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A coordination network that reversibly switches between two nonporous polymorphs and a high surface area porous phase

Ai-Xin Zhu,†‡§ Qing-Yuan Yang,†‡§¶ Amrit Kumar,‡ Clare Crowley,‡ Soumya Mukherjee,‡ Kai-Jie Chen,‡ Shi-Qiang Wang,‡ Daniel O’Nolan,‡ Mohana Shivanna,‡ and Michael J. Zaworotko*‡

†Faculty of Chemistry and Chemical Engineering, Yunnan Normal University, Kunming 650500, China.
‡Department of Chemical Sciences and Bernal Institute, University of Limerick, Limerick V94 T9PX, Republic of Ireland.
§School of Chemical Engineering and Technology, Xi’an Jiaotong University, Xi’an 710049, China

Supporting Information Placeholder

ABSTRACT: We report a 2-fold interpenetrated primitive cubic (pcu) network X-pecu-5-Zn, [Zn(2)(DMTDC)(dpe)] (H2DMTDC = 3,4-dimethylthieno[2,3-b]thiophene-2,5-dicarboxylic acid, dpe = 1,2-dif-4-pyridyl)ethylene), that exhibits reversible switching between an as-synthesized “open” phase, X-pecu-5-Zn-α, and two nonporous or “closed” polymorphs, X-pecu-5-Zn-β and X-pecu-5-Zn-γ. There are two unusual features of X-pecu-5-Zn. The first relates to its sorption properties, which reveal that the α form exhibits high CO2 uptake (ca. 255 cm3/g at 195K) via reversible closed-to-open switching (type F-IV isotherm) of the type desirable for gas and vapor storage; there are only three other reports of porous materials that combine these two features. Second, we could only isolate the β form by activation of the CO2 loaded α form and it persists through multiple CO2 adsorption/desorption cycles. We are unaware of a new polymorph having been isolated in such a manner. The observed phase changes of X-pecu-5-Zn-α occur in single-crystal-to-single-crystal fashion enabled structural characterization of the three forms; γ is a coordination isomer of α and β, both of which are based upon “paddlewheel” clusters.

That we are in the “Age of Gas” requires development of more energy efficient technologies for gas storage and/or delivery.1 Considerable attention has been directed toward the use of porous crystalline adsorbents with high surface area2 as an alternative to existing energy intensive technologies such as compression and liquefaction. Metal-organic materials (MOMs),3 especially metal-organic frameworks (MOFs)4 and porous coordination polymers (PCPs),5 have emerged as a class of porous materials that offers great potential for gas storage/delivery applications, especially natural gas (NG) storage. They are of interest thanks to their modularity, high porosity and pore tunability.6 However, no rigid MOM yet meets the requisite properties for practical deployment in NG storage applications owing to reduced working capacity that results from the type I isotherms characteristic of microporous materials.7 Flexible MOMs (FMOMs) offer a potential solution to this problem as they can “breathe”, i.e. contract under reduced gas pressure and expand under increased pressure. Consequently, they tend to exhibit ‘S-shaped’ or stepped adsorption isotherms that result from guest-induced structural transitions.8 Such adsorption isotherms can enhance working capacity between the storage and deliverable pressures.9 However, although there are >20,000 porous MOMs reported in the literature,10 most of them are rigid physiosorbents with type-I sorption isotherms. Our survey of the literature revealed ca. 150 FMOMs and most transform between less open (small pore) and more open (large pore) phases (Type F-I and Type F-II isotherms).10 Unfortunately, such isotherms offer little advantage over Type I isotherms as they retain adsorbate at low (deliverable) pressure. FMOMs with Type F-IV isotherms that switch between nonporous and porous phases represent the most desirable type for pressure swing adsorption (PSA) gas storage. Unfortunately, there are very few reports of FMOMs with Type F-IV isotherms. Indeed, only DUT-8(Ni),11 X-dia-1-Ni12 and Co(bdp) (bdp2-1,4-benzenedipyrazolate)12 exhibit porous phases with saturation uptake >250 cm3/g.9 Further, multiple cycles of adsorption/desorption cause the gate-opening pressure of DUT-8(Ni) to shift13 and X-dia-1-Ni to degrade.14 In addition, X-dia-1-Ni exhibits strong hysteresis which can also reduce the working capacity. Cu(bdp) (bdp2-1,4-benzenedipyrazolate)12 is the only FMOM with both high working capacity and good recyclability yet it must be handled in a glove box.9b Herein, we introduce a new FMOM that meets the aforementioned criteria, [Zn(2)(DMTDC)(dpe)] (X-pecu-5-Zn, Scheme 1).
Solvothermal reaction of H$_2$DMTDC and dpe with Zn(NO$_3$)$_2$·6H$_2$O in DMF at 105 °C afforded pale yellow, needle-shaped crystals of X-pcu-5-Zn. Previous work on X-pcu-5-Zn-$\alpha$ Single-crystal X-ray diffraction (SCXRD) revealed that X-pcu-5-Zn-$\alpha$ crystallized in triclinic space group P-1. The structure is comprised of dinuclear Zn(II) tetracarboxylate paddlewheels linked via DMTDC ligands to form a square lattice, sql, network (Figure 1a). The sql nets are pillared by dpe linkers to afford a pcu topology net. X-pcu-5-Zn-$\alpha$ is therefore a variant of DMOF-1 with 2-fold offset interpenetration. X-pcu-5-Zn-$\alpha$ exhibits 1D channels with an effective pore diameter of ca. 5.1 × 4.6 Å$^2$ along the c-axis (Figure S1) and calculated guest-accessible volume of 45.7%. TGA revealed that as-synthesized X-pcu-5-Zn-$\alpha$ loses guest molecules (obs. 21.86%; cal. 21.74%) by 110 °C and is stable to 320 °C (Figure S20).

The sql net is once again distorted into a rhombus (Figure 1c) and the interpenetration is centered (Figure S2 and Table S2). PLATON calculations revealed that the $\gamma$ phase is nonporous. TGA of X-pcu-5-Zn-$\gamma$ revealed no weight loss until decomposition at 320 °C (Figure S20). Despite bond breakage, the $\gamma$ form readily reverted to the $\alpha$ form when soaked in DMF at room temperature for 1 d (Figure S8). X-pcu-5-Zn-$\gamma$ was stable in air after exposure to 75% relative humidity (Figure S10) with little water vapor uptake at 298 K (Figure S23). The crystal structures are analysed in Table S2 and Figures S1-S5.

That X-pcu-5-Zn-$\beta$ and X-pcu-5-Zn-$\gamma$ are nonporous but prepared from a porous phase suggested to us that they might exhibit switching to X-pcu-5-Zn-$\alpha$ when exposed to gases. The $\beta$ form indeed exhibited gate-opening for N$_2$ at 77 K with an onset pressure of 340 mmHg but saturation was not attained with uptake of 136 cm$^3$/g at 745 mmHg (Figure 2a). The CO$_2$ sorption isotherm at 195 K displayed switching behaviour (227 mmHg, $P/P_0 = 0.30$) with saturation (ca. 250 cm$^3$/g) at 0.6 bar. In contrast, the $\gamma$ form exhibited no N$_2$ (77 K) induced switching up to 1 bar. CO$_2$ (195 K) sorption revealed a Type F-IV isotherm and saturated uptake (256 cm$^3$/g at 1 bar, gate-opening pressure of 272 mmHg, $P/P_0 = 0.36$) (Figure 2b). Adsorption kinetics were observed to be slower than desorption (Figure S25). Pore volumes of 0.45 cm$^3$/g and 0.46 cm$^3$/g for the $\beta$ and $\gamma$ forms were calculated by assuming liquid filling of CO$_2$ when saturated. These values are close to the 0.43 cm$^3$/g estimated from the crystal structure of X-pcu-5-Zn-$\alpha$. The Langmuir surface areas for the $\alpha$ form calculated from the CO$_2$ sorption isotherms of the $\beta$ and $\gamma$ forms at 195K are 1318 and 1441 m$^2$/g$^3$, respectively. The desorption isotherms exhibit hysteresis with adsorbed CO$_2$ retained for both the $\beta$ and $\gamma$ phases around 183 mmHg ($P/P_0 = 0.24$). Other FMOMs that exhibit single step Type F-IV isotherms are tabulated in Table S4; DUT-8 exhibits similar switching pressures.$^{11}$ Most CO$_2$ isotherms for FMOMs exhibit several steps,$^{14}$ or one step with a much lower closing pressure.$^{15}$ Such stepped isotherms are rare and are yet to be classified by IUPAC.$^{9}$ That X-pcu-5-Zn-$\gamma$ exhibits high CO$_2$ uptake (ca. 255 cm$^3$/g) makes it one of only four FMOMs that exhibit both a Type F-IV isotherm and a saturation uptake >250 cm$^3$/g.$^{9,16}$

PXRD indicated that X-pcu-5-Zn-$\beta$ was recovered after N$_2$ or CO$_2$ sorption (Figure 2c) whereas X-pcu-5-Zn-$\gamma$ had transformed to X-pcu-5-Zn-$\beta$ after CO$_2$ desorption (Figure 2d). Reversible Zn-carboxylate bond rearrangement induced by gases has been reported$^{13,16}$ but to our knowledge X-pcu-5-Zn-$\gamma$ is the first example induced by CO$_2$. To further investigate these transformations, five consecutive cycles of CO$_2$ adsorption at 195 K were conducted for the $\beta$ and $\gamma$ forms (Figure 2e). The switching onset pressure for the first run of X-pcu-5-Zn-$\beta$ is slightly higher than that of the remaining cycles. Previous reports$^{8,17}$ indicate that this observation could be the result of a phase change during degassing (Figure S11). Alternatively, Long and co-workers suggested that a slightly higher energy barrier might be required for the first expansion of a freshly packed sample.$^{9}$ Nevertheless, saturation uptakes and desorption profiles for all cycles are equivalent. The corresponding cycles for X-pcu-5-Zn-$\gamma$ reveal that the gate opening pressure for the second cycle (216 mmHg, $P/P_0 = 0.28$) is below that of the first cycle (272 mmHg, $P/P_0 = 0.36$, Figure 2f). The stress of multiple sorption cycles resulted in reduction in crystallite size (Figures S34-35) but adsorption capacity was unaffected. X-pcu-5-Zn-$\beta$ obtained from exposure of X-pcu-5-Zn-$\gamma$ to CO$_2$ is unstable in air overnight (Figure S13), partially reverting to X-pcu-5-Zn-$\gamma$.
DSC measurement of X-pcu-5-Zn-β after methanol exchange revealed a broad exotherm at 150 °C (Figure S21) suggestive of a polymorphic transformation. PXRD measurements confirmed that the β form and γ form are monotropic polymorphs (Figures S26-27). These samples also converted to the α form after CO₂ sorption at 268 K was performed on X-pcu-5-Zn-β (Figure 3). Once more, the gate adsorption pressure of the α form after multiple cycles of CO₂ sorption/desorption cycles, the Raman bands of X-pcu-5-Zn-γ form also exhibit bands at 1420 cm⁻¹ and 1404 cm⁻¹ corresponding to ν_{vib}(COO⁻) vibration whereas the β form also exhibits a small peak at 1397 cm⁻¹ and a larger peak at 1422 cm⁻¹. A single band at 1419 cm⁻¹ was measured for X-pcu-5-Zn-γ. After both low and high-pressure CO₂ sorption/desorption cycles, the Raman bands of X-pcu-5-Zn-γ became consistent with X-pcu-5-Zn-β.

The single crystal structures of X-pcu-5-Zn-α, X-pcu-5-Zn-β and X-pcu-5-Zn-γ revealed sliding of the two inter-penetrated nets and distortion of the sql nets (Table S2) accompanied transformation between the closed phases and the porous phase. There are no π-π interactions (centroid-centroid distance are >4.0 Å) in any phase but C-H-π interactions exist in the α phase (Figure S3). C-H-O interactions between interpenetrated nets exist in the α and γ forms (Figures S4-5) but there are no such interactions in the β form. Others have suggested that framework flexibility can be associated with sliding of interpenetrated nets, rotation and distortion of organic linkers,9b,12,19 and/or reorientation of coordination bonds.20 These features are observed herein.

In summary, we report a flexible, 2-fold interpenetrated coordination network, X-pcu-5-Zn, with three crystal forms, two
which are non-porous polymorphs. There are three primary messages from this study. First, the $\beta$ form represents to our knowledge the first example of polymorph discovery by desorption. Given the importance of polymorphism in pharmaceutical compounds,22 the approach used herein could supplement crystallization screens to discover new polymorphs.22 Second, the two closed forms, $\beta$ and $\gamma$, exhibit type F-I$\nu$ isotherms with CO$_2$ uptakes >250 cm$^3$/g at cryogenic temperatures and survive multiple adsorption/desorption cycles. X-peu-5-Zn is therefore only the second example of an FMONM that exhibits a type F-I$\nu$ isotherm with uptake capacity of >250 cm$^3$/g and it is recyclable over multiple cycles. Third, X-peu-5-Zn is a variant of DMFOF-12, as such it belongs to one of the most compositionally diverse platforms of coordination networks and we have recently reported on related coordination networks that also exhibit multiple phase transformations.9b,13b Many related compounds with multiple phases are anticipated based upon these observations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXXX. Materials and methods, supporting figures, supporting tables, and supporting references (PDF)

Crystallographic information files (CIF)

AUTHOR INFORMATION

Corresponding Author

*Michael.Zaworotko@ul.ie

Author Contributions

$^\dagger$These authors contributed equally.

Notes

The authors declare no conflicts of interest.

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