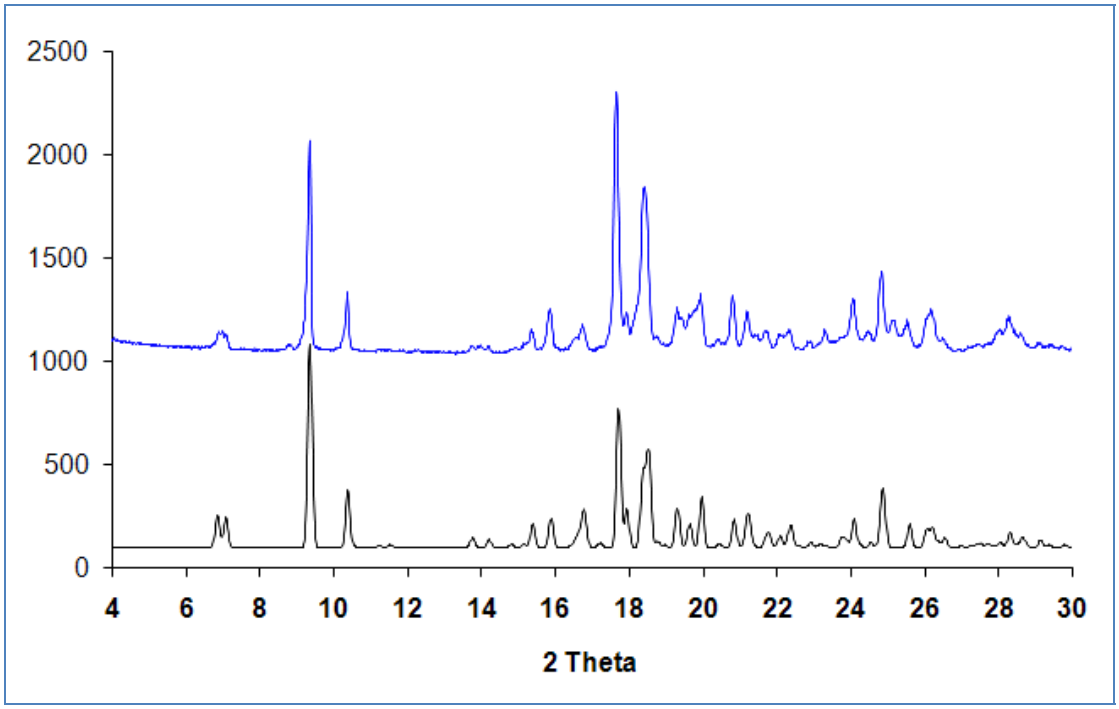



**Figure S4**. Experimental and calculated powder X-ray diffraction patterns for **1**a crystals obtained by triple sublimation of **1** at 175 ºC under vacuum. (Blue: experimental; Black: simulated).

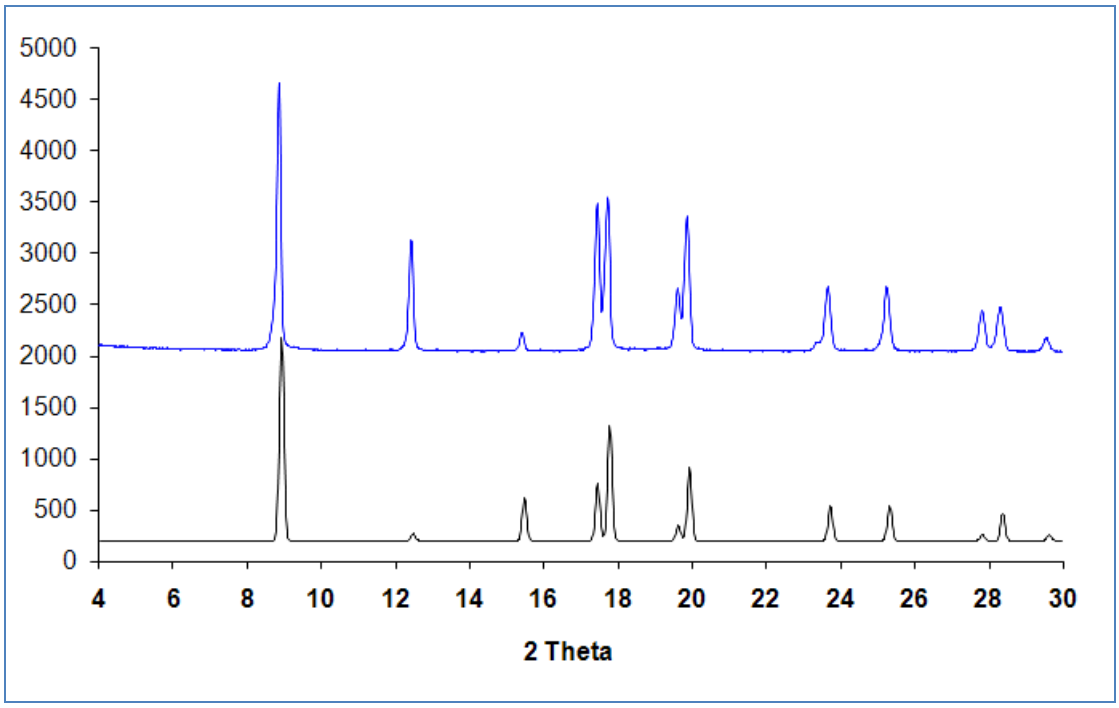



**Figure S5**. (Top) Experimental powder X-ray diffraction patterns of **1b** solids obtained by pressurization of **1a** solid with 350 psi $CO_2$ for 3 hrs. (Bottom) Simulated powder X-ray diffraction pattern from single crystal X-ray data of **1b** (CSD **DOFSUM01**).[1]

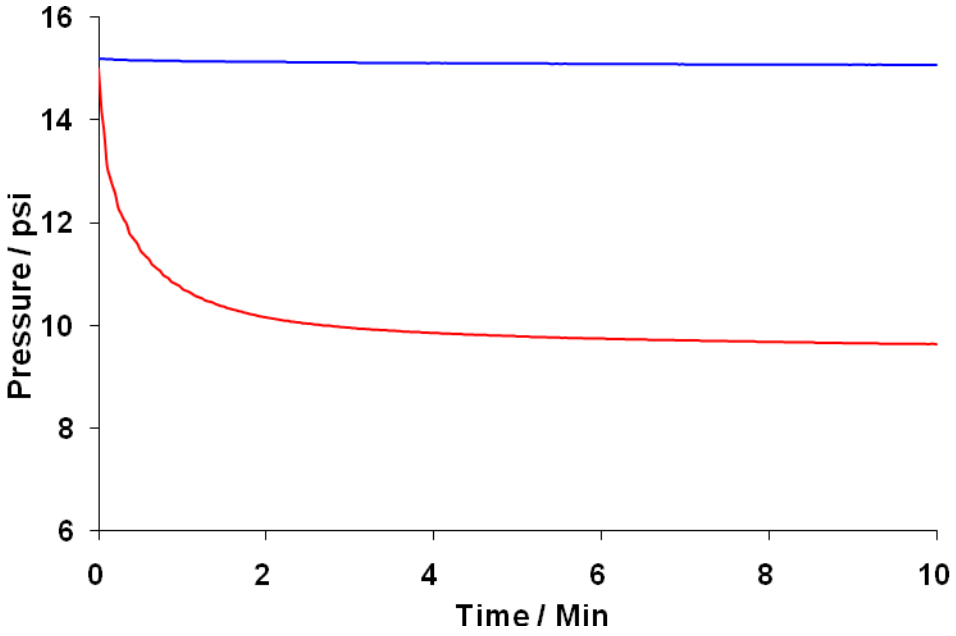



**Figure S6**. (Blue) Fresh **1a** solid shows no uptake of $CO_2$ at 1 bar and room temperature, consistent with its nonporous nature. (Red) **1b** converted from **1a** shows an uptake of $CO_2$ up to 4.5 wt % at 1 bar and room temperature.

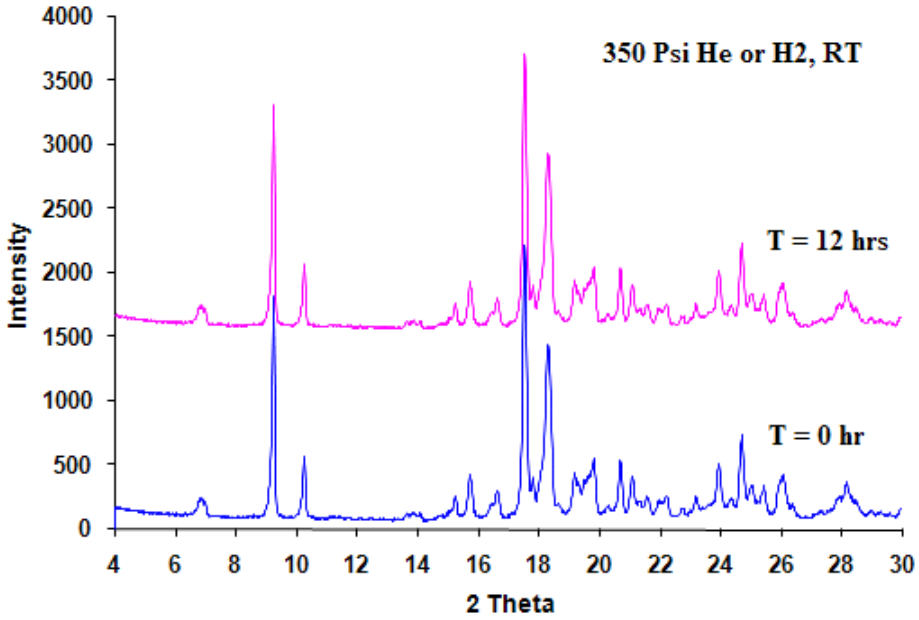



**Figure S7.** Effect of Hydrogen and Helium gases on **1a** at 350 psi and room temperature over 12 hrs indicates no phase transformation.

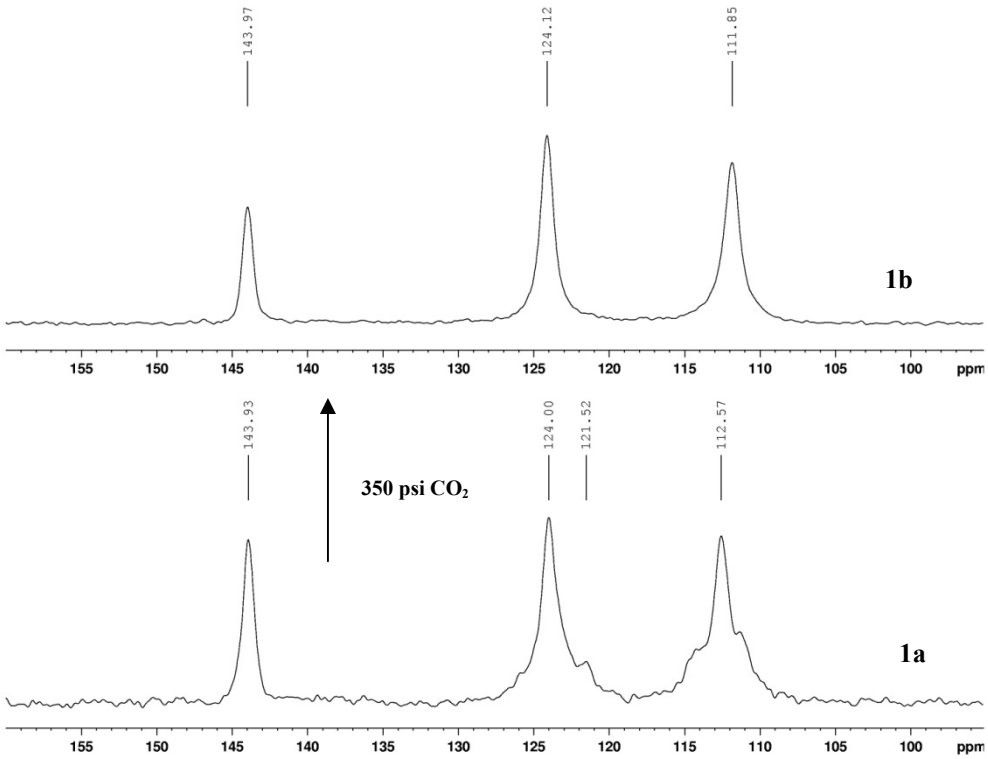



**Figure S8**. Solid state $^{13}C$ NMR studies of **1a** show the peaks of aromatic carbons of **1** become narrower and more uniform after transformation, indicating the host molecule changes its conformation to higher symmetry ($D_{3h}$). The external chemical shift reference was the CO carbon of glycine at 176.03 PPM.

Reference:

1 P. Sozzani, S. Bracco, A. Comotti, L. Ferretti, R. Simonutti, *Angew. Chem.; Int. Ed*. **2005**, 44, 1816. Also see the supporting information.

2 The structure of **1a** is recollected in order to calculate the volume of lattice voids in **1a** crystals.

3 The structure of **1b** reported in ref 1 (CSD **DOFSUM01)** was used to generate the figures.