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 compound at 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

![Diagram of TPPO](image)

2. **Single crystal X-ray Collection:** Single crystal X-ray data of 1a crystals was collected under N₂ flow at 173 K on a Bruker Apex II diffractometer equipped with a fine-focus sealed-tube X-ray source (Mo-Kα radiation, $\lambda$ =0.71073 Å).²

**Crystal data of 1a:** C₃₆H₂₄N₆O₁₂P₆, $M = 918.43$, 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, $\beta = 96.015(3)^\circ$, $V = 3746.7(15)$ Å$^3$, $Z = 4$, 29147 reflections collected, 5430 unique ($R_{int} = 0.0514$). Final $GooF = 1.104$, $R_I = 0.1129$, $wR_2 = 0.3025$, $R$ indices based on 4821 reflections with $I > 2\sigma(I)$ (refinement on $F^2$).

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

**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 ($\lambda = 1.5418$ Å). Measurements were made using a step-scanning technique with a fixed time of 0.02° /min 2θ. Data points were obtained from 5 to 30° 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. 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 1a crystals obtained by triple sublimation of 1 at 175 °C 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<sub>2</sub> for 3 hrs. (Bottom) Simulated powder X-ray diffraction pattern from single crystal X-ray data of 1b (CSD DOFSUM01).<sup>1</sup>
**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.