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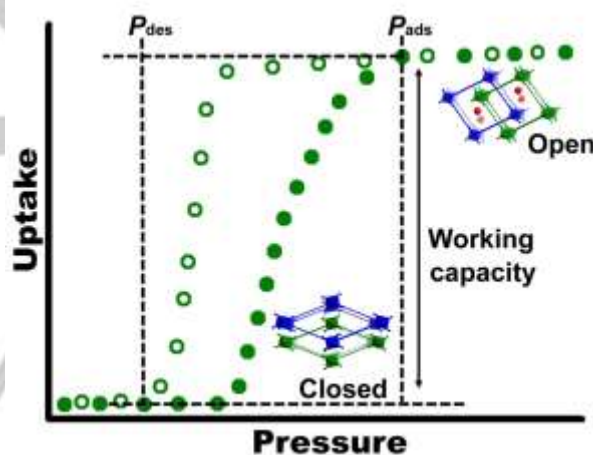
Tuning the gate-opening pressure in a switching pcu coordination network, X-pcu-5-Zn, by pillar ligand substitution

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Abstract: Coordination networks that reversibly switch between closed and open phases are of topical interest since their stepped isotherms can offer higher working capacity for gas storage applications than related rigid porous coordination networks. In order to be of practical utility, the pressures at which switching occurs, the gate-opening and gate-closing pressures. Here we study the effect of linker substitution to fine-tune gate-opening and gate-closing pressure. Specifically, three variants of a previously reported pcu topology MOF, X-pcu-5-Zn, have been prepared. X-pcu-6-Zn, **6** = 1,2-bis(4-pyridyl)ethane (bpe), X-pcu-7-Zn, **7** = 1,2-bis(4-pyridyl)acetylene (bpa) and X-pcu-8-Zn, **8** = 4,4'-azopyridine (apy), each exhibited switching isotherms but at different gate-opening pressures. The N₂, CO₂, C₂H₂ and C₂H₄ adsorption isotherms consistently indicated that the most flexible dipyridyl organic linker, **6**, afforded lower gate-opening and gate-closing pressures. This simple design principle enables rational control of the switching behaviour in adsorbent materials.

Metal-organic materials (MOMs),^[1] especially metal-organic frameworks (MOFs)^[2] and porous coordination polymers (PCPs)^[3] have received considerable attention with respect to their potential utility in gas storage/delivery, especially for natural gas (NG) storage. However, no rigid MOM yet meets the requisite efficiency for practical utility in NG storage due to reduced working capacity that results from their typical type I isotherms.^[4] Approaches to address this challenge include monolithic or hierarchal variants of MOFs^[5] and the development of flexible MOMs (FMOMs), especially those with type F-IV isotherms that result when an FMOM switches between nonporous and porous phases^[6a]. Such isotherms are of interest because they can enhance working capacity between the storage and deliverable pressures (Scheme 1).^[6] Whereas > 20,000 porous MOFs are reported in the literature,^[7] there are few reports of FMOMs with type F-IV isotherms,^[6,8-10] including just six with uptake capacities

> 250 cm³/g,^[6a-b,8-9] and only two with good sorption recyclability.^[6b,9] It should be noted that the gate-opening / gate-closing pressures of Type F-IV isotherms can offer optimal working capacity if the loading/deliverable pressures match the phase change pressures. Moreover, different sorbates require result in different gate-opening/gate-closing pressures because each sorbate has distinct interactions with the same MOM. Ability to fine-tune the phase change pressure in FMOMs is crucial to enabling the development of bespoke porous materials for gas storage/delivery applications.



Scheme 1. Unlike rigid porous materials, the working capacity of a switching material with a type F-IV isotherm will be equal to the uptake capacity if the switching events between open and closed phases occur at the right pressure.

Crystal engineering approaches can be used to tailor the structural of FMOMs remains understudied.^[11-17] In this context, linker ligand modification is perhaps the most established strategy to modulate flexibility and porosity.^[12-17] For example, the phase change pressures of MIL-53,^[13] [Co(bdp)],^[14] and some pillared-layered structures^[15] can be systematically controlled by altering ligand functionality. Nevertheless, little attention has been paid to exploiting ligand functionality to modulate those FMOM platforms that feature type F-IV isotherms.^[14,16,17] Kitagawa and Rosseinsky's groups independently reported the fine-tuning of CO₂ gate-opening pressures by varying ratios of two constituent functional groups.^[16,17] Long *et al.* demonstrated that CH₄ induced gate-opening pressures in flexible frameworks can be systematically controlled by ligand functionalization.^[14] Herein we address the use of ligand substitution to control the flexibility and switching features of certain classes of FMOMs.

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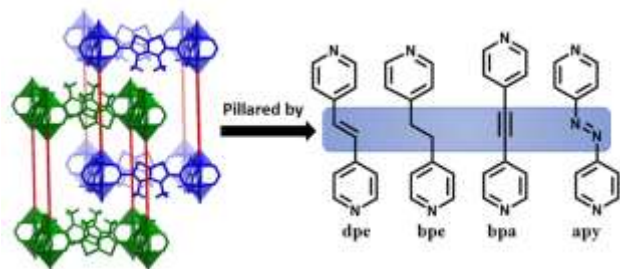
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Scheme 2. A family of 3D two-fold interpenetrated **pcu** frameworks was prepared by varying pillar linker ligands across the **X-pcu-n-Zn** platform.

Very recently, we reported a new FMOM, the 2-fold interpenetrated coordination network **X-pcu-5-Zn** ($[\text{Zn}_2(\text{DMTDC})_2(\text{dpe})]$).^[9] **X-pcu-5-Zn** is only the second example of an FMOM that exhibits following features: a type F-IV isotherm; high CO_2 uptake ($> 250 \text{ cm}^3/\text{g}$); good recyclability. In this contribution, we report the synthesis, structure and properties of three isorecticular analogues of **X-pcu-5-Zn** that were obtained by substituting the dpe pillar ligand with three dipyriddy type ligands of similar length but with different functionality and conformational freedom: 1,2-bis(4-pyridyl)ethane (bpe), **X-pcu-6-Zn**; 1,2-bis(4-pyridyl)acetylene (bpa), **X-pcu-7-Zn**; 4,4'-azopyridine (apy), **X-pcu-8-Zn** (Scheme 2). This systematic approach enabled by crystal engineering is expected offer insights into structure-property relationships concerning framework flexibility and how this in turn impacts the switching pressures of sorbents that exhibit type F-IV isotherms.

X-pcu-6-Zn- α , **X-pcu-7-Zn- α** and **X-pcu-8-Zn- α** were obtained by the same method used for **X-pcu-5-Zn- α** ,^[9] solvothermal reaction of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, H_2DMTDC , and the respective linker ligand (Scheme 2) in *N,N*-Dimethylformamide (DMF). Single-crystal X-ray diffraction (SCXRD) studies revealed that the open phases, **X-pcu-6-Zn- α** , **X-pcu-7-Zn- α** and **X-pcu-8-Zn- α** , are isostructural to **X-pcu-5-Zn- α** and crystallize in the triclinic space group *P*-1. All four compounds can be regarded as derivatives of the parent material **DMOF-1** but with 2-fold interpenetration.^[18] Their structures can be described as being comprised of square lattice, **sql**, networks formed by dinuclear $\text{Zn}(\text{II})$ tetracarboxylate paddlewheel molecular building blocks (MBBs) linked by DMTDC ligands. These **sql** nets are in turn pillared by the respective dipyriddy linker ligands to form **pcu** topology nets. Despite 2-fold interpenetration, the frameworks exhibit 1D channels with effective pore diameters of *ca.* 4.6×5.1 , 3.7×4.6 , 4.0×4.4 and $3.8 \times 6.1 \text{ \AA}^2$ that lie parallel to the crystallographic *c*-axes (Figure 1), and calculated guest-accessible volumes of 45.7 %, 45.5 %, 46.0 % and 46.6% were found in **X-pcu-5-Zn- α** , **X-pcu-6-Zn- α** , **X-pcu-7-Zn- α** and **X-pcu-8-Zn- α** , respectively. Thermogravimetric (TGA) traces revealed that the as-synthesized α phases of **X-pcu-6-Zn**, **X-pcu-7-Zn** and **X-pcu-8-Zn** lose their guest molecules below $145 \text{ }^\circ\text{C}$ and remain stable to $320 \text{ }^\circ\text{C}$ (Figures S15-S17).

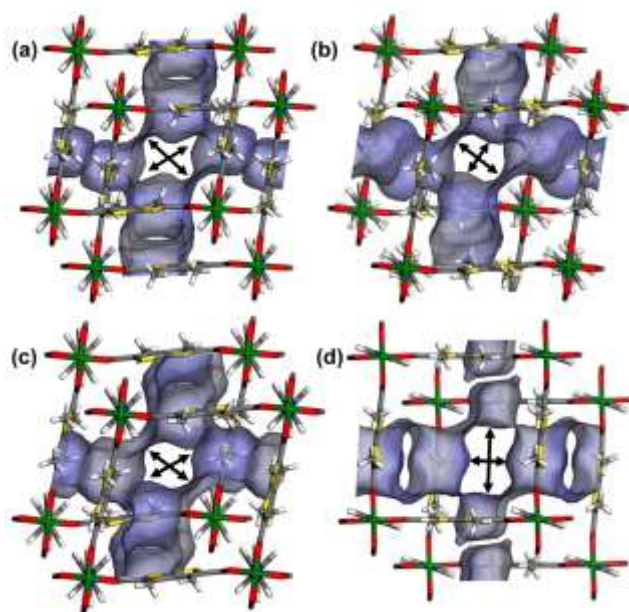


Figure 1. Illustrations of the 3D frameworks, their channel structures and pore diameters viewed along the crystallographic *c*-axes for **X-pcu-5-Zn- α** (a), **X-pcu-6-Zn- α** (b), **X-pcu-7-Zn- α** (c) and **X-pcu-8-Zn- α** (d).

Our previous study revealed that **X-pcu-5-Zn- α** undergoes a single-crystal-to-single-crystal (SCSC) transformation following methanol exchange to form the closed phase **X-pcu-5-Zn- β** . We observed that heating the α forms of **X-pcu-6-Zn** and **X-pcu-8-Zn** affords the respective closed or β forms (Figures S8 and S10), whereas **X-pcu-7-Zn- β** was obtained by evacuating at ambient temperature (Figures S6 and S9). SCXRD studies revealed that the β forms are isostructural to **X-pcu-5-Zn- β** (Figure 2) *i.e.* contorted versions of the α forms with the same connectivity, different space groups and centered interpenetration. **X-pcu-5-Zn- β** and **X-pcu-6-Zn- β** crystallized in orthorhombic space group *Pbca* and underwent shrinkages of *ca.* 33.6% and 31.9%, respectively, to their unit-cell volumes vs. the corresponding α forms. **X-pcu-7-Zn- β** and **X-pcu-8-Zn- β** crystallized in orthorhombic space group *Fmmm* and underwent 36.9% and 38.2% shrinkages to their unit-cell volumes vs. the corresponding α forms. PLATON calculations revealed that **X-pcu-5-Zn- β** and **X-pcu-6-Zn- β** contain no residual solvent accessible void, whereas **X-pcu-7-Zn- β** and **X-pcu-8-Zn- β** have negligible void volumes of 3.9% and 1.8%, respectively. The structural results indicate that all four β forms are nonporous. TGA and FT-IR studies confirmed the absence of guest molecules in the β forms (Figures S15-20). As for **X-pcu-5-Zn- β** ,^[9] the three new β forms were observed to revert to the respective α forms when soaked in DMF at room temperature for one day (Figures S1-S3). These results suggest that the extreme structural transformations required to transform between the α and β form are reversible.

Analysis of the crystal structures reveals that the metal-carboxylate junction $\text{Zn}_2=\text{O}_2 > \text{C}$ in the α phases approaches linearity with dihedral angles (Table S5) between the $\text{Zn}_2=\text{O}_2$ plane and the carboxylate group $\text{O}_2 > \text{C}$ covering the range of 3.6° - 7.9° , 3.5° - 8.6° , 5.5° - 12.8° and 0.2° - 6.0° for **X-pcu-5-Zn- α** , **X-pcu-6-**

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Zn- α , **X-pcu-7-Zn- α** and **X-pcu-8-Zn- α** , respectively (Table S5). Conversely, in the β phases the metal-carboxylate junctions bend with dihedral angles of 17.5°-29.9° and 15.1°-30.7° for **X-pcu-5-Zn- β** and **X-pcu-6-Zn- β** , and 25.5° and 26.0° for **X-pcu-7-Zn- β** and **X-pcu-8-Zn- β** , respectively. In the α phases there are no π - π interactions (centroid-centroid distances are > 4.5 Å) whereas C-H... π interactions and weak C-H...O hydrogen bonding exist except in **X-pcu-6-Zn- α** (Tables S14 and S15). With respect to the β phases, aromatic stacking interactions (Table S13) with distances between centroids are ordered as follows: **X-pcu-6-Zn- β** (4.32 Å) > **X-pcu-5-Zn- β** (4.30 Å) > **X-pcu-8-Zn- β** (4.04 Å) > **X-pcu-7-Zn- β** (4.02 Å).

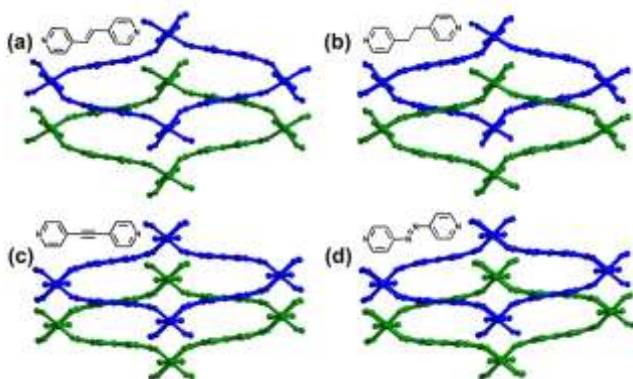


Figure 2. Views of the 2-fold interpenetrated 3D frameworks along the crystallographic a -axes for **X-pcu-5-Zn- β** (a), **X-pcu-6-Zn- β** (b) and along the b -axes for **X-pcu-7-Zn- β** (c), **X-pcu-8-Zn- β** (d).

In order to study the impact of pillar substitution on structural flexibility and the associated gate-opening pressures, single gas sorption isotherms were collected for N₂, CO₂, C₂H₂ and C₂H₄. As revealed by Figure S21, **X-pcu-6-Zn- β** and **X-pcu-7-Zn- β** exhibit gate-opening for N₂ at 77 K with onset pressures of $P/P_0 = 0.20$ and 0.68, respectively. **X-pcu-5-Zn- β** was reported to exhibit gate opening at $P/P_0 = 0.44$.^[9] **X-pcu-6-Zn- β** reaches saturation with an uptake of 293 cm³/g whereas saturation in **X-pcu-5-Zn- β** and **X-pcu-7-Zn- β** was not reached with uptakes of 136 and 217 cm³/g at $P/P_0 = 0.97$ and 0.99, respectively. **X-pcu-8-Zn- β** exhibited no N₂ (77 K) induced switching up to 1 bar.

CO₂ (195 K) sorption isotherms, which are indicative of uptake capacity for all gases, were recorded for **X-pcu-6-Zn- β** , **X-pcu-7-Zn- β** and **X-pcu-8-Zn- β** and compared to that of **X-pcu-5-Zn- β** (Figure 3). All four β forms were found to exhibit type F-IV isotherms with saturation uptakes of 254, 245, 267 and 243 cm³/g at 1 bar and gate-opening at $P/P_0 = 0.30$, 0.17, 0.33 and 0.39 for **X-pcu-5-Zn**, **X-pcu-6-Zn**, **X-pcu-7-Zn** and **X-pcu-8-Zn**, respectively. To the best of our knowledge, only two other FMOMs exhibit CO₂ saturation uptakes > 200 cm³/g with type F-IV isotherms (Table S17).^[8a,8b] Langmuir surface areas for the α forms calculated from the CO₂ sorption isotherms at 195 K are 1163, 1318, 1362, and 1375 cm² g⁻¹, respectively. Pore volumes of 0.45, 0.44, 0.48, and 0.43 cm³/g, respectively for the β forms of **X-pcu-5-Zn**, **X-pcu-6-Zn**, **X-pcu-7-Zn** and **X-pcu-8-Zn** were calculated by assuming liquid filling of CO₂ when saturated. These

values are close to the ones estimated from the crystal structures: 0.42, 0.43, 0.43 and 0.44 cm³/g, of **X-pcu-5-Zn- α** , **X-pcu-6-Zn- α** , **X-pcu-7-Zn- α** and **X-pcu-8-Zn- α** , respectively. The desorption isotherms exhibit hysteresis with gate-closing pressures around $P/P_0 = 0.20$, 0.16, 0.29 and 0.33 for **X-pcu-5-Zn**, **X-pcu-6-Zn**, **X-pcu-7-Zn** and **X-pcu-8-Zn**, respectively. Unlike **X-pcu-5-Zn**,^[9] there is no γ phase observed for **X-pcu-6-Zn**, **X-pcu-7-Zn**, **X-pcu-8-Zn** after the CO₂ adsorption (Figures S5-S7).

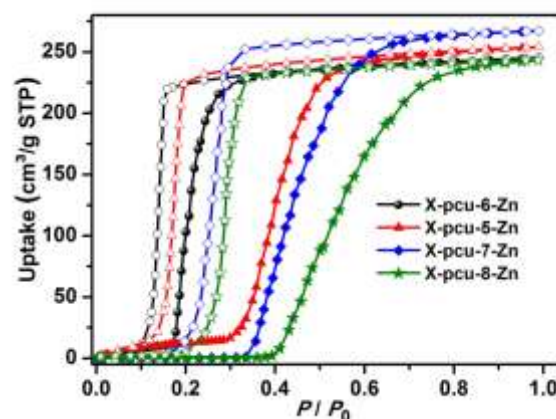


Figure 3. CO₂ (195K) sorption isotherms of **X-pcu-5-Zn- β** (red), **X-pcu-6-Zn- β** (black), **X-pcu-7-Zn- β** (blue) and **X-pcu-8-Zn- β** (green). Adsorption and desorption branches are shown with solid and open symbols, respectively.

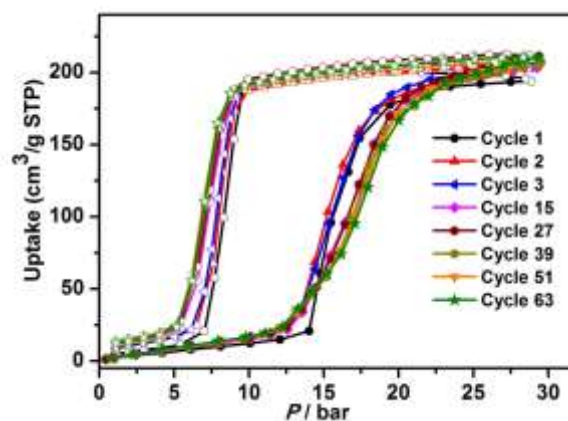


Figure 4. High-pressure CO₂ sorption isotherms for **X-pcu-6-Zn- β** at 273 K obtained during cyclic sorption studies.

High-pressure CO₂ sorption isotherms at 273 K were also collected (Figure S29). The gate opening (P_{g0}) and gate closing pressures (P_{gc}) were found to follow the same trend as the 77 K N₂ and 195 K CO₂ isotherms: **X-pcu-6-Zn- β** < **X-pcu-5-Zn- β** < **X-pcu-7-Zn- β** < **X-pcu-8-Zn- β** . **X-pcu-6-Zn- β** is the only variant that reached saturation at 273 K with $P_{g0} = 14.0$ bar. **X-pcu-6-Zn- β** was found to exhibit good sorption recyclability over > 60 consecutive adsorption-desorption cycles (Figure 4 and Figure S30). Whereas **X-pcu-5-Zn** exhibited structural transformation

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across three phases,^[9] **X-pcu-6-Zn** recycles between only the α and β phases. That the related pillared-layered networks **DUT-8(Ni)**^[19] and **X-pcu-3-Zn-3i**,^[20] which contain the short pillar dabco and rigid pillar 1,4-bis(4-pyridyl)benzene, respectively, offer much lower recyclability suggests that flexible dipyridyl type ligands may induce greater framework reversibility and recyclability.

C_2H_2 and C_2H_4 adsorption experiments were conducted at 195 K. Figure 5 reveals that, although **X-pcu-5-Zn- β** , **X-pcu-6-Zn- β** , **X-pcu-7-Zn- β** and **X-pcu-8-Zn- β** exhibit comparable C_2H_2 uptakes at 195 K, P_{go} values for C_2H_2 differ but follow the same overall order: **X-pcu-6-Zn- β** < **X-pcu-5-Zn- β** < **X-pcu-7-Zn- β** < **X-pcu-8-Zn- β** . **X-pcu-8-Zn- β** did not reach saturation for C_2H_4 adsorption at 195 K, with an uptake of just 54 cm^3/g at 757 mmHg.

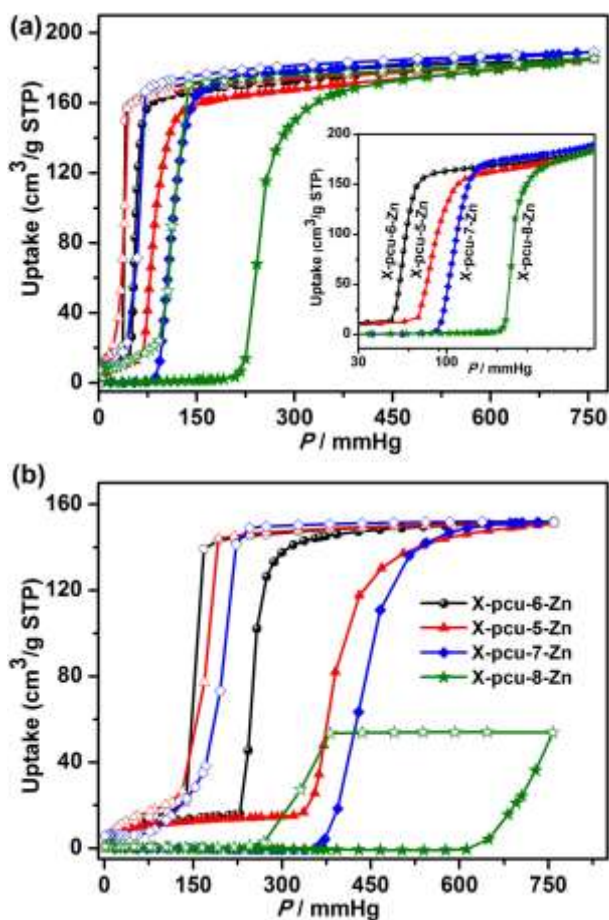


Figure 5. C_2H_2 (a, 195 K) and C_2H_4 (b, 195 K) sorption isotherms of **X-pcu-5-Zn- β** (red), **X-pcu-6-Zn- β** (black), **X-pcu-7-Zn- β** (blue) and **X-pcu-8-Zn- β** (green). Adsorption and desorption branches are shown with solid and open symbols, respectively.

In-situ CO_2 -loaded PXRD data indicate that the CO_2 loaded porous phases are isostructural with the as-synthesized α phases (Figures S11-S14). PXRD patterns from samples collected after the sorption experiments further indicate that structural transformations between the β and α phases are reversible (Figures S4-S7). Since the respective β and α forms are isostructural, we attribute the different adsorption properties to the

different pillar ligands. **X-pcu-6-Zn- β** was found to consistently exhibit the lowest P_{go} values. We attribute this to the relative conformational flexibility of the ethane moiety ($-CH_2CH_2-$) of the bpe linker. The ethylene group ($-C=C-$) of **X-pcu-5-Zn- β** and the ethyne ($-C\equiv C-$) moiety of **X-pcu-7-Zn- β** exhibited higher P_{go} values. The azo group ($-N=N-$) of **X-pcu-8-Zn** afforded the highest P_{go} . A CSD survey (Figure S36) is consistent with P_{go} order. In particular, bpe linker ligands were found to exhibit a wide distribution of torsion angles. Conversely, dpe and apy linker ligands offer the narrowest ranges of torsion angle distribution with the ethylene and azo moieties, respectively, retaining trans-configurations. The ethyne group enforces linearity and also induces planarity in the majority of bpa structures archived in the CSD. The degree of structural variability of the four pillar ligands therefore correlates with the observed P_{go} values.

The results of the structural studies revealed that the transformations between the nonporous closed phases and porous open phases are accompanied by distortion of the **sql** nets and sliding of the interpenetrated nets (Tables S7-S12). The degree of network distortion follows the order **X-pcu-6-Zn** < **X-pcu-7-Zn** < **X-pcu-5-Zn** < **X-pcu-8-Zn** (Table S7) whereas the repeat distance contraction between adjacent nets is ordered as follows: **X-pcu-5-Zn** < **X-pcu-6-Zn** < **X-pcu-7-Zn** < **X-pcu-8-Zn** (Table S9). The shortest distances between ring centroids in the β phases are ordered as follows: **X-pcu-7-Zn** (4.02 Å) < **X-pcu-8-Zn** (4.04 Å) < **X-pcu-5-Zn** (4.30 Å) < **X-pcu-6-Zn** (4.32 Å) (Table S13). Meanwhile, $C-H\cdots\pi$ and $C-H\cdots O$ interactions between interpenetrated nets exist in the α forms of **X-pcu-5-Zn**, **X-pcu-7-Zn** and **X-pcu-8-Zn** (Tables S14 and S15) but there are no such interactions in the α form of **X-pcu-6-Zn**. These results collectively help to explain why **X-pcu-6-Zn** exhibits the lowest gate-opening pressure of the four compounds studied. Rotation of organic linkers and a hinge-like motion associated with carboxylate coordination was also observed during the transformation between α and β forms. In **X-pcu-6-Zn**, bpe ligands afford the highest dihedral angle change between two pyridine rings (Table S4), and the highest bending angles for the $Zn_2=O_2 > C$ junctions (Table S5), further suggesting that **X-pcu-6-Zn** exhibits the highest framework flexibility among the flexible networks studied herein. The single-crystal structures are in accord with CSD search results (Figure S36) in that they both indicate that the ethane group offers the most rotational variability.

In summary, we report an isorecticular family of four flexible, 2-fold interpenetrated **pcu** networks that exhibit reversible structural transformations between open porous phases and closed nonporous phases. All four sorbents exhibit type F-IV isotherms with high uptake capacities. That the gate opening/closing pressures of these networks are influenced by substitution of the pillar ligands has enabled us to fine-tune these important parameters in a systematic, consistent and rational fashion. Specifically the N_2 , CO_2 , C_2H_2 and C_2H_4 adsorption isotherms all suggest that the most flexible dipyridyl organic linker results in lower gate-opening pressures. These changes are quite substantial in that the relative differences between gate-opening pressures differ as follows: the gate-opening pressures of **X-pcu-6-Zn** was reduced by 31–55% (depending upon sorbate) vs. **X-pcu-5-Zn** whereas the gate-opening pressures of **X-pcu-7-Zn** and **X-pcu-8-Zn** were increased by 8–55% and 30–206%. This work provides a simple design principle to enable rational up/down control of the gate-

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opening and/or gate-closing pressures of switching adsorbent materials.

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Conflicts of interest

The authors declare no conflict of interest.

Keywords: flexibility • gate-opening pressure • ligand substitution • switching sorbents • type F-IV isotherm

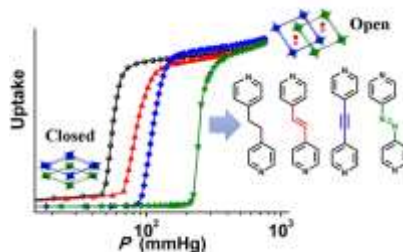
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The crystal engineering approach of pillar substitution enables the gate-opening / gate-closing pressures of a family of flexible coordination networks to be fine-tuned. That linker flexibility favours lower gate-opening pressure and vice-versa has broad implications for controlling a key parameter of switching adsorbent materials.



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Tuning the gate-opening pressure in a switching pcu coordination network, X-pcu-5-Zn, by pillar ligand substitution

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