Porous Materials

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Mesoporous Metal–Organic Framework with Rare etb Topology for Hydrogen Storage and Dye Assembly**

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Metal–organic frameworks (MOFs) have attracted much attention owing to their enormous variety of interesting molecular topologies and wide potential applications as functional materials.[1] Over the past decade, discrete clustered metal carboxylate secondary building units (SBUs) have been constructed to produce a new generation of highly porous MOFs.[2,3] Recently, infinite rod-shaped metal carboxylate SBUs have provided effective routes to obtain novel MOFs without interpenetration because of the intrinsic packing arrangement of the rods in the crystal structure.[4,5] As a typical example of an infinite rod-shaped metal carboxylate SBU, Riou, Férey, and co-workers synthesized MIL-47, the structure of which consists of rigid organic linkers that connect chains of corner-sharing transition-metal octahedra.[4a] Furthermore, Yaghi, O'Keeffe, and co-workers have systematically studied such rod-shaped metal carboxylate SBUs and reported the preparation, characterization, and crystal structures of 14 new MOFs with 12 different structure types; they also demonstrated how their structures are related to basic nets.[5a] Concerning rare-earth rod-shaped MOFs, Devic, Férey, and co-workers have, for the first time, synthesized the 3D lanthanide-based MOF MIL-103 with large one-dimensional tunnels and a high surface area.[6] In our previous studies, we have also successfully prepared a series of novel 3D rare-earth MOFs with rod-shaped SBUs by the reaction of rare-earth ions with 4,4′-biphenyldicarboxylic acid (H_2bpdc).[7] However, such MOFs involving infinite rod-shaped metal carboxylate SBUs still remain largely unexplored.

Herein, our strategy for preparing non-interpenetrating large porous frameworks is to construct infinite rod-shaped cadmium carboxylate SBUs. To implement this design, we use a rigid, linear organic O-donor ligand, H_2bpdc, as a linker, which has been shown to exhibit a variety of flexible coordination forms.[8] H_2bpdc is longer (11.3 Å) than common linear organic O-donor ligands, such as H_2bdc (H_2bdc = 1,4-benzenedicarboxylic acid, 7.7 Å), and will have the potential to construct large porous MOFs. Herein, we describe the synthesis and structure of a novel metal–organic framework, $[Cd_3(bpdc)_3(dmf)]\cdot 5\,dmf\cdot 18\,H_2O$ (named JUC-48, JUC = Jilin University China), constructed from rod-shaped Cd^{II} carboxylate SBUs. Of particular interest is that these rod-shaped SBUs are interconnected through the biphenyl groups of bpdc to generate a 3D non-interpenetrating extended network with rare etb[5a] topology and 1D hexagonal nanotube-like channels of 24.5 Å × 27.9 Å. To our knowledge, JUC-48 is the MOF with the largest 1D nanotube-like channels reported to date.[6,9] The high-pressure hydrogen storage and fluorescence properties of JUC-48 have been examined. Additionally, for the first time, JUC-48 can be assembled with nanosized rhodamine 6G dye molecules (Rh6G), and the product (JUC-48·Rh6G) shows favorable temperature-dependent luminescent properties.

X-ray crystallography reveals that JUC-48 crystallizes in the orthorhombic system, space group *Pbcn* (No. 60).[10] The fundamental building unit of JUC-48 contains three cadmium centers, three bpdc ligands, one coordinated dmf ligand, five guest dmf molecules, and eighteen guest H_2O molecules. Two crystallographically distinct Cd atoms adopt distorted octahedral coordination geometries with six oxygen atoms from five carboxylate groups of bpdc. The third Cd center is coordinated by seven oxygen atoms from five carboxylate groups of bpdc and one terminal dmf ligand. Each bpdc ligand coordinates to five different Cd^{II} ions through two different coordination modes: bidentate and chelating/bisbridging bidentate. The six- and seven-coordinate Cd^{II} ions are linked together by carboxylate groups of bpdc to construct 1D Cd-O-C chains running along the [001] direction. These Cd-O-C chains, as rod-shaped SBUs, are interconnected through biphenyl groups of bpdc to generate a 3D non-interpenetrating extended network with 1D hexagonal channels of 24.5 Å × 27.9 Å (measured between opposite atoms) viewed along the [001] direction (Figures 1 and 2). When van der Waals radii of the atoms are taken into account, these channels are 21.1 Å × 24.9 Å, in which the vacancies are filled with one coordinated dmf ligand, five guest dmf molecules,

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

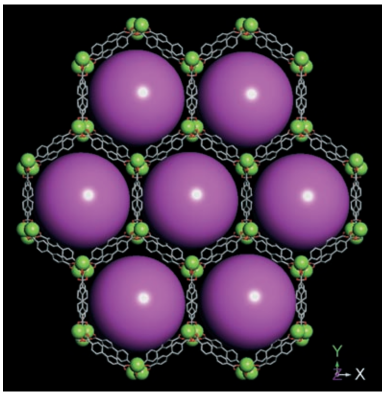

Figure 1. The network of JUC-48 with 1D hexagonal nanotube-like channels, which are indicated by pink spheres of diameter 21.1 Å viewed along the [001] direction. Cd green (ball), O red, C gray.

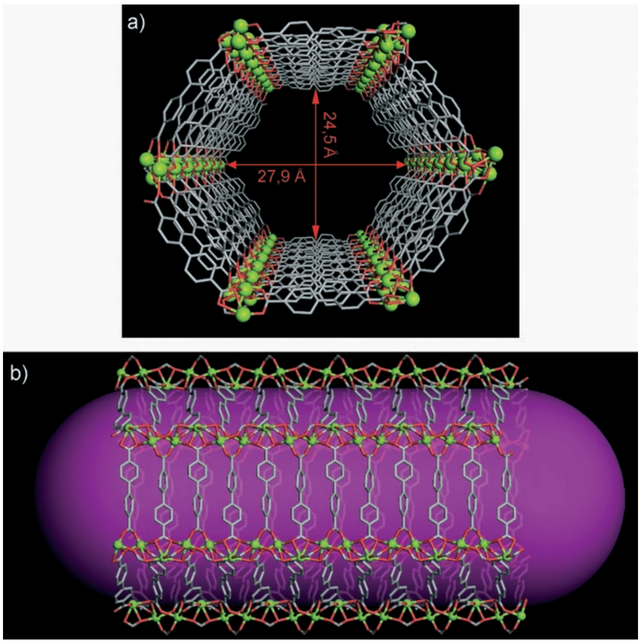

Figure 2. Respresentation of a hexagonal nanotube-like channel of JUC-48 of dimensions 24.5 Å×27.9 Å viewed along the [001] (a) and [100] (b) direction. Cd green (ball), O red, C gray.

and eighteen guest H_2O molecules per formula unit, as established by elemental analysis, inductively coupled plasma (ICP) analysis, and thermogravimetric (TG) analysis. Without guest molecules, the effective free volume of JUC-48 is calculated by PLATON analysis[12] to be 69.8% of the crystal volume (7085.1 $Å^3$ of the 10154.0-$Å^3$ unit cell volume). The permanent porosity of JUC-48 is confirmed by its N_2 adsorption isotherm, which reveals a Langmuir surface area of 880 $m^2 g^{-1}$, pore volume of 0.19 $cm^3 g^{-1}$, and pore size of 18.8 Å.

It is notable that each hexagonal channel of JUC-48 can be viewed as a nanotube-like architecture. As shown in Figure 2, the distance between adjacent bpdc linkers is about 3.8 Å (measured between carbon atoms of adjacent bpdc ligands), which indicates that strong CH⋯π interactions exist between them. Additionally, if van der Waals radii of the carbon atoms (1.7 Å) and hydrogen atoms (1.2 Å) are taken into account, these biphenyl rings of the bpdc ligands construct an impenetrable wall of bpdc units, and it is impossible for additional ligands to fill in between adjacent biphenyl groups.[5b] Thus, an interpenetration structure is prohibited, and a novel architecture with hexagonal nanotube-like channels is formed.

Futher insight into the structure of JUC-48 can be gained by reducing multidimensional structures to simple rod geometries and associated nets.[5] As shown in Figure 3, the carboxylate carbon atoms of the 1D Cd-O-C chain constituting the rod-shaped SBU can be connected to construct a pseudo 3_1 or 3_2 helix. The helices are then linked by linear biphenyl groups of bpdc ligands to generate bnn[5a] parallel rod packing. Considering only the carboxylate carbon atoms as threefold connected nodes of extension and bpdc as bridged ligands, the resulting structure of JUC-48 is a threefold connected 3D network, and its Schläfli symbol is (8^3), which is a rare etb topology in MOFs.[13]

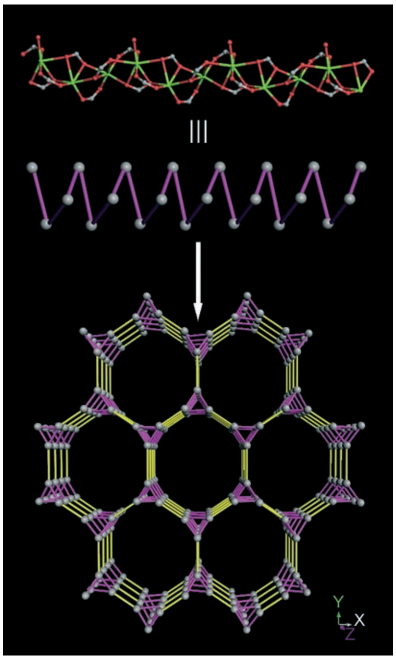

Figure 3. Development of the structure of JUC-48: top, the Cd^{II} ions are linked together by carboxylate groups of bpdc to construct 1D Cd-O-C chains as rod-shaped SUBs (the terminal dmf molecules except for their oxygen atoms are omitted for clarity); middle, the carboxylate carbon atoms of the chain can be connected to construct a pseudo 3_1 or 3_2 helix; bottom, the helices are linked by biphenyl groups (yellow lines) of bpdc to generate bnn parallel rod packing with etb topology. Cd green, O red, C gray.

The high-pressure hydrogen storage capability of JUC-48 was evaluated both at 77 K and at room temperature (298 K). Before the measurements, the sample of JUC-48 was soaked in $CHCl_3$ for 48 h and then evacuated under dynamic vacuum at room temperature for 24 h to remove the included solvent molecules. The hydrogen adsorption isotherm (Figure 4) was recorded using a RUBOTHERM magnetic suspension balance (Ankersmid B.V., Netherlands). At 77 K, the sorption

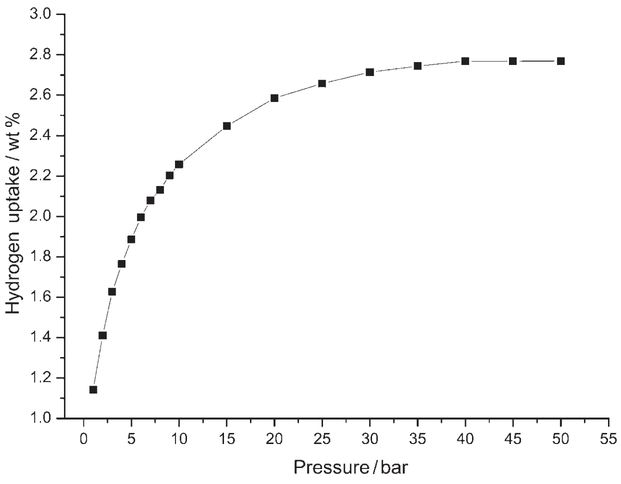

Figure 4. High-pressure hydrogen adsorption isotherm for JUC-48 at 77 K.

isotherm of JUC-48 has a type I profile which is saturated at 40 bar with a hydrogen uptake of about 2.8 wt%, which corresponds to a H_2 storage capacity of 311.1 mLg^{-1} and is equivalent to the adsorption of about 12 H_2 molecules per formula unit. The room-temperature hydrogen storage capacity of JUC-48 is expected to be about 1.1 wt% at 100 bar, and the H_2 uptake increases linearly with increasing hydrogen pressure. Although the hydrogen uptake of JUC-48 is lower than some reported MOFs with high hydrogen storage (such as MIL-101,[14] MOF-177[15] and $[Zn_3(bdt)_3(dmf)_4(H_2O)_2]\cdot 3.5\,CH_3OH$[16]; bdt = 1,4-benzeneditetrazolate), to our knowledge it is comparable with many MOFs and is higher than "active" carbon (CECA, France) and purified single-walled carbon nanotubes.[17,18]

Encouraged by the single-crystal X-ray diffraction results, JUC-48 was assembled with nanosized Rh6G dye molecules (Figure 5 a, inset) by adding Rh6G in ethanol (0.2 mL, 10^{-3} M) to the growth solution; the amount of Rh6G in the red-colored doped crystals was about 0.046%, as determined by TG, ICP, and elemental analysis (see the Supporting Information). Rh6G is a xanthene derivative used as a gain medium in dye lasers, and it exhibits strong absorption in the visible region and a very high fluorescence quantum yield.[19] Recently, an increasing number of studies have tried to incorporate Rh6G into hybrid organic–inorganic materials for applications in fields such as solid-state lasing, optical filters, and optoelectronics.[20] Figure 5 a shows the fluorescence spectra for JUC-48·Rh6G. Clearly, the strongest emission peak for JUC-48·Rh6G is at 563 nm with the excitation peak at 541 nm at room temperature, which is similar to the previous results obtained on Rh6G-doped mesostructured materials.[21] Furthermore, JUC-48·Rh6G can be also obtained by immersing JUC-48 for 36 h in solutions of Rh6G in ethanol with different concentrations (10^{-3}, 10^{-4}, and 10^{-5} M). However, the emission peaks exhibit a blue shift (574 nm, 567 nm, and 555 nm, respectively) when the concentration of the Rh6G solution used to prepare JUC-48·Rh6G is decreased from 10^{-3} to 10^{-5} M (see the Supporting Informationn), which implies that the Rh6G dye in the crystals is present as free monomer molecules and shows fine fluorescence properties.[22] The emission spectra of JUC-48·Rh6G are also temperature-dependent. Figure 5 b shows the emission spectra of JUC-48·Rh6G recorded at different temperatures (298–77 K). The peak location of JUC-48·Rh6G at 563 nm remains unchanged with decreasing temperature, while the intensity of the signal is enhanced linearly, which reveals that JUC-48·Rh6G will be a potential candidate for applications in temperature-sensing devices.[23]

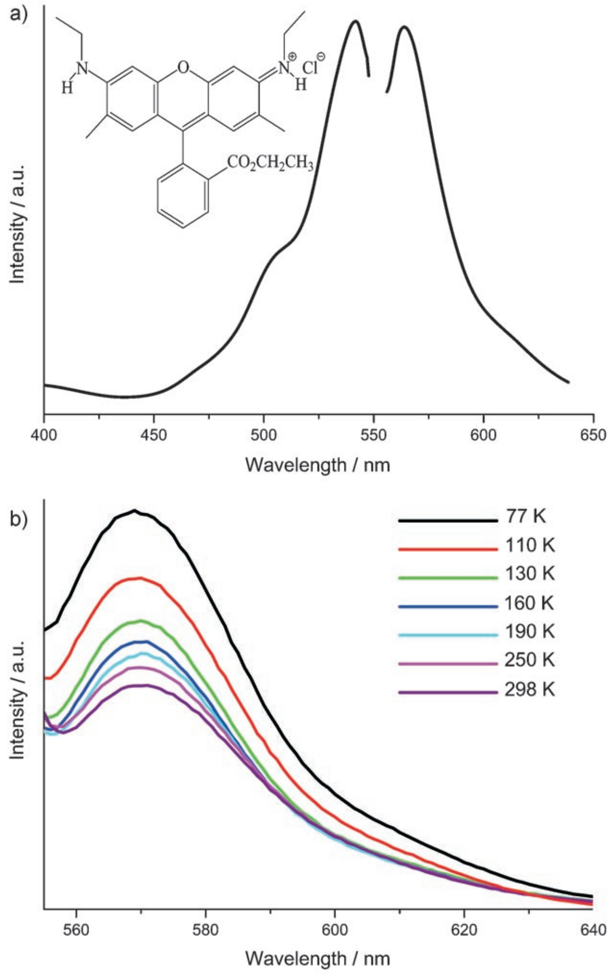

Figure 5. Fluorescence spectra of JUC-48·Rh6G a) at room temperature and b) at different temperatures. In a), the inset shows the molecular structure of Rh6G.

In conclusion, we have successfully synthesized a new MOF, $[Cd_3(bpdc)_3(dmf)]\cdot 5\,dmf\cdot 18\,H_2O$ (JUC-48), with the largest reported 1D hexagonal nanotube-like channels of 24.5 Å × 27.9 Å and rare etb topology, constructed from rod-shaped cadmium carboxylate SBUs. JUC-48 exhibits good fluorescence properties and substantial hydrogen uptake. In addition, for the first time, JUC-48 was assembled with Rh6G dye molecules, and JUC-48·Rh6G shows favorable temperature-dependent luminescent properties. It is believed that these results will further facilitate the exploration of such MOFs as new types of functional materials for applications in fields such as optical materials, high-pressure hydrogen storage, and temperature-sensing materials.

Experimental Section

JUC-48: A mixture of $Cd(NO_3)_2{\cdot}4H_2O$ (0.15 g, 0.5 mmol), H_2bpdc (0.05 g, 0.25 mmol), and dmf (50.0 mL) was stirred in air for 2 h. Subsequently, triethylamine (0.5 mL) in dmf (15.0 mL) was slowly diffused in at 60 °C over three days. The resulting colorless rod-shaped crystals of JUC-48 were collected in 80 % yield based on cadmium. The complex was insoluble in common organic solvents such as acetone, methanol, ethanol, dichloromethane, acetonitrile, chloroform, and dmf. Elemental anal. and ICP analysis calcd (%) for $C_{60}H_{102}N_6O_{36}Cd_3$ (1820.72): C 39.58, H 5.65, N 4.62, Cd 18.52; found: C 39.63, H 5.69, N 4.58, Cd 18.50. FT-IR (KBr): $\tilde{\nu} = 3423$ (m), 2929 (w), 2362 (w), 1653 (s), 1577 (s), 1522 (s), 1390 (s), 1176 (w), 1105 (w), 1005 (w), 854 (m), 771 (s), 681 (w), 432 (w) cm^{-1}.

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[10] A colorless, rod-shaped crystal of $[Cd_3(bpdc)_3(dmf)]{\cdot}5\,dmf{\cdot}18\,H_2O$ (JUC-48, $C_{60}H_{102}N_6O_{36}Cd_3$, $M_w = 1820.72$) was selected for X-ray structural analysis on a Bruker SMART CCD diffractometer at 293 K. The complex crystallized in the space group *Pbcn*, orthorhombic, dimensions $0.45 \times 0.20 \times 0.16$ mm, $a = 24.498(5)$, $b = 45.853(9)$, $c = 9.0389(18)$ Å, $V = 10154(4)$ Å^3, $Z = 4$, $\lambda = 0.71073$ Å, $\rho_{calcd} = 0.740\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 0.651\ mm^{-1}$, $F(000) = 2224$. A total of 49 999 reflections were collected in the range of $2.37 < \theta < 25.00$, of which 8704 were unique. The structure was solved and refined by full-matrix least-squares on F^2 values (SHELXL-97).[11] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at calculated positions and refined using a riding mode. The final $R1(wR2)$ value was 0.0727 (0.2326) for 6608 independent reflections $[I > 2\sigma(I)]$. CCDC-622797 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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