

Synthesis and characterization of recyclable porous materials

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Introduction

Zeolites are solid materials that contain rigid frameworks and accessible internal channels or cages. They have been used in many applications in areas of catalysis and phase separation.[1] Recent work has shown that porous metal organic materials have properties that mimic and sometimes are superior to those of zeolites.[2] Novel metal organic framework structures with specific functionality can be designed and rationally synthesized, by selecting suitable organic ligands and metal centers. In this paper, we describe our recent study of a group of organic framework structures based on the metal cobalt and the organic ligands biphenyldicarboxylate (bpdc) and bipyridine (bpy), RPMs (Rutgers Recyclable Porous Materials) that are porous and recyclable.[3] This remarkable structural recyclability makes these systems highly promising for use as host materials in ship-in-bottle catalysis.

RPM1-Co

Single crystals of three-dimensional (3D) $[\text{Co}_3(\text{bpdc})_3\text{bpy}] \cdot 4\text{DMF} \cdot \text{H}_2\text{O}$ (RPM1-Co) (DMF = dimethyl formamide) were grown by the solvothermal method.[4] The compound is stable in common organic solvents but can be quickly converted to a one-dimensional chain like structure, $[\text{Co}(\text{bpdc})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ [4], when immersed in water. The crystal structure of RPM1-Co was determined by single crystal X-ray diffraction to reveal a two-fold interpenetrating 3D network based on a unique building block that contains two independent cobalt centers (Fig. 1). Octahedral Co1 located in 2-fold rotation center connects to two adjacent distorted trigonal bipyramidal Co2 centers through six distinct bpdc ligands in different orientations. Each of the two Co1-Co2 pairs is connected by three carboxylate groups via two μ_2 and one μ_3 bonding modes. The Co3 unit, acting as a node, is connected to six adjacent nodes via six bpdc to form a two-dimensional (2D) layer parallel to the *ab* (*xy*) plane. The remaining coordination sites of the two Co2 in each building block are occupied by nitrogen atoms of bpy ligand acting as pillars, which bind the adjacent 2D layers to generate a pillared 3D framework. Two of these pillared 3D motifs, identical in structure, interpenetrate to yield a new type of catenated network consisting of a uniquely shaped one-dimensional (1D) channels (see Fig. 2). All aromatic rings are approximately parallel to the *z*-axis, acting as sidewalls of the channels. As shown in Fig. 2a, the cross-section of the narrow windows is $\sim 8 \times 8 \text{ \AA}$

and the size of supercage is $\sim 11 \times 11 \times 5 \text{ \AA}$, calculated by subtracting the Van der Waals radii of carbon atoms 1.65-1.70 \AA . DMF and H_2O molecules fill in these channels (Fig. 2a). The thermal stability of RPM1-Co was examined by thermogravimetric (TG) experiment in either air or under nitrogen atmosphere. Both experiments indicated a weight loss of $\sim 22.7\%$ around $180 \text{ }^\circ\text{C}$, corresponding to the weight of all guest water and DMF molecules (calc. 22.7%). Upon further heating, the desolvated samples showed no signs of decomposition up to $400 \text{ }^\circ\text{C}$.

RPM1-Co showed strong sorption capacity for hydrocarbons. At $80 \text{ }^\circ\text{C}$, the measured sorption capacities for propylene (600 Torr), n-hexane (vapor, 90 Torr), and cyclohexane (vapor, 60 Torr) were 12, 15, and 19 wt%, measured relative to mass of RPM1-Co, respectively. The sorption capacity for cyclohexane (19 wt%) was even larger than that of one of the most open zeolites, H-Y (17 wt%), which demonstrated the high porosity of our coordination polymer. Experimental sorption isotherms for n-hexane and cyclohexane at various temperatures were determined. Fits to the Langmuir equation yielded isosteric heats of sorption, 72 and 65 kJ/mol for n-hexane and cyclohexane, respectively. The heat of n-hexane sorption on RPM1-Co was considerably larger than that for a typical zeolite (e.g., 53 kJ/mol for H-Y), and was close to, although not as large as, that for H-ZSM-5 (82 kJ/mol). The large isosteric heat suggested the strong sorption of these hydrocarbons in the pores of RPM1-Co.

The photolysis of o-MeDBK (DBK = dibenzylketone) on RPM1-Co was investigated using a 500 W medium-pressure mercury lamp. When adsorbed on FAU or MFI zeolites, o-MeDBK typically undergoes two photoreactions: (a) α -cleavage followed by loss of carbon monoxide to form a geminate pair of hydrocarbon radicals, which undergo geminate (product AB) or random combination (products AA, AB and BB), and (b) an intramolecular hydrogen abstraction followed by cyclization to form a cyclopentanol, CP. Photolysis of o-MeDBK on RPM1-Co produced only AB with 60% yield in reaction (a), corresponding to a "cage effect" of 100% (compared to a cage effect of 70% for photolysis of o-MeDBK in NaX) [6]. The yield of CP was 40% in reaction (b). This yield of CP is much higher than the values found in other zeolites, for example, NaX, where the maximum yield is $\sim 10\%$. In addition, it was observed that only $\sim 50\%$ of the overall products could be extracted before breaking the RPM1-Co framework. The remaining 50% of the products were recovered only after RPM1-Co was immersed in water and completely converted to the 1D $[\text{Co}(\text{bpdc})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$, giving a 100% mass balance. For NaX, the mass balance of the same experiment was 60-70%. The results from the photolysis experiment show the potential of RPM1-Co to be used as "smart" porous host for "ship-in-bottle" synthesis.

RPM2-Co

A second member of the RPMs is RPM2-Co or $[\text{Co}(\text{bpdc})(\text{bpy})] \cdot 0.5\text{DMF}$, DMF = dimethylformamide, synthesized by mixing $[\text{Co}(\text{bpdc})(\text{py})_2] \cdot \text{H}_2\text{O}$ (py = pyridine), a two-dimensional structure,[5] and bpy in the molar ratio of 1:4. The reaction was carried out in a Teflon-lined autoclave containing 5mL of DMF and heated at 120 °C for one day. RPM2-Co was insoluble in common solvents including methanol, DMF, ether, acetonitrile, chloroform, benzene and toluene. However, it can be readily transformed to the same 1D structure $[\text{Co}(\text{bpdc})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ as in the case of RPM1-Co, when immersed in a hot water/ethanol solution. Upon a mild chemical process,[5] the 1D structure can be converted back to $[\text{Co}(\text{bpdc})(\text{py})_2] \cdot \text{H}_2\text{O}$, thus completing the cycle. X-ray analysis performed on a single crystal of RPM2-Co revealed a structure possessing a non-interpenetrating, three-dimensional network as shown in Fig. 3a. The basic building block, $\text{Co}_2(\text{bpdc})_4(\text{bpy})_4$, is shown in Fig. 3b. The structure contains 1D rectangular channels with a cross section of $\sim 5.6 \times 3 \text{ \AA}$ calculated based on van der Waals radius of carbon. These channels run along the α -axis. The solvent molecules (DMF) are arranged in a head-to-tail fashion within these channels.

Under a nitrogen environment, thermal gravimetric analysis (TGA) performed on the as-synthesized RPM2-Co showed one step weight loss of 10 % in the range of 160-250 °C, equivalent to the loss of two DMF. The framework structure was stable up to 350 °C. Like RPM1-Co, RPM2-Co also displayed a high sorption capacity for hydrocarbons. The adsorption capacities were 9 wt%, 11 wt% and 15 wt% for cyclohexane, propene, and ortho-xylene, respectively.

In conclusion, we have designed and synthesized a unique group of recyclable porous materials that show unprecedented sorption and catalytic properties. We have also investigated their sorption properties. Future work will focus on new members of RPMs with various pore size and shape, and on their possible applications.

Experiment

Synthesis of RPM1-Co: In a typical synthesis, 0.3 mmol of $[\text{Co}(\text{bpdc})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (white-gray), prepared as previously reported, and bpy (0.1 mmol) were stirred in DMF (10mL) and well mixed. The solution was then transferred into an acid digestion bomb, closed and heated at 150 °C for 3 days, giving rise to deep-purple columnar crystals of RPM1-Co [7] in high yield (129.1mg, ~94.5%). A 13.5 mg of the round product was immersed in distilled water for 30 min, yielding $[\text{Co}(\text{bpdc})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ in quantitative yield (10.4mg, cal. 10.5mg).

Synthesis of RPM2-Co: A 2D compound $[\text{Co}(\text{bpdc})(\text{py})_2] \cdot \text{H}_2\text{O}$ and bpy in the molar ratio of 1:4 were reacted in a Teflon-lined autoclave (5 mL of DMF) at 120 °C for one day. Orange needle-like crystals of RPM2-Co were obtained as the major phase in 90% yield.[8]

Acknowledgment

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- [6] X. Lei, Jr. C. E. Doubleday, M. B. Zimmt, N. J. Turro, *J. Am. Chem. Soc.*, **1986**, 108, 2444.
- [7] Crystal data of $[\text{Co}_3(\text{bpdc})_3(\text{bpy})]\cdot 4\text{DMF}\cdot \text{H}_2\text{O}$ (RPM1-Co): orthorhombic crystal system, space group *Pbcn*, $a = 14.195(3)$, $b = 25.645(5)$, $c = 18.210(4)$ Å, $V = 6629(2)$ Å³, $Z = 4$, $d_{\text{calc}} = 1.367$ g cm⁻³, $\rho(\text{MoK}_\alpha) = 0.71073$ Å. The structure was solved by direct methods. The refinement by full-matrix least squares gave final $R_1 = 0.056$ from 3662 reflections with intensity $I \geq 2\sigma(I)$; 2% sgr; (I) for 384 variables. Powder X-ray diffraction (PXRD) analysis of the polycrystalline samples was in excellent agreement with the calculated PXRD pattern produced by single crystal data.
- [8] Crystal data of $[\text{Co}(\text{bpdc})(\text{bpy})]\cdot 0.5\text{DMF}$ (RPM2-Co): monoclinic crystal system, space group *C2/c*, $a = 9.523(2)$, $b = 20.618(4)$, $c = 25.814(5)$ Å, $\beta = 96.20(3)^\circ$, $V = 5050.5(17)$ Å³, $Z = 4$, $d_{\text{calc}} = 1.294$ g cm⁻³. All measurements were made on a Enraf-Nonius CAD4 diffractometer with graphite-monochromated MoK_α Radiation. $R_1 = 0.123$ from 2030 reflections with intensity $I > 2\sigma(I)$.

Figures and Captions

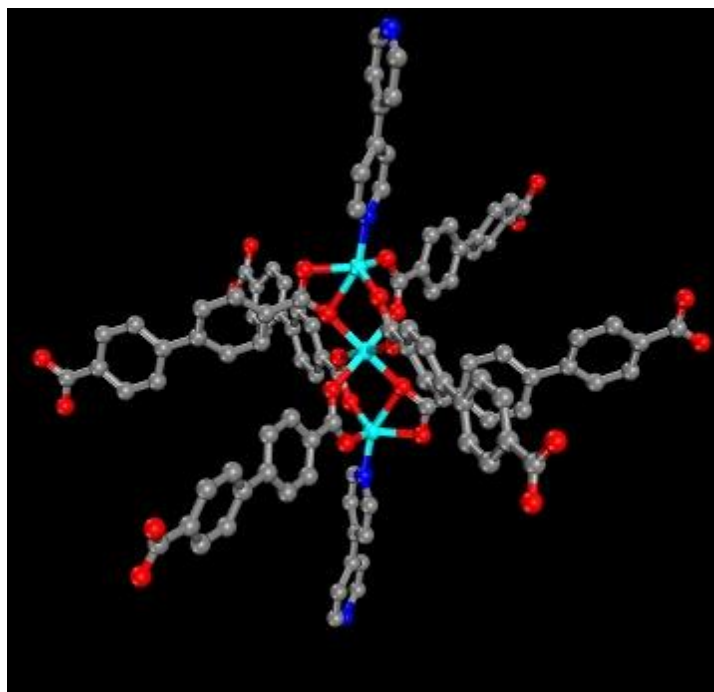


Figure 1. The $\text{Co}_3(\text{bpdc})_6(\text{bpy})_2$ building unit in RPM1-Co. Co (light blue), O (red), N (blue), C (gray).

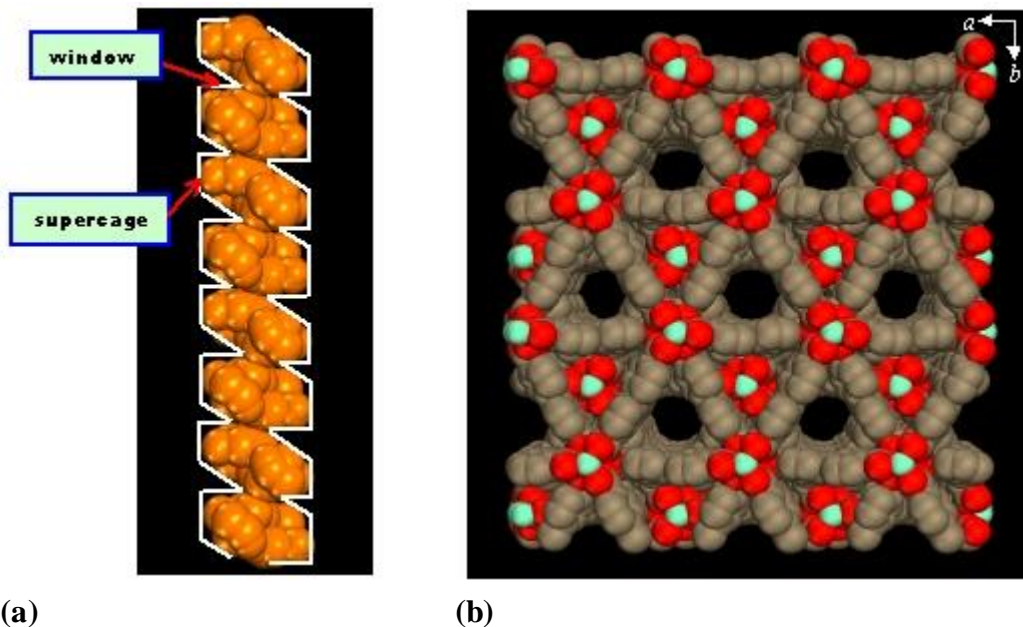


Figure 2. (a) Side (100) view of one-dimensional channel in RPM1-Co with solvent molecules (gold). (b) Top (001) view of the channels showing the window openings.

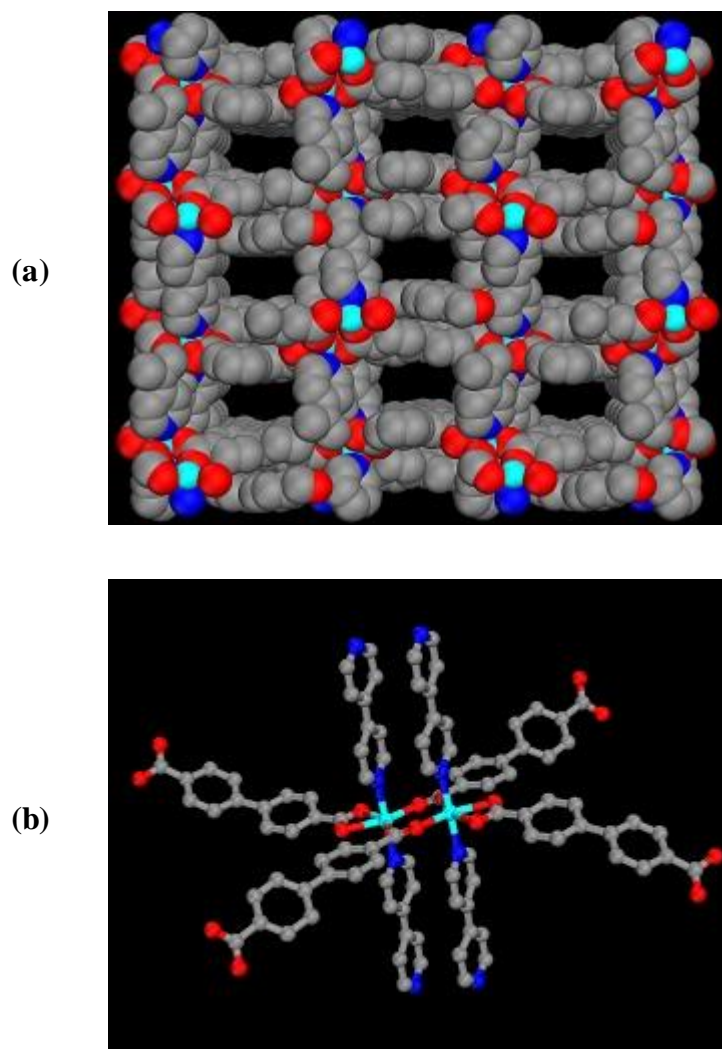


Figure 3. (a) View of RPM2-Co structure along the α -axis; (b) The basic building unit of RPM2-Co, $\text{Co}_2(\text{bpdc})_4(\text{bpy})_4$.

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