ℝPM-2: A recyclable porous material with unusual adsorption capability: self assembly via structural transformations

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Structural transformation via deliberate and partial topological changes in a grid network structure has led to a three-dimensional, fully recyclable porous material (ℝPM-2) with a very high sorption capability.

Self-assembly of molecular electronics and smart materials will bring a new era in the field of material science.[1] However, effective control of a self-organization process towards targeted products still remains an enormous challenge in both static self-assembly and dynamic self-assembly.[2] Realization of new crystalline architectures with desired topology and specific properties often suffers from numerous factors that are difficult to control, for example, various ways in which a metal and a ligand may form a bond and different geometries that a metal may adopt, as well as unforeseen ways of crystal packing. While much effort has been made recently in this regard,[3] accurate prediction of structures for even the simplest type of crystalline solids from a knowledge of their chemical composition is still unachieved.[4] We and others have noted that partial topological changes of a framework can be achieved effectively through structural transformations.[5] The secondary building unit (SBU)[6] approach may be extended to include 1D and 2D structural motifs. Assembly of a targeted 3D structure using these structural motifs can, thus, be carried out in a more controllable manner, due to their well-defined topology and rigid backbone structure that effectively reduce the unpredictable factors. Scheme 1 illustrates such an example where a 2D structure (or SBU) transforms to a 3D network by a simple ligand exchange. Furthermore, if such a transformation is reversible between a porous and a nonporous structure, some important applications can be envisioned. Our recent exploratory study on such a structure, the 3D porous ℝPM-1 (ℝPM: Rutgers Recyclable Porous Material) system,[7] has demonstrated its potential to be used as a host material in "ship-in-bottle" synthesis. Herein, we report another 3D porous compound, ℝPM-2, obtained by a structural transformation from a 2D precursor (or SBU). In the present case, the 2D sheets of the 2D structure are present in the 3D structure but as interpenetrating pairs of identical sheets, requiring a partial restructuring of the single 2D sheets during the transformation. The process is fully recyclable.

Using 2D $[Co(bpdc)(py)_2]\cdot H_2O$ (**1**)[5a] as a precursor, 3D structure $[Co(bpdc)(bpy)]\cdot 0.5DMF$ (**2**) (bpy = 4,4′-bipyridine, bpdc = biphenyldicarboxylate, DMF = dimethylformamide), or ℝPM-2, was assembled by mixing **1** and bpy in the molar ratio of 1:4 in 5 mL of DMF at 120 °C for one day under autogenous pressure in a Teflon-lined autoclave. Orange needle-like crystals of **2** were obtained in 90% yield.[8] Compound **2** was insoluble in common solvents such as methanol, DMF, ether, acetonitrile, $CHCl_3$, benzene and toluene. However, it can be readily transformed to a 1D $[Co(bpdc)(H_2O)_2]\cdot H_2O$ (**3**)[5a] structure upon immersion in a hot water/ethanol solution.[8] Upon a mild chemical process, structure **3** can be converted back to **1**,[5a] thus completing the cycle (see below).

$$\mathbf{1}\ (2D)\ \rightarrow\ \mathbf{2}\ (3D)\ \rightarrow\ \mathbf{3}\ (1D)$$
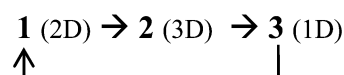
X-ray analysis‡ performed on a single crystal of **2** revealed a porous structure (Fig. 1) possessing a three-dimensional network containing rectangular-shaped 1D open channels along the *a*-axis (window size: ~ 5.6 × 3.0 Å). Fig. 2 shows the structural relation between **1** and **2**. Structure **1** is a 2D network built on $Co_2(bpdc)_4(py)_4$ basic building blocks (Fig. 2a). Its backbone structure, Co(bpdc), is a 2D motif shown in Figure 2b. Each Co of the Co_2 pair in the building block is four-fold coordinated to oxygen atoms through chelating and μ_2-bridging carboxylate ions of bpdc, forming a noninterpenetrating 2D lattice with quadrilateral shaped grids (Fig. 2b). Structure **1** is resulted by completing the metal octahedral coordination with four pyridines going into the apical positions (two per metal). The same Co(bpdc) motif forms the backbone structure of **2**, except that the 2D lattice now contains two identical, interpenetrating units (Fig. 2d). Replacing apical pyridines by exo-bidentate ligand 4,4′-bpy results in 3D porous network structure **2**.

The basic building block of **2**, $Co_2(bpdc)_4(bpy)_4$, is shown in Figure 2c. Unlike in **1**, where the two benzene rings of bpdc are essentially in plane, they are severely bent in **2** (the dihedral angles of the two benzene rings in two bpdc are 41.20 and 17.25°, respectively). This distortion[9] is required to make room to accommodate the two interlocking Co(bpdc) layers (Fig. 3). As a result, the planar lattice of quadrilateral shaped grids in **1** is replaced by an undulating network with irregular rhombus (Fig. 3). Interconnection of the adjacent wave-like layers by
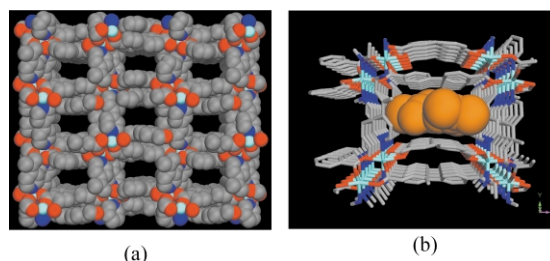

Scheme 1

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(a)   (b)
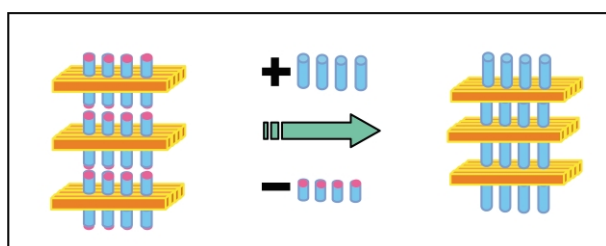
Fig. 1 (a) View of ℝPM-2 (**2**) structure along the *a*-axis. (b) View showing a 1D open channel filled with DMF solvent molecules.

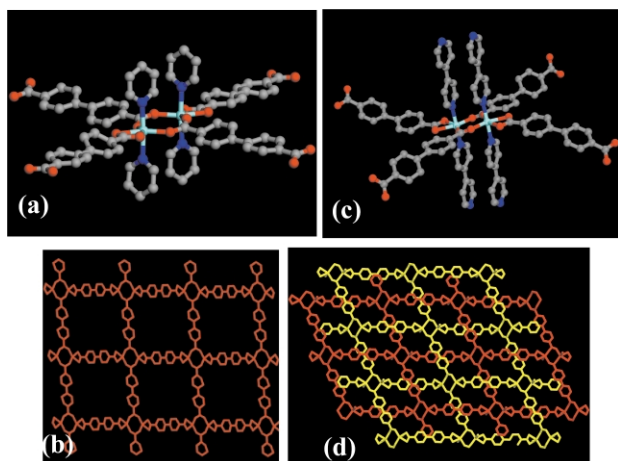**Fig. 2** (a) Basic building block [Co$_2$(bpdc)$_4$(py)$_4$] in **1**. Co (light blue), O (red), N (blue), C (gray). (b) 2D Co(bpdc) backbone structure motif in **1**. (c) Basic building block [Co$_2$(bpdc)$_4$(bpy)$_4$] in **2**. (d) Two-dimensional slab in **2** composed of two identical and interpenetrating Co(bpdc) backbone structure motifs.

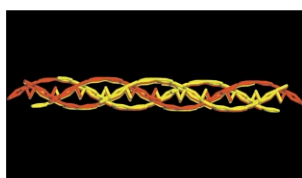**Fig. 3** Side view of the two identical and interlocking Co(bpdc) layers in **2**.

4,4′-bpy as pillars gives rise to a non-interpenetrating 3D framework with 1D rectangular channel (~ 5.6 × 3 Å based on van der Waals radius of carbon) running along the *a*-axis. (Fig. 1a). The solvent molecules (DMF) are arranged in a head-to-tail fashion within every channel (Fig. 1b). Calculation of the pore volume in **2** reveals that 28.6% of the structure is occupied by guest molecules.

Under nitrogen environment, thermogravimetric analysis (TGA) performed on the as-synthesized ℝPM-2 showed one-step weight loss of DMF in the range of 160–200 °C. The framework structure is stable up to 350 °C. PXRD analysis indicated Co$_3$O$_4$ as the only residue after the sample was heated to 700 °C. For gas adsorption experiments, the sample was heated to 200 °C to remove the guest molecules. The PXRD pattern showed no change compared to the simulated pattern produced from the single crystal XRD based structure.

ℝPM-2 displays high (reversible) sorption capacity for hydrocarbons (Table 1), despite its small 1D channels. While its adsorption properties resemble those of zeolites they are clearly

Table 1 Sorption properties of ℝPM-2

Hydrocarbon	P/P^{oa}	Sorption (wt.%)
Propene	0.063	11
n-Hexane	0.48	10
Cyclohexane	0.45	9
p-Xylene	0.34	11
o-Xylene	0.37	15
Mesitylene	0.27	11
Triisopropylbenzene	~ 0.9	1

^{a} P is the sorption partial pressure of a sorbate, and P^o is the calculated vapor pressure at the sorption temperature at 30 °C.

unique owing to its hydrocarbon based surface and distinctive pore structure. The adsorption capacities range from 9 to 15 wt% for the sorbed gases. The uptake of large molecules such as cyclohexane, xylenes and mesitylene is unexpected for ℝPM-2 with a channel opening of 5.6 × 3 Å. In particular, the uptake of large mesitylene molecules, which are too large for ZSM-5, a zeolite with 5.5 × 5.5 Å channels, is surprising. This suggests flexibility of ℝPM-2's channel windows (composed of aromatic hydrocarbons) and also reflects the difficulty of precisely calculating the pore size of the hydrocarbon based pores. Triisopropylbenzene (8.5 Å) is excluded, consistent with ℝPM-2′s pore diameter. At 30 °C, ℝPM-2's adsorption capacity for ortho-xylene, 15 wt% (0.17cm^3 g^{-1}), is unusually larger than for other hydrocarbon gases (~ 10 wt%). Also, an unexpected increase in *o*-xylene capacity is observed for 60 → 40 °C, ~ 4 wt% while for *p*-xylene the difference is only ~ 1 wt%. This is attributed to more efficient packing of *o*-xylene. The isosteric heat of adsorption of n-hexane at zero coverage of ~ 68 kJ $^{-1}$ was obtained from adsorption isotherms. This heat of sorption is considerably larger than that of H–Y (45.5 kJ mol^{-1}), and is close to that of H-ZSM-5 (68.8 kJ mol^{-1}).[10] The heat of sorption for ℝPM-2 is close to that for ℝPM-1 (66 kJ mol^{-1})[7] indicating that both ℝPM-1 and ℝPM-2 interact strongly with n-hexane.

In conclusion, deliberate replacement of ligands via a structural transformation of a coordination motif has led to a porous 3D network with essentially the same backbone structure. This network structure can be recycled via a three-step process. This approach may become a practical route for partial modification of structure topology in crystal engineering. The porosity and unusual sorption capability of ℝPM-2 are of significant interest for applications in sorption, separation, and shape-selective reactions.

Notes and references

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