

An unusual case of symmetry-preserving isomerism†

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Two isomeric phases of the NbO-type structure have been discovered: PCN-16 (α phase) and PCN-16' (β phase), and gas sorption studies revealed that the α phase possesses a larger surface area, leading to higher hydrogen and methane storage capacity as compared with the β phase.

Framework isomerism, which was previously classified as part of the supramolecular isomerism,¹ has been of continuous interest in the crystal engineering field. The most common framework isomerism is the structural isomerism originated from differences in atomic connectivity, which is similar to that in the structural chemistry of discrete molecules.² Framework isomerism also has its own characteristics not commonly known in the structural chemistry of discrete molecules. For instance, in discrete molecules, conformers separated by small energy barriers are difficult, if not impossible, to isolate. However, in frameworks, even conformers with the most unstable conformation can be readily stabilized and isolated.³ The energy penalty received due to the unstable conformation can be compensated by the formation of an overall stable framework. Another type of isomerism unique in framework chemistry is the catenation isomerism in the form of interpenetration and noninterpenetration.^{1,4}

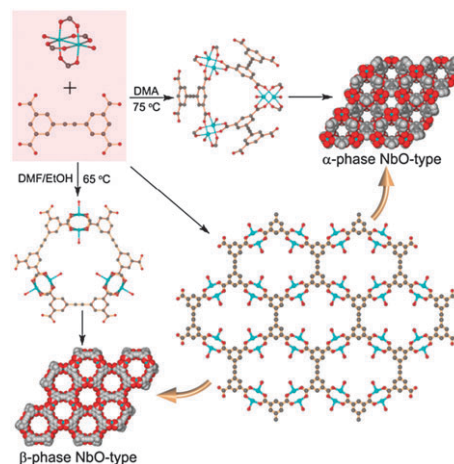
Recently, we and others have become interested in utilizing tetracarboxylate ligands for the preparation of porous metal-organic frameworks (MOFs) with high hydrogen and methane adsorption capacities.^{3,5} The assembly of the tetracarboxylate ligands with dicopper paddlewheel secondary building units (SBUs) usually leads to NbO-type three-dimensional networks containing two types of open channels. One channel type is predefined by the geometry of the $[\text{Cu}_2(\text{O}_2\text{CR})_4]$ paddlewheel SBU and the span of the two dicarboxylate groups of an isophthalate moiety on each terminus of the bridging linker. These channels are “hexagonal” ($-3m$) in shape viewed along the c -axis with a diameter of ~ 8 Å (atom to atom distance throughout this communication).⁵ The other channel type has

an open window on the $[0, 15, 13]$ plane, and the channel size is determined by the length of the linker.⁵

For a tetracarboxylate ligand rectangular in shape, as a discrete species, the “portrait” and “landscape” orientations are structurally and chemically indistinguishable. However, in a framework, the two orientations can potentially lead to two isomers crystallizing in the same space group. In other words, in addition to the NbO-type phase that has been commonly found, there, perhaps, exists a new phase that has the same composition, atom-to-atom connectivity, and symmetry, but only different in the orientation of the rectangular ligand.

Indeed, we have observed the formation of a new phase of NbO-type structure. The two phases are symmetry-preserving isomers of each other. Both phases are generated from the assembly of dicopper paddlewheel SBUs and the tetracarboxylate ligand, 5,5'-(1,2-ethynediyl)bis(1,3-benzenedicarboxylate) (*ebdc*)⁶ (Scheme 1).

The reaction of H_4ebdc and $\text{Cu}(\text{NO}_3)_2$ in dimethylacetamide (DMA) at 75 °C afforded the crystals of PCN-16 (PCN represents “porous coordination network”) with a NbO-type structure designated as the α -phase.⁶ In contrast, the reaction of the same starting materials in dimethylformamide (DMF) and ethanol at 65 °C gave rise to an isomer, PCN-16', which also possesses the NbO-type structure named



Scheme 1 The formation of the two symmetry-preserving NbO-type phases. Each consists of three “honeycomb”-type nets. The difference between the two isomers is how the three nets are connected: in the α -phase, the three nets are linked through carboxylate groups from the same end of the tetracarboxylate ligand but in the β -phase, the three nets are connected through carboxylate groups from the opposite ends of the ligand. Color scheme: C, grey; O, red; and Cu, aqua blue.

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as the β -phase. Remarkably, the two isomers possess the same space group symmetry.

Single crystal X-ray crystallographic studies (see ESI†) confirmed that both PCN-16 and PCN-16' adopt the dicopper paddlewheel clusters as SBUs and crystallize in $R\bar{3}m$ space group. Their structural difference, however, can be clearly discerned from the space-filling models viewed along the c -axis as shown in Scheme 1. Both are isostructural with previously reported NbO-type MOFs prepared from tetracarboxylates and each structure has two distinct types of cavities.⁵

In PCN-16, the first type consists of twelve ebdc ligands connecting six paddlewheel SBUs to form a pseudo-octahedral (based on the metal clusters) cavity, in which each ligand utilizes only two of its four carboxylate groups (Fig. S1a†) to support the cavity; the other two carboxylate groups in each ebdc are utilized to link adjacent cavities. In each cavity, one half of the 12 ebdc ligands join adjacent SBUs through carboxylate groups from the same phenyl ring and the other half use carboxylates from the opposite ends of the ligand for the same purpose (Fig. S1†). The dimensions of the open windows leading to the cavity are about $10 \times 10 \text{ \AA}$ and $8 \times 8 \text{ \AA}$. The second type of cavities, which is elliptical, is formed from six ebdc ligands connecting twelve paddlewheel SBUs (Fig. S1b†). In this type, each ligand uses all of its four carboxylate groups to support the cavity. The dimensions of the open windows leading to the elliptical cavity are also $10 \times 10 \text{ \AA}$ and $8 \times 8 \text{ \AA}$. These two types of cavities are connected to each other by sharing three paddlewheel SBUs between two adjacent ones of different type leading to a 3D framework with the NbO-type topology (Fig. S2†). The dimensions of the $-3m$ (in space group $R\bar{3}m$) open channels are about $8 \times 8 \text{ \AA}$ along the c -axis (Scheme 1), consistent with the size of the channels in the previously reported NbO-type MOFs.^{4,5} The solvent accessible volume in the dehydrated structure is 72.5% calculated from PLATON/SOLV.⁷

The structure of PCN-16' is very similar to that of PCN-16 except that the $-3m$ open channels ($11 \times 11 \text{ \AA}$) are larger than those in PCN-16 (Scheme 1). The solvent accessible volume in the dehydrated structure is 70.1% calculated from PLATON/SOLV,⁷ which is slightly smaller than that of PCN-16.

Topologically, both PCN-16 and PCN-16' have the NbO network as shown in Fig. 1, with the short vertex symbol of $[6^4.8^2]$ when considering both the ligand and the dinuclear $\text{Cu}_2(\text{CO}_2)_4$ SBU as planar four-connected nodes.⁵ Again, symmetry is preserved in the two isomers. Clearly, the ligand orientation difference between the two is not represented in the vertex symbol. Alternatively, the structures can also be topologically represented by viewing the $\text{Cu}_2(\text{CO}_2)_4$ SBUs as planar four-connected nodes and the ligands as two three-connected nodes centered between two phenyl rings, leading to two different (3,4)-connected nets. In this view, PCN-16 has a short vertex symbol of $[6.8^2][6^2.8^2.10^2]$ (the α phase), but PCN-16' has a symbol of $[7^3][7^4.10^2]$ (β phase). The topological representations of the two isomers are presented schematically in Fig. 2a and b, respectively. From these two figures the difference between the two nets becomes clear. Simply, the coupled three-connected nodes representing the

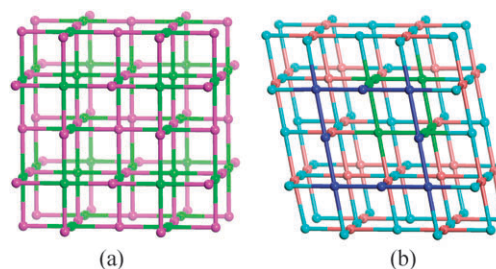


Fig. 1 Schematic representations of (a) the standard NbO network and (b) distorted NbO network in PCN-16 and PCN-16'; Ligands and $\text{Cu}_2(\text{CO}_2)_4$ SBUs are represented by brown and aqua blue spheres, respectively. All nodes are topologically identical, and both six- (green) and eight- (blue) membered rings are highlighted.

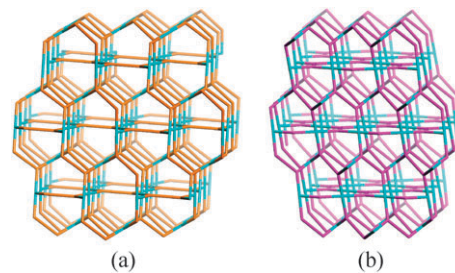


Fig. 2 Schematic representation of the topological net in (a) PCN-16 (α phase) and (b) PCN-16' (β phase) when considering each ligand as two 3-connected nodes and each $\text{Cu}_2(\text{CO}_2)_4$ SBU (aqua blue) as a four-connected node.

ligand have different orientations within the “hexagonal” channels, parallel in PCN-16 but perpendicular in PCN-16'.

Alternatively, both isomers can be structurally constructed with the same squashed 2D honeycomb-net (Scheme 1). Both consist of three parallel sets of squashed-honeycomb-nets (Fig. S3†) connected through the three dimetal paddlewheel units centred on each $-3m$ site in the $R\bar{3}m$ space group (Scheme 1). The only structural difference is that the α phase is formed by connecting the three sets of honeycomb nets through the two carboxylate groups from the same isophthalate moiety, whereas in the β phase the three sets of 2D nets are linked by two carboxylates that are *cis* to each other from the two different isophthalate moieties (Scheme 1). Thus the pores residing on the $-3m$ sites of the $R\bar{3}m$ space group in the β phase are larger than those in the α phase. In other words, the pores of PCN-16' ($11 \times 11 \text{ \AA}$) have been augmented from those in PCN-16 ($8 \times 8 \text{ \AA}$) without changing either the linker/SBU or the space group symmetry. It is also important to note that although all previously reported MOFs based on two linearly-coupled isophthalates have formed in the α phase,⁵ the β phase presumably should also exist.

While the structural difference between the isomer pair is rather subtle, the isomerism leads to significant disparity in physical properties such as gas adsorption.

To check the permanent porosities of the pair of isomers, N_2 sorption isotherms at 77 K were collected for the dehydrated samples. As shown in Fig. 3a, both PCN-16 and PCN-16' display typical Type-I sorption behaviour. PCN-16 has a BET surface area of $2273 \text{ m}^2 \text{ g}^{-1}$ (Langmuir surface area,

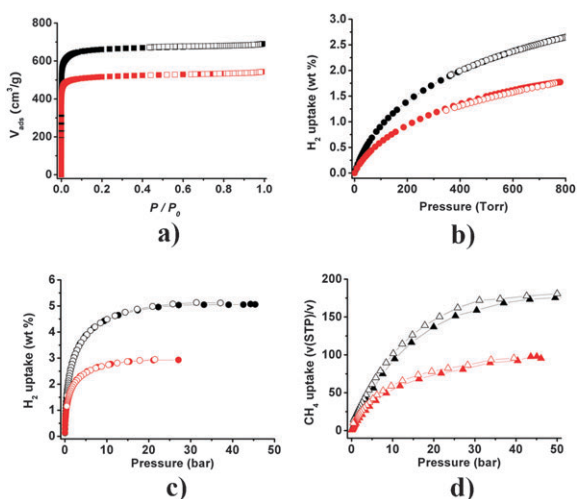


Fig. 3 Gas sorption isotherms of PCN-16 (black) and PCN-16' (red): (a) N_2 at 77 K; (b) low-pressure H_2 at 77 K; (c) high-pressure H_2 at 77 K; (d) high-pressure CH_4 at 300 K (calculated assuming perfect single crystal 'bulk' density). (solid, adsorption; open, desorption). The values are reported as excess adsorption.

$2800 \text{ m}^2 \text{ g}^{-1}$) and a total pore volume of $1.06 \text{ cm}^3 \text{ g}^{-1}$ while PCN-16' possesses a $1760 \text{ m}^2 \text{ g}^{-1}$ BET surface area (Langmuir surface area, $2200 \text{ m}^2 \text{ g}^{-1}$) and a $0.84 \text{ cm}^3 \text{ g}^{-1}$ pore volume.

The differing pore structures as evidenced by the BET surface areas directly impact the adsorption capacities for hydrogen and methane as indicated in Fig. 3c and d, PCN-16 demonstrates significantly higher hydrogen adsorption capacity than PCN-16'. At 77 K and 760 torr, PCN-16 can adsorb 2.6 wt% hydrogen, comparable to the values observed in other α phase NbO-type copper MOFs.⁵ In contrast, PCN-16' can only adsorb 1.7 wt% hydrogen, much lower than that in PCN-16. This difference persists at higher pressures where the excess hydrogen uptake of PCN-16 saturates at 5.1 wt%, while the saturation for PCN-16' occurs with the value of only 2.9 wt%. A similar trend is also reflected in the room temperature methane adsorption (Fig. 3d) where PCN-16 has a much higher capacity of $175 \text{ cm}^3(\text{STP})/\text{cm}^3$ at 45 bar compared to just $97 \text{ cm}^3(\text{STP})/\text{cm}^3$ for PCN-16' under the same pressure.

Because PCN-16 and PCN-16' are isomers of each other and both crystallize in the same space group and contain similar nanoscopic cages,⁸ the superior gas adsorption properties of PCN-16 can mainly be attributed to the pore size,⁹ which is smaller than that of PCN-16'. The small pores lead to an increased effective surface area,⁹ offering more adsorption sites for hydrogen and methane. Indeed, the saturation uptake of hydrogen at 77 K for each isomer is consistent with the different BET surface areas, as explained in a recent analysis.¹⁰ The results above also suggest that α phase NbO-type copper MOFs should be better for gas storage than their β phase counterparts.

In summary, controlled assembly of copper paddlewheel SBUs and ebdc ligands results in the formation of two supramolecular stereo-isomers crystallizing in the same $R\bar{3}m$ space group. This represents an unusually rare instance of symmetry-preserving isomerism. Gas sorption studies revealed

that PCN-16 possesses smaller pores and a larger surface area than PCN-16', leading to higher hydrogen and methane adsorption capacities in the former. Theoretically, both α and β phase isomers should exist for all NbO-type structures based on rectangular tetracarboxylate linkers and paddlewheel SBUs, though only α phase structures have been reported before this work. Attempts to synthesize the β phases for the other reported NbO-type copper MOFs is underway in our lab.

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