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Non-, Micro-, and Mesoporous Metal−Organic Framework Isomers: Reversible Transformation, Fluorescence Sensing, and Large Molecule Separation

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Over the past few years, metal−organic frameworks (MOFs) have attracted tremendous attention owing to their intriguing structural topologies and wide potential applications as functional materials.[1,2] The porosity of MOFs plays crucial roles in gas storage and separation, transport of organic substrates and products in catalysis, etc.[1b,2] Significant challenges remain although some strategies have been developed for achieving large porosity in MOFs in recent years.[1b,c,2c] So far, in the limited mesoporous MOFs, mesoporous cages are included in most cases[3] whereas MOFs with 1D mesoporous channels are particularly rare.[4] Introducing longer bridging ligands as a main strategy, nevertheless, reduced porosity imposed by interpenetration, which is almost unavoidable.[5] It is still elusive, although framework interpenetration was suppressed in a few MOFs.[4a,5a,6] The only case of controlling interpenetration with the same reactants in one-pot synthesis was reported very recently.[6b] Yet, the systematic modulation of pore size, currently, mostly depends on size-alterable organic linkers.[1b,2c] However, to the best of our knowledge, no MOFs with continuously tunable pore sizes based on the same ligands and metal centers/SBUs were reported to date. Herein, for the first time, we prepared nonporous to microporous MOFs by interpenetration control from the same reactants and further enlarged micropores to mesopores by simply decreasing reactant concentrations and reaction time. All three MOFs are isomers based on the same dicadmium(II) SBU and ligands. Strikingly, the microporous and mesoporous MOFs have been demonstrated to be reversibly transformed. In addition, the microporous MOF could be a promising luminescent probe and the mesoporous MOF has been evaluated as a chromatographic stationary phase for large molecule (dye) separation.

Solvothermal reactions of $Cd(NO_3)_2 \cdot 4H_2O$, 4,4′-bipyridine (bpy), and 2-amino-1,4-benzenedicarboxylic acid (**L**) in DMF yielded Cd(**L**)(bpy) (**1**, *C*2/*m*), Cd(**L**)(bpy)·$4H_2O$·2.5DMF (**2**, *Pbam*), and Cd(**L**)(bpy)·$4.5H_2O$·3DMF (**3**, *P*6/*m*) with the same framework formula but different isolated solvents based on single crystal X-ray structural, thermogravimetric (TG), and elemental analyses.[7]

The asymmetric unit of nonporous **1** contains one Cd atom and two half **L** ligands, having a half occupancy factor, and one-half bpy. The Cd atom coordinates to two nitrogens from two bpy ligands and five carboxylate oxygens from three different **L** ligands, two **L** ligands adopt different coordination modes, and bpy bridges two Cd atoms (Figure 1a). Such connectivity leads to a 3D 2-fold interpenetrated network of **1**, in which each network has a pillared-layer structure with bpy as a pillar and a planar channel size of 1.3 × 1.7 nm^2 surrounded by Cd(II) and **L** ligands (Figure 1b). The channels nearly disappear with a free volume of only 3.4% upon interpenetration.[7,8] Further examinations reveal that **1** adopts two interpenetrating 6-connected α-Po net with the Schläfli symbol of $(4^{12}6^3)$ (Figure 1c).

By merely lowering the reaction temperature, microporous **2** was obtained. It adopts a similar framework structure with the single network of **1**, but slight distortion to the structure and pores inevitably occurs to meet the systematic stability of **2**, in which interpenetration is suppressed. There is one Cd atom, one **L** ligand with a half occupancy factor, and a half bpy in the asymmetric unit. The coordination environments of Cd(II) and bpy in **1** and **2** are the same. The unique **L** ligand in **2** has the same coordination functions with the two independent **L** in **1** (Figure 1a, 1d),[7] leading to the same 6-connected topology of **1** and **2** (Figure 1c, 1f). The resultant pillared-layer framework with bpy as the pillar has a planar channel size of 1.1 × 1.9 nm^2 surrounded by Cd(II) and **L** (Figure 1e).[7] PLATON calculation gives a free volume in **2** of 61.2% upon interpenetration control, much higher than that of **1** (3.4%).[8]

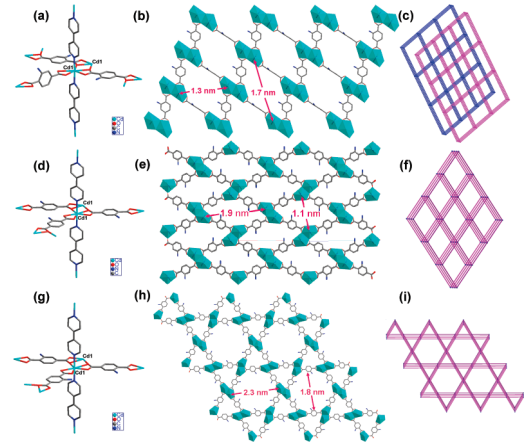

Figure 1. Coordination environments of Cd and ligands in (a) **1**, (d) **2**, and (g) **3**. (b)View of the single network in **1** and (c) topological view of **1** down the *b*-axis. (e) View and (f) topological view of **2** down the *c*-axis. (h) View and (i) topological view of **3** down the *c*-axis. For clarity, the only position was kept for the disordered N atom in amino group.

In contrast to **2**, upon decreasing the concentrations of the reactants and reaction time, mesoporous **3** was successfully prepared. In the asymmetric units of **2** and **3**, all are the same except that a 180° planar turning happens to one of the three **L** ligands connected to Cd(II),[7] leading to two types of channels in **3** along the *c*-axis (Figure 1d−h). In addition to the triangular channel, the larger hexagonal open-channel has a mesoporous size of 1.8 × 2.3 nm^2 parallel to the *ab* plane. As in the case of **1** and **2**, the bpy linker still acts as the pillar in **3** to connect Cd-**L** layers, resulting in a 3D open framework with enormous open channels and a very high free volume of 68.2%.[8] Its structure can be simplified to a rarely reported 6-connected **kag** net with a Schläfli symbol of $(3^2 \cdot 4^8 \cdot 6^5)$ (Figure 1i).[9a,b]

It is very interesting to note that the reversible transformation occurs for compounds **2** and **3** with different sizes of channels. Compound **3** undergoes spontaneous transformation to **2** in air upon losing isolated solvents. The framework of **3** remains over 2 months when it is immersed in mother liquor/DMF, showing its stability. The transformation starts once it is taken out, and the process can be finished in 4 days in air along with the decrease/disappearance

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of the characteristic peak at ~3.9° (Figure 2a).[7] It is proposed that the transformation is triggered by solvent departure, which results in an unstable framework of **3** with too large and bare pores. A theoretical calculation carried out with a VASP program showed the energy of **3** was slightly higher than that of **2**, which revealed the feasibility of reversible transformation between **2** and **3**.[7,9c] With this in mind, our efforts of stretching the pores of **2** with more solvents at higher temperature have successfully converted **2** to **3** under a pressure estimated to be ~265 kPa (Figure 2a).[7] It is assumed that the flexibility of **L** ligand benefits its turning, finally leading to the reversible transformation between **2** and **3**.

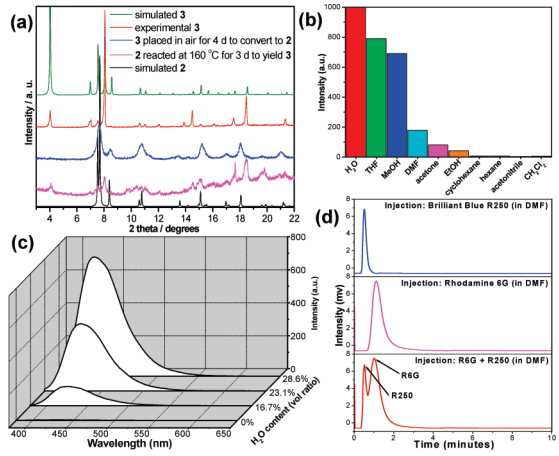

Figure 2. (a) Powder XRD patterns for the reversible transformation between **2** and **3**. (b) PL intensities of **2a** introduced into various pure solvents and (c) PL spectra of **2a** acetonitrile emulsion in the presence of various amounts of H_2O under $\lambda_{ex} = 362$ nm. (d) Separation of R250 and Rhodamine 6G achieved using **3** as the stationary phase (the flow rate of mobile phase (DMF): 0.5 mL/min; detected wavelength: 540 nm).

TG analyses in a He stream show that **1** starts to lose weight and decompose above 260 °C, whereas heating **2** and **3** results in the loss of H_2O and DMF from room temperature to ~300 °C and ~215 °C (corresponding to weight losses of 35.1% for **2** and 40.5% for **3**), respectively, followed by framework combustion.[7] The solid-state photoluminescence (PL) spectra of as-synthesized **1**−**3** were investigated under $\lambda_{ex} = 362$ nm. Compound **1** exhibited weak bands at ~435 and ~525 nm, which could be attributed to the ligand-to-metal charge transfer (LMCT) and intraligand fluorescent emission, respectively.[10] Compounds **2** and **3** displayed strong emission at ~435 nm assigned to LMCT.[10] Interestingly, the PL of desolvated **2** (denoted as **2a**) was almost quenched upon desolvation and presented similar emissions as those in **1**, possibly due to the distortion of framework. Strikingly, the PL spectra of **2a** in different solvent emulsions exhibited excellent fluorescence sensing for small molecules. As shown in Figure 2b, the PL intensity was strongly dependent on the solvent molecule. When **2a** was dispersed in acetonitrile, the fluorescence intensity gradually increased with increasing amounts of H_2O (Figure 2c), where the system rapidly reached the equilibrium state. It is assumed that the restoration of distorted framework **2a** in different solvents is responsible for the fluorescence enhancement. The encouraging result reveals **2a** could be a promising luminescent probe for detecting small molecules.[11] Significantly, **3** was approved to be effective for size-exclusion dominant liquid chromatographic (LC) separation of Rhodamine 6G (larger than the pore of **2** whereas smaller than that of **3**) and Brilliant Blue R-250 dyes (larger than pores of **2** and **3**) whereas **2** with smaller pores was not (Figure 2d).[7] As far as we know, this is the first report on a mesoporous MOF as an LC stationary phase for large dye separation, although limited MOFs for small molecule LC separations were reported.[12] The study could open up a new avenue to large molecule separation.

In conclusion, for the first time, three MOF isomers based on the same structural units but hierarchical pores were prepared, in which not only interpenetration control was realized but also the micro- and meso-porous MOFs can be transformed reversibly. Compounds **2** and **3** could be a potential luminescent probe and an LC stationary phase, respectively. In addition, the available amino groups and hierarchical pores in these MOF isomers make them good candidates for postsynthetic covalent modification for further applications;[13] efforts to realize these are underway.

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Supporting Information Available: Complete refs 2c, 3e, and 12a; full preparation details; and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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