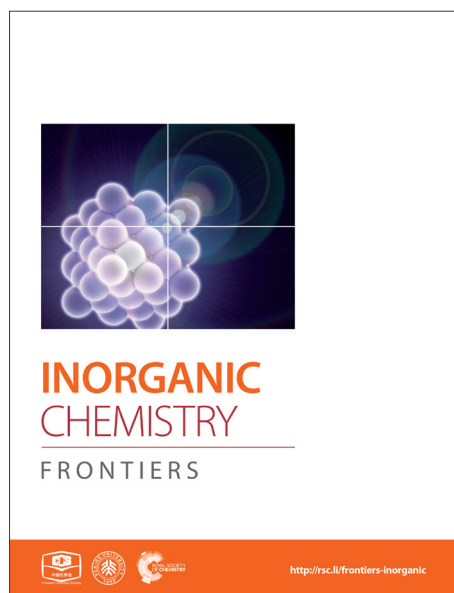
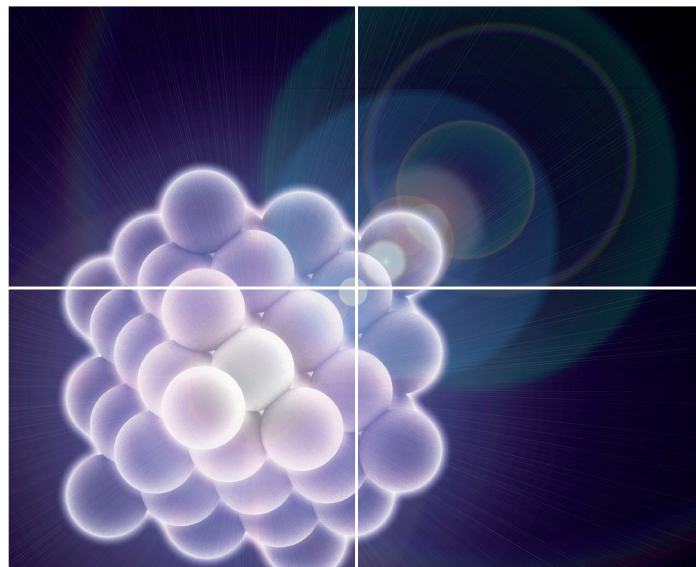


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ARTICLE TYPE

## Syntheses, structures and gas sorption properties of two coordination polymers with a unique type of supramolecular isomerism

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The solvothermal reaction of a short bridging ligand 1*H*-pyrazole-4-carboxylic acid (H<sub>2</sub>pc) and Zn(NO<sub>3</sub>)<sub>2</sub> in mixed solvent containing *N,N*-dimethylacetamide (DMA) at 110 °C produced two genuine supramolecular isomers [Zn<sub>2</sub>(pc)<sub>2</sub>(DMA)] (**1**) and [Zn<sub>2</sub>(pc)<sub>2</sub>]-DMA (**2**). Single-crystal X-ray diffraction studies showed that **1** is a densely packed layer structure with DMA molecules coordinated on the layer surface, and **2** is a porous three-dimensional framework structure with DMA molecules filling inside the pore without coordination to any metal ion, which represent a rare case of coordination-sphere isomerism in coordination polymers. Removal of the coordinated DMA molecules in **1** happens at high temperatures, accompanying the irreversible formation of an unidentified nonporous phase. On the other hand, the guest DMA molecules in **2** can be readily removed at mild conditions to give a porous new phase [Zn<sub>2</sub>(pc)<sub>2</sub>] (**2'**). Gas-sorption measurements of **2'** revealed that the framework has significant flexibility and selective CO<sub>2</sub> adsorption at room temperature.

### Introduction

Porous coordination polymers (PCPs) or metal-organic frameworks (MOFs) have attracted much attention partly because of their rich structural diversity and potential applications.<sup>1</sup> Supramolecular isomerism in coordination polymers is the existence of more than one type of network superstructure from the same building blocks, which is caused from the structural uncertainty in the self-assembly processes, but can be also regarded as an invaluable opportunity for the study of the self-assembly and crystal growth processes, as well as the structure-property relationship of these interesting materials.<sup>2</sup>

According to the type of structure differences, supramolecular isomerism in PCPs can be categorized into many classes, such as structural isomerism, topological isomerism, and interpenetration isomerism, etc.<sup>3</sup> For example, in the isomers [Cu(SCN)(dpt)] (dpt = 2,4-bis(4-pyridyl)-1,3,5-triazine) reported by Champness et al., Cu(I) cation coordinated with SCN anions and dpt ligands to construct N<sub>3</sub>S and N<sub>2</sub>S<sub>2</sub> coordination spheres, respectively, forming 3D porous framework structure with 6<sup>5</sup>.8 topology and a stair-like chain.<sup>3b</sup> With the same coordination geometries, the building units can be linked to form extended networks with different topologies, which can be defined as topological isomers. For example, Maverick et al. found that Cu(II) ion tends to coordinate with two β-ketonate and two pyridyl groups from four 3-(4-pyridyl)pentane-2,4-dionate ligands to form a square-planar 4-connected node, which can be linked to form two-dimensional (2D) **sql** network or 3D **nbo** networks depending on the solvent used in the syntheses.<sup>3c</sup> With identical coordination environments and topologies, porous networks may interpenetrate differently to

form interpenetration isomers.<sup>3j, k</sup> Comparison experiments indicate that larger interpenetration number usually leads to increase in the low-pressure adsorption performance, although the porosity and saturated adsorption capacity are decreased.<sup>4</sup> Also, the interpenetration number is an important influencing factor of framework flexibility.<sup>5</sup> In PCPs, supramolecular isomerism usually refers to the coordination frameworks rather than the whole crystal. Strictly, most supramolecular isomers in PCPs are not genuine supramolecular isomers because there are different guest molecules in the pore systems.<sup>3</sup>

Herein, we report two new coordination polymers, namely [Zn<sub>2</sub>(pc)<sub>2</sub>(DMA)] (**1**) and [Zn<sub>2</sub>(pc)<sub>2</sub>]-DMA (**2**) (H<sub>2</sub>pc = 4-carboxylpyrazole, DMA = *N,N*-dimethylacetamide) showing a new type of supramolecular isomerism, in which the crystals have the same chemical composition but the coordination frameworks consist of different components. Because the DMA molecules serve as terminal coordination molecules and guests, respectively, the two isomers display totally different porosity and sorption behavior.

### Experiment Section

#### Materials and Methods.

The ligand H<sub>2</sub>pc was synthesized according to the literature method.<sup>6</sup> Other reagents and solvents were commercially available and used without further purification. Elemental analyses (C, H, N) were performed with a Vario EL elemental analyzer. FT-IR spectra were obtained from KBr pellets on a Bruker EQUINOX 55 FT-IR spectrometer in the 4000–400 cm<sup>-1</sup> region. Powder X-ray diffraction (PXRD) patterns were recorded

on a Bruker D8 ADVANCE or a D8 DAVINCI X-ray powder diffractometer (Cu K $\alpha$ ). Thermogravimetry (TG) analyses were performed using a TA Q50 instrument. Each sample was heated from room temperature to 700 °C with a heating rate of 5.0 °C/min under nitrogen atmosphere. Gas sorption isotherms were measured on a Belsorp MAX or a Micromeritics ASAP 2020M volumetric adsorption apparatus. The sample was placed in the sample tube and dried under high vacuum at 170 °C for 4 h to remove the remnant solvent molecules prior to measurements.

## 10 Synthesis

**[Zn<sub>2</sub>(pc)<sub>2</sub>](DMA) (1).** A mixture of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.2 mmol, 0.059 g), H<sub>2</sub>pc (0.2 mmol, 0.022 g), H<sub>2</sub>O (6.0 mL), and DMA (1.5 mL) was sealed in a 12-mL Teflon-lined reactor, heated at 110 °C for 3 days and cooled to room temperature at a rate of 5 °C/h. Colorless plate-like crystals of **1** were collected by filtration (yield 20% on the basis of Zn). Elemental analysis (%) calculated: C, 32.90, H, 2.99, N, 15.99; found: C, 32.92, H, 2.98, N, 15.91. FT-IR (cm<sup>-1</sup>): 3097(w), 2933(w), 1610(m), 1555(s), 1510(m), 1454(m), 1405(w), 1296(s), 1170(w), 1056(m), 1006(m), 898(w), 797(m), 626(w), 589(w).

**[Zn<sub>2</sub>(pc)<sub>2</sub>](DMA) (2).** A mixture of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.2 mmol, 0.059 g), H<sub>2</sub>pc (0.2 mmol, 0.022 g), methanol (MeOH, 6.0 mL), and DMA (1.5 mL) was sealed in a 12-mL Teflon-lined reactor, heated at 110 °C for 3 days, cooled by 5 °C/h to room temperature and colorless plate-like crystals of **2** were collected by filtration (yield 70% on the basis of Zn). Elemental analysis (%) calculated: C, 32.90, H, 2.99, N, 15.99; found: C, 32.87, H, 3.03, N, 15.79. FT-IR (cm<sup>-1</sup>): 3072(m), 2933(w), 1638(ms), 1555(s), 1461(ms), 1391(m), 1296(s), 1176(w), 1056(m), 1012(m), 949(w), 879(w), 803(ms), 595(w).

## Crystal Structure Determination.

Diffraction data were collected on a Bruker Apex CCD diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Absorption corrections were applied by using the multi-scan program SADABS.<sup>7</sup> The structures were solved with the direct method and refined with the full-matrix least-squares technique with the SHELXTL program package.<sup>8</sup> Anisotropic thermal parameters were applied to all non-hydrogen atoms. All hydrogen atoms were generated geometrically. The disordered bridging ligands and terminal coordinated DMA molecules were subjected to geometric restraints during the refinements.

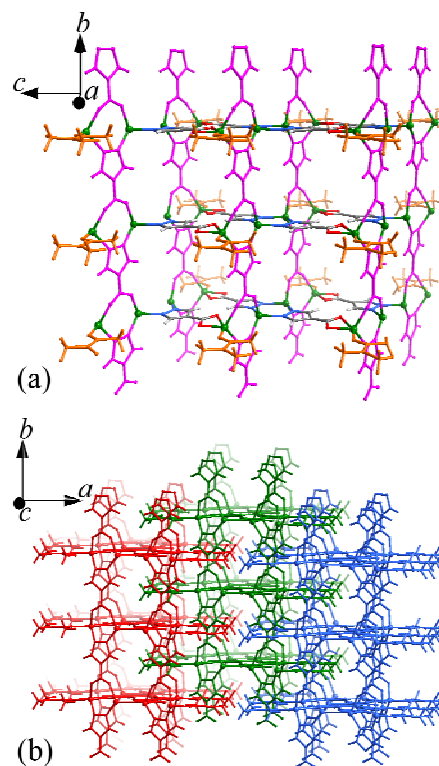
## Results and Discussion

### Syntheses and structures.

Both **1** and **2** were synthesized under similar, mild solvothermal conditions, except that H<sub>2</sub>O and methanol were used as the main solvents, respectively. Small amount of DMA was added to serve as not only necessary component of **1** and **2**, but also a base to deprotonate the H<sub>2</sub>pc ligands. Without addition of DMA, no precipitation formed after the solvothermal reactions. Infrared spectra of **1** and **2** show different adsorption peaks around 1640 ~ 1450 cm<sup>-1</sup>, suggesting that the DMA molecules reside at different environments or the carboxylate groups adopt different coordination modes (Fig. S1).

**1** crystallizes in the C<sub>2</sub>/m space group, containing two Zn atoms (Zn1 at a C<sub>2v</sub> axis, 1/2 occupancy, Zn2 at a mirror plane,

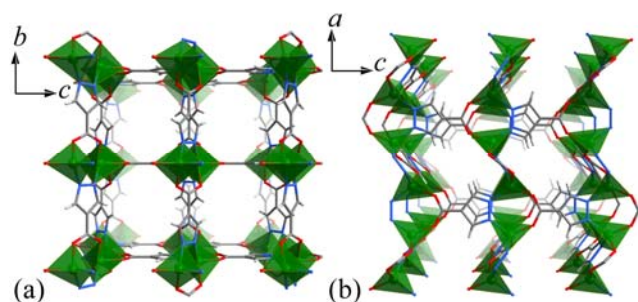
1/2 occupancy), two fully deprotonated pc<sup>2-</sup> ligand both locating at mirror planes with 1/2 occupancies (the molecular axis of one is parallel to its mirror plane, while that of another is perpendicular to its mirror plane; so the pyrazolate and carboxylate ends of the latter one are statistically disordered), and one DMA molecule (lying on the same mirror plane with Zn2, 1/2 occupancy) in the asymmetric unit. As shown in Fig. 1 and S2, Zn1 is tetrahedrally coordinated by two pyrazolate nitrogen atoms (Zn1—N1 1.994(4), Zn1—N2 2.005(4) Å) from two ordered pc<sup>2-</sup> ligands and two carboxylate/pyrazolate donors (Zn1—O3 1.995(7) and Zn1—N4 1.909(6) Å) from two symmetrically disordered pc<sup>2-</sup> ligands. Zn2 coordinates with a chelating carboxylate from the ordered pc<sup>2-</sup> (Zn2—O1 2.416(5) and Zn2—O2 1.996(3) Å) and an carbonyl oxygen (Zn2—O5 2.000(3) Å) of DMA, as well as two carboxylate oxygen/pyrazolate nitrogen atoms [Zn2—N3 1.910(6) and Zn2—O4 2.048(8) Å] from the symmetrically disordered pc<sup>2-</sup> to form a seriously distorted triangular-bipyramidal coordination environment. All the Zn—N and Zn—O bond length are consistent with the expected values.<sup>9</sup> The ordered and symmetrically disordered pc<sup>2-</sup> ligands are both four coordinated, but they serve as three- and four-connected linkers, respectively, which bridge the Zn atoms along two mutually perpendicular directions to form a thick, porous 2D layer extending across the bc-plane with DMA molecules pointing outwards (Fig. 1a). These layers interdigitate to form the final 3D structure with DMA molecules inserting into pores of adjacent layers, so that no solvent accessible free volume is found in **1** (Fig. 1b).



**Fig. 1** Perspective views of the (a) 2D layer (the symmetrically disordered pc<sup>2-</sup> ligands are highlighted in magenta, and only one possible orientation is shown; the coordinated DMA molecules are highlighted in orange) and (b) 3D packing (adjacent layers are shown in different colours to highlight the interdigitation) of **1**.



**2** crystallizes in the *Pnma* space group containing a Zn atom (Zn1 at a mirror plane, 1/2 occupancy), two fully deprotonated  $pc^{2-}$  ligand (both at  $C_{2h}$  axis with 1/4 occupancy so that all the pyrazolate and carboxylate ends are symmetrically disordered) and a non-coordinated DMA molecule (at a mirror plane, 1/2 occupancy) in the asymmetric unit. As shown in Fig. S3, Zn1 is tetrahedrally coordinated by four disordered carboxylate/pyrazolate donors (Zn1—N/O 1.9300(4)–1.9785(3) Å) from four  $pc^{2-}$  ligands. Each  $pc^{2-}$  ligand also adopts the same coordination environment linking to four Zn1 atoms with exo-tetradentate coordination to construct a 3D porous framework (void 27%). There are small narrow 3D channels consisting of small cavities of  $4.0 \times 5.1 \times 3.8$  Å<sup>3</sup> (filled with DMA molecules) and even smaller apertures of  $2.5 \times 5.0$  Å<sup>2</sup>,  $1.6 \times 2.4$  Å<sup>2</sup>, and  $1.5 \times 4.0$  Å<sup>2</sup> running along *a*-, *b*-, and *c*-axes, respectively, taking into account the van der Waals radii (Fig. 2).



**Fig. 2** Perspective views of the 3D coordination framework structure of **2** along the (a) *a*- and (b) *b*-axis. Note that all  $pc^{2-}$  ligands have statistically disordered prazolate/carboxylate ends, and only one possible ligand orientation is shown.

In **1** and **2**, many of the pyrazolate and carboxylate groups are statistically disordered, because pyrazolate usually adopts a similar bidentate bridging coordination mode as carboxylate. Several PCPs based on bifunctional pyrazolate-carboxylate ligands have been reported, some of which also show statistically disordered pyrazolate and carboxylate groups.<sup>9-10</sup> The key structural difference between **1** and **2** is the role of the DMA molecules, which reside at different coordination spheres. Interestingly, the H<sub>2</sub>O and MeOH molecules do not participate in the crystal composition although they are the main solvents and should serve as important additives in the syntheses of the two isomers.<sup>2b</sup> In **1**, the DMA molecules coordinate to the surface of the grid layer, preventing it from extending along the *a*-axis into a 3D structure. Also because of the coordination of DMA molecules, the  $pc^{2-}$  ligands in **1** connect with less Zn atoms as compared with those in **2**. On the other hand, the DMA molecules fill inside the grid layer in **2**, so that the coordination network is extended into a microporous 3D framework. In most cases, DMA serves merely as a solvent or a basic agent for deprotonating the ligand, rather than a ligand. It should be noted that, the crystal composition of **1** and **2** are the same, meaning that they are genuine supramolecular isomers. Further, supramolecular isomerism based on this type of structural difference has not been reported for coordination polymers in the literature so far.

### Thermal Stability.

Thermal stabilities of **1** and **2** were studied by TG and PXRD. As shown in Fig. S5a, the PXRD pattern of as-synthesized **1** is

consistent well with the single crystal X-ray diffraction data. A small weight loss of ca. 2.4% was observed from 180 °C to 220 °C (Fig. S4), which might be attributed to the DMA molecules coordinated on the external surface of the crystals (calculated weight loss for all the coordinated DMA molecules is 20%). At 200 °C, displacement and splitting of diffraction peaks in the PXRD patterns between 11° and 13° suggest obvious distortion of the framework (Fig. S5a). Another weight loss of 17.2% appears in the range of 310 ~ 400 °C, which corresponds to all the other coordinated DMA molecules inside the crystals. The widening and displacement of the diffraction peaks above 200 °C indicate that the framework kept distorting during the loss of DMA molecules before decomposition. As proved by PXRD, the original framework cannot be recovered by dipping the desolvated samples (after heated at 350 °C) in DMA for 3 days (Fig. S4a), which suggests that the framework was irreversibly damaged upon the loosing of coordinated DMA molecules and no porosity can be found in the desolvated structure. For **2**, all DMA guest molecules escape at 170 ~ 220 °C (Fig. S4), and the distorted guest-free framework **2'** decomposes over 400 °C (Fig. S3 and S4b). Obvious framework distortion can be found after the loss of guest molecules and the original framework structure **2** can be recovered by exposing **2'** in MeOH vapor at room temperature, which suggests that **2** is a flexible framework and MeOH molecules can act as guest molecules to fill the pore system and drive the structural transformation of the host framework. On the other hand, structural transformation of **2'** to **2** can be realized by heating **2'** in DMA at 140 °C, instead of dipping **2'** in DMA at room temperature, which can be attributed to the bigger volume of DMA molecules, preventing them from getting across the small apertures under ambient temperature (Fig. S5b).

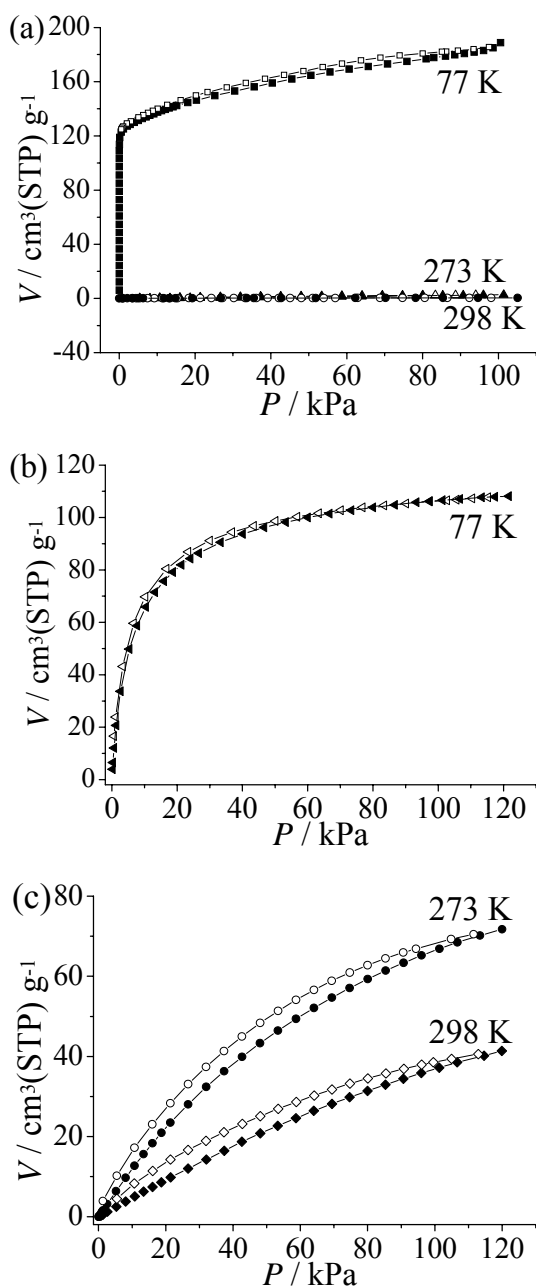
Although **1** and **2** cannot transform to each other at high temperatures (Fig. S5), we tried to explore if the structural transformation of the two isomers could happen by either refluxing or solvothermal reaction in the solvent used for the syntheses of their counterparts. Nevertheless, no structural transformation between **1** and **2** can be observed (Fig. S6). By comparing the asymmetric units and packing structure of the two isomers, we can find that the transformation from **1** to **2** requires the departure of the coordinated DMA molecules, change of connection number of the  $pc^{2-}$  ligands from three to four, and translation of the disordered  $pc^{2-}$  ligands, which can only happen after network dissociation (Fig. S7).

### Gas sorption

To examine the pore characteristics and gas adsorption property of guest-free **2'**, CO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub> isotherms were measured (Fig. 3). A type-I-like N<sub>2</sub> sorption isotherm at 77 K with an apparent Langmuir surface area of 781 m<sup>2</sup> g<sup>-1</sup> was obtained. Being different from the typical type I adsorption isotherm, the sorption amount keeps increasing at high pressures. The adsorption amount at  $P/P_0 = 0.01$  and 0.95 are about 125 and 183 cm<sup>3</sup>(STP) g<sup>-1</sup>. For comparison, the value calculated from the single-crystal structure is 122 cm<sup>3</sup>(STP) g<sup>-1</sup> (Fig. 3a). These results further confirm the significant flexibility of **2'** and it can be speculated that **2'** may expand to a state more porous than the as-synthesized one.<sup>11</sup>

The H<sub>2</sub> sorption isotherm of **2'** measured at 77 K shows a type-

I characteristic. The sorption amount is near to saturation at low pressure ( $86 \text{ cm}^3(\text{STP}) \text{ g}^{-1}$  at 0.26 bar) and the uptake increases gradually to  $107 \text{ cm}^3(\text{STP}) \text{ g}^{-1}$  or 0.7 wt% at 1 atm (Fig. 3b). The relatively low saturated sorption amount is mainly caused from the small pore volume. The  $\text{H}_2$  density can be calculated to be  $0.064 \text{ g}\cdot\text{cm}^{-3}$  in the pore system of **2'**, which is very close to the density of liquid  $\text{H}_2$  ( $0.07 \text{ g}\cdot\text{cm}^{-3}$ ).<sup>12</sup>



**Fig. 3** (a)  $\text{N}_2$ , (b)  $\text{H}_2$  and (c)  $\text{CO}_2$  adsorption (solid) and desorption (open) isotherms of **2'**.

$\text{CO}_2$  adsorption isotherms were measured for **2'** at 273 K and 298 K, which show moderate sorption amounts of 67 and 37  $\text{cm}^3(\text{STP}) \text{ g}^{-1}$  at 1 atm, respectively (Fig. 3c). Using the Virial fitting method and the Clausius-Clapeyron equation, the  $\text{CO}_2$  adsorption enthalpy on **2** is calculated to be around  $25 \text{ kJ mol}^{-1}$  at zero coverage (Fig. S8), which is relatively low among PCPs.<sup>13</sup>

Further, **2** shows only surface adsorption for  $\text{N}_2$  at 273 K and 298 K ( $2.0 \text{ cm}^3(\text{STP}) \text{ g}^{-1}$  and  $0.45 \text{ cm}^3(\text{STP}) \text{ g}^{-1}$  at  $P = 101 \text{ kPa}$  respectively). The  $\text{CO}_2/\text{N}_2$  selectivity is estimated to be ca. 47 at 273 K and 17 at 298 K by comparing the  $\text{CO}_2$  and  $\text{N}_2$  uptakes at the relevant partial pressures for flue gas ( $\text{CO}_2$  0.15 atm;  $\text{N}_2$  0.75 atm),<sup>13b</sup> which is similar to that of zeolite 13X (ca. 20) used for  $\text{CO}_2$  capture.<sup>14</sup>

## Conclusions

In short, two genuine supramolecular isomers, with a layer structure and a flexible microporous 3D framework, have been synthesized under similar solvothermal conditions using water and methanol as the main solvents, although water or methanol does not participate in the crystal composition. More interestingly, DMA molecules, as the minor component of the mixed solvents used for the syntheses, are included in the isomers as either terminal ligands on the layer structure or lattice guest molecules in the pores of the 3D framework, representing a new type of supramolecular isomerism in coordination polymers. Interestingly, the 3D framework isomer can be activated to form an ultramicroporous material with high framework flexibility and adsorption affinity for  $\text{H}_2$ . These results highlight that, even subtle modification of the synthetic condition in the very simple metal-ligand system can produce very different outcomes in the context of material structures and properties.

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- † Electronic Supplementary Information (ESI) available: [Summary of the crystal data, additional structural plots, adsorption enthalpies of  $\text{CO}_2$ , and X-ray crystallographic files in CIF format.]. See DOI: 10.1039/b000000x/
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*Short text and illustration for table of contents:*



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Two genuine supramolecular isomers with a unique type of structural difference and completely different porous properties have been synthesized and characterized.

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