Benzene-Templated Hydrothermal Synthesis of Metal–Organic Frameworks with Selective Sorption Properties

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Abstract: In this paper, we report two metal–organic frameworks $[Co_3(ndc)_3(bipyen)_{1.5}]\cdot H_2O$ (**1**) and $[Co_2(ndc)_2(bipyen)]\cdot C_6H_6\cdot H_2O$ (**2**) (bipyen = *trans*-1,2-bis(4-pyridyl)ethylene, H_2ndc = 2,6-naphthalenedicarboxylic acid). These compounds were both synthesized from identical hydrothermal reaction conditions except that benzene was added to the reaction for **2**. Crystal structures show that the two compounds have triply interpenetrated three-dimensional frameworks and these frameworks have the same primary structure of a two-dimensional network of interconnected $[Co_2(O_2CR)_{4/2}]$ (R = naphthalene group) paddle-wheels and bridging bipyen ligands. Both compounds have guest water molecules and, in addition, **2** has guest benzene molecules. Structural transformations of the host accompanied guest removal, which can be monitored by powder X-ray diffraction. N_2 adsorption data of **2** show that there are two different types of pores corresponding to the benzene and water pores. Upon exposure to vapors of several organic molecules, the heat-treated sample of **2** adsorbs benzene and cyclohexene, but does not adsorb toluene, (*o*-, *m*-, and *p*-)xylenes, cycloheptatriene, or cyclohexane.

Keywords: adsorption • benzene templates • host–guest systems • hydrothermal synthesis • metal–organic frameworks

Introduction

With the potential for tailor-made syntheses of sorption hosts with molecule-specific adsorption properties, various kinds of porous materials have been investigated.[1,2] Metal-organic frameworks (MOFs) are the most recently highlighted class of materials in this regard.[3–9] Unfortunately, MOFs often have structures with interpenetrated frameworks producing only small pores, especially when synthesized under hydrothermal conditions.[8] This has been considered as a major obstacle for endowing sorption properties to MOFs, and several solutions have been proposed to prevent the formation of the interpenetration structures.[4,5] In fact, most of the MOFs with accessible pores described in the literature have been synthesized from low-temperature reactions in nonaqueous media (i.e., diffusion reactions).[6–9]

In most of the MOFs, the (potential) pore walls are formed by the hydrophobic parts of ligand molecules. We envisioned that these pores tend to be small to avoid the unfavorable contact with solvent water molecules under typical hydrothermal reaction conditions. Conversely, if there are hydrophobic molecules present during MOF formation, they may function as guests occupying the pores through hydrophobic interactions with the ligands and consequently promote the formation of large pores. With this idea in mind, we have explored such possibilities and found a novel MOF system that formed either an inclusion compound with benzene as a guest or a simple triply interpenetrated structure depending on whether benzene was present in the reaction mixture during the syntheses. The MOF from the benzene-containing reaction shows specific adsorption properties for benzene and cyclohexene as opposed to other ring compounds. Herein, the details of syntheses and characterization are reported.

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Results and Discussion

Hydrothermal reactions of $Co(NO_3)_2{\cdot}6H_2O$, 2,6-naphthalenedicarboxylic acid (H_2ndc), and *trans*-1,2-bis(4-pyridyl)ethylene (bipyen) in water produced the MOF $[Co_3(ndc)_3(bipyen)_{1.5}]{\cdot}H_2O$ (**1**) in which two-dimensional networks of interconnected $[Co_2(O_2CR)_{4/2}]$ (R = naphthalene group) paddle-wheels[5] are bridged by the bipyen ligands to form triply interpenetrated three-dimensional frameworks (Figure 1). Two of the three frameworks are generated by the paddle-wheels of Co1/Co2 and the third one by those of Co3. The two types of framework have essentially the same structure and the one of Co3 is shown in Figure 1b with a schematic drawing of the unit mesh to show the dimensions of the framework. The interpenetrated structure leaves three-dimensional interconnected channels between the neighboring frameworks of Co1/Co2, which are occupied by water molecules. When benzene was added to the reaction mixture and the other conditions were kept unchanged, the reaction produced a different MOF $[Co_2(ndc)_2(bipyen)]{\cdot}C_6H_6{\cdot}H_2O$ (**2**) that shows another triply interpenetrated structure of the same primary framework as **1** (Figure 2).

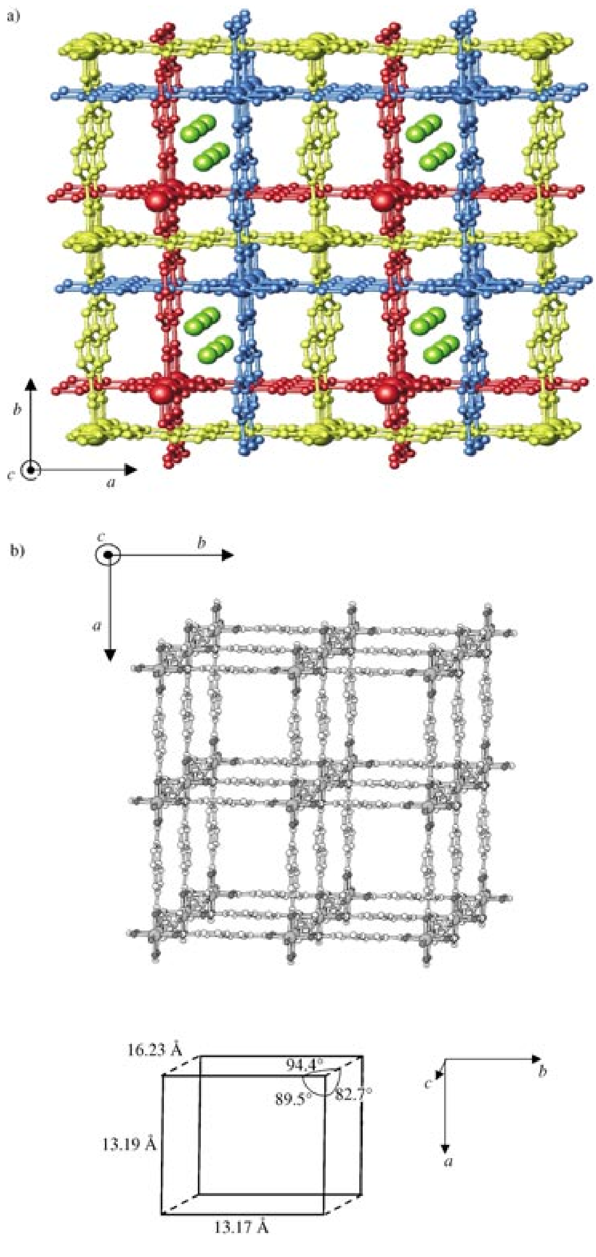

Figure 1. a) Triple interpenetration structure of **1**. Red and blue frameworks are inversion-related to each other and are formed by Co1 and Co2; yellow framework is formed by Co3. The oxygen atoms of the guest water molecules are shown as green spheres. b) Single framework structure of Co3 and its mesh dimensions. Gray, white, hatched, and dark spheres are cobalt, carbon, nitrogen, and oxygen atoms, respectively.

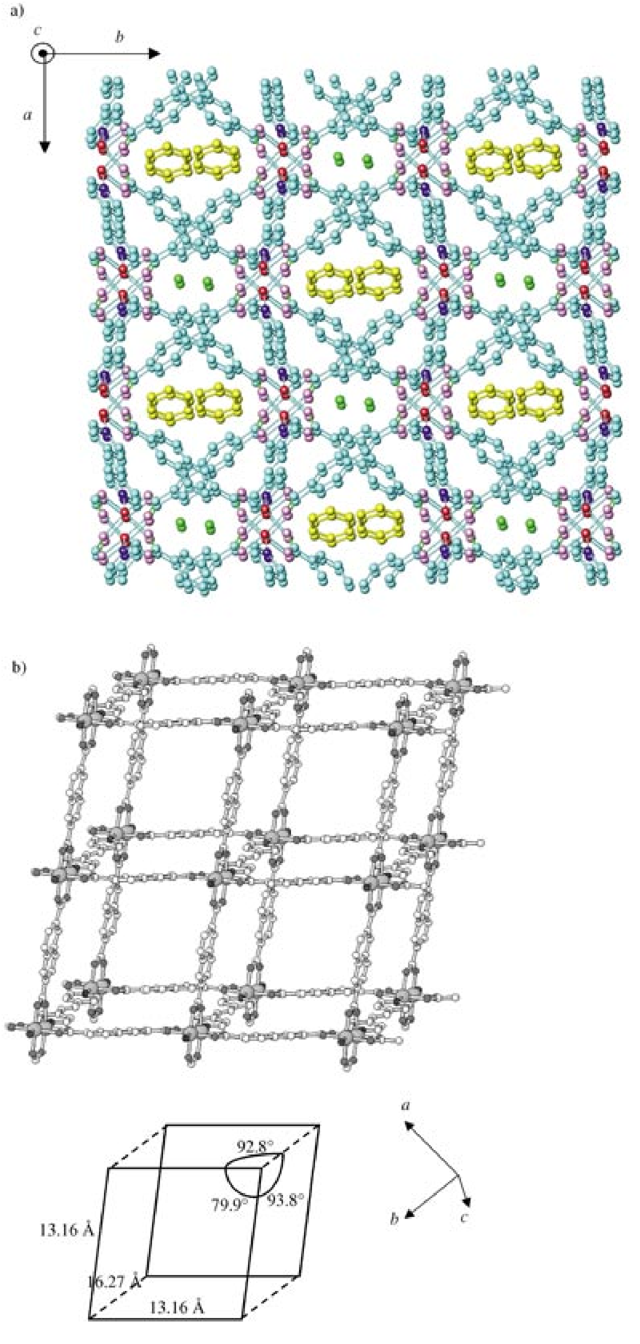

Figure 2. a) Structure of **2** with the benzene and water guest molecules. Red, purple, blue, and light blue spheres of the framework are cobalt, oxygen, nitrogen, and carbon atoms, respectively. Guest benzene and water molecules are in yellow and green, respectively. b) Single framework structure and its mesh dimensions. Gray, white, hatched, and dark spheres are cobalt, carbon, nitrogen, and oxygen atoms, respectively.

The unit mesh is considerably distorted compared with that of **1**. Because of the distortion, there are free volumes generated between the frameworks that are occupied by lattice water and benzene molecules. Based on the crystallographic data and the van der Waals radii of atoms, the pore cross sections are calculated to be 4.3×4.3 Å^2 in **1** and 6.6×6.2 (benzene pore) and 4.4×3.5 Å^2 (water pore) in **2** (Figure 3). There are two papers concerning benzene-clathrated crystals in the literature, one about a one-dimensional MOF[9] and the other about an organic crystal with internal hydrogen bonds forming a network structure.[10]

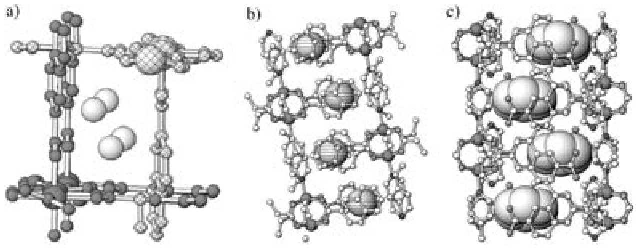

Figure 3. Immediate environments around the guests: a) water molecules in **1**, b) water, and c) benzene molecules in **2**.

Although there are already many examples of MOFs with incorporated guest molecules, it is notable that most of them are from diffusion reactions in nonaqueous solvents under ambient pressures and low temperatures.[6,7] The guest molecules in these cases are either the solvent molecules or molecules that dissolve in the solvents. Both of the benzene-clathrated crystals mentioned above were also formed from low-temperature reactions in nonaqueous solvents. In contrast, our compound **2** is formed by means of a hydrothermal reaction using high temperature, high pressure, and water as the solvent. Because of these conditions, hydrothermal reactions typically produce MOFs with densely packed structures or a high degree of interpenetration. In order to overcome this problem, we used a hydrophobic template. Although the incorporation of benzene molecules does not influence the primary structure of the framework or the triple-interpenetration structure, it changes the structure and creates pores.

The two compounds show contrasting sorption properties for the guest molecules. Thermogravimetric analysis (TGA) data of **1** show that it loses lattice water at 100–140 °C by 1.8% (calcd 1.6%). The TGA data of **2** show a benzene-loss step below 110 °C by 10.1% (calcd 9.4%) and water-loss step at 320 °C by 1.8% (calcd 1.93%) (Figure 4a).

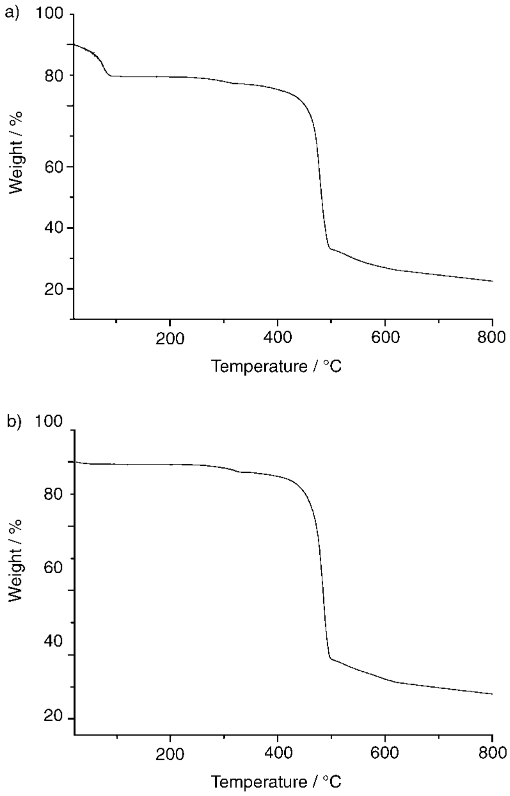

Figure 4. TGA curves of a) **2** and b) **2a**.

We have found that the two MOFs undergo structural transformations on removing the guest molecules, which can be readily monitored by powder X-ray diffraction (XRD). As can be seen in Figure 5a, the water molecules of **1** can be removed by heating at 200 °C for 2 h, but they cannot be reinserted by exposing the water-desorbed crystals to water vapor at room temperature for 48 h. The benzene molecules

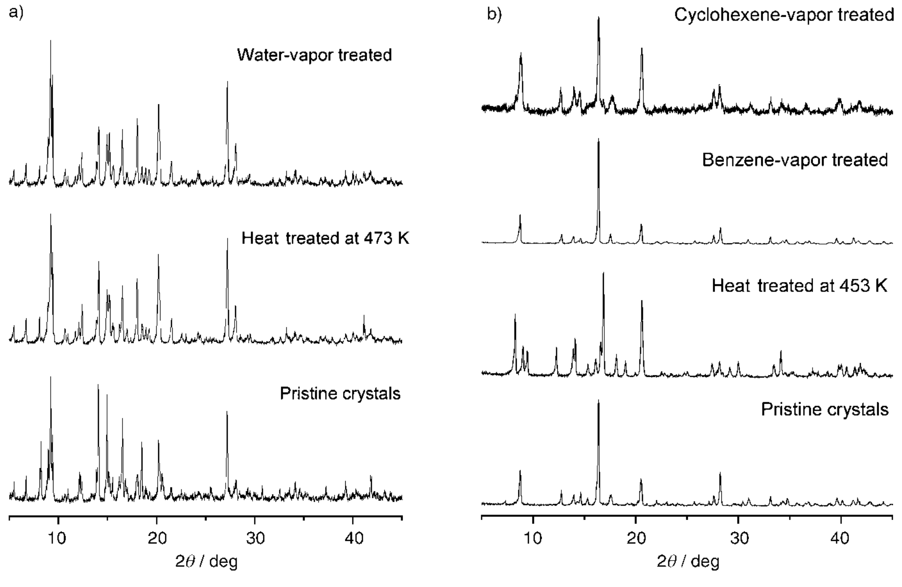

Figure 5. Powder X-ray diffraction patterns of a) **1** and b) **2** treated under various conditions.

of **2** can be removed by heating at 180°C for 1 hour or by vacuum treatment at room temperature, as can be seen by the TGA data (Figure 4b). However, this process can be reversed by exposing the benzene-desorbed sample (hereafter **2a**) to benzene vapor for 7 days at room temperature (Figure 5b). In addition to the XRD data, this benzene-readsorbed sample of **2a** shows practically the same TGA curve as the original crystals of **2**, suggesting that the benzene desorption–adsorption processes of **2** are reversible. The larger pore size and the more favorable host–guest interactions of **2** compared with **1** are probably the main reasons for the different sorption characteristics of the two compounds.

The N_2 adsorption isotherm of **2**, taken at 77 K after evacuation at 100°C and 10^{-4} Pa for 2 h, shows two pore-filling steps at $P/P_0 < 0.01$ and $P/P_0 = 0.1$ (Figure 6). The steep uptake at $P/P_0 < 0.01$, due to monolayer adsorption on micropore walls, can be assigned to the micropore filling of N_2 into the benzene pores that have enhanced adsorbent–adsorbate interactions. The second steep uptake at $P/P_0 = 0.1$ is assigned to a block in the entrance of the water pores, since the size of the water pore is almost equal to that of an N_2 molecule. A similar pore-blocking phenomenon has been reported for another MOF crystal with a small pore.[11] This almost vertical adsorption uptake at $P/P_0 = 0.1$ also strongly suggests that the size of the water pore is very uniform. The "knees" of the isotherm at points A and B are very sharp, indicating that pore-size distributions of both pores are extremely narrow.

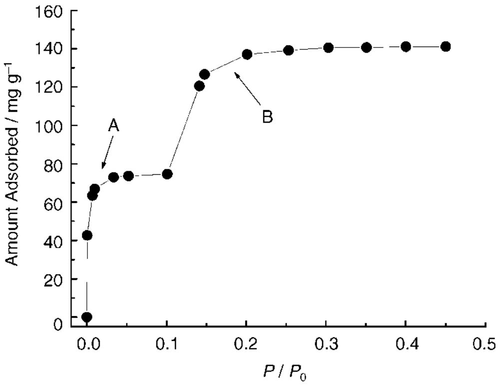

Figure 6. N_2 adsorption isotherm of **2** at 77 K.

Using the Brunauer–Emmett–Teller (BET) and Dubinin–Radushkevich methods on the isotherm data, we have calculated the specific surface areas and micropore volumes of the benzene and water pores of **2**. The larger surface area (254 m^2g^{-1}) and volume (0.11 mLg^{-1}) of the benzene pore compared with those of the water pore (230 m^2g^{-1} and 0.07 mLg^{-1}) are consistent with the crystallographic pore dimensions. However, their differences are not as large as is expected from the crystallographic data. Such discrepancies can be explained by the different packing densities of N_2 within the two pores because of the incompatible dimensions of the adsorbate molecules and the pores. Through the structural change accompanying the sorption–desorption of the guest molecules, the change in the pore dimensions from those of the crystal structure **2** may also contribute to these discrepancies.

We have also studied the sorption properties of **2a** for other organic molecules. On exposing **2a** to a vapor of cyclohexene for 10 days at room temperature, we obtained an XRD pattern similar to that of **2** (Figure 5b). However, the increased background and broadened peaks indicate that the adsorption of cyclohexene may induce structural tension, probably because of the (slight) difference in the dimensions. On the contrary, similar experiments with toluene, (*o*-, *m*-, and *p*-) xylenes, cycloheptatriene, and cyclohexane did not change the XRD pattern of **2a**. Clearly, these experiments demonstrate that **2a** has selective adsorption properties for benzene and cyclohexene as opposed to toluene, xylenes, cycloheptatriene, or cyclohexane. These results bear significant relevance to the petroleum industry, such as in the separation of benzene and toluene from crude oil or gasoline, and the separation of benzene and cyclohexene from cyclohexane. The prevailing methods for these have been fractional-distillation techniques; the products are mixtures with a certain degree of benzene or cyclohexene enrichments, requiring repetitive operations.[12] There are a few reports of using zeolites for these purposes, but the separation by zeolites is based mainly on preference not selectivity of target adsorbents; that is, a small amount of toluene is always adsorbed along with benzene.[13,14] Although not so important in terms of industrial applications, the distinction of benzene from cyclohexane, which have close kinetic diameters of 5.85 and 6.0 Å, respectively,[15] by **2a** is unprecedented by any other sorption host ever reported. Zeolites and reported porous MOFs have selective sorption properties based on the size of the pore openings; any molecules of sizes smaller than a critical kinetic diameter can be adsorbed. On the contrary, with the crystal structure of **2** in which benzene molecules are nested in the pores, we believe that the selectivity of **2a** for benzene over toluene by adsorption arises from the size of the pore, a "final-state effect", rather than the size of the pore opening. Similar high specificity in the clathration was discovered in other MOFs and this discrimination of the isomers in the clathration has been applied to their separation.[16]

The sorption properties of crystal **2a** specific for benzene and cyclohexene might be explained in terms of tailor-made pore structures. That is, because the pores are formed around benzene templates, they have just the right size and shape only for benzene molecules and the right environment to have favorable π–π interactions with benzene molecules. Using this principle, we have also attempted to synthesize other MOFs with hydrophobic guests. Unfortunately, our preliminary experiments employing many different combinations of metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}), dicarboxylate ligands (H_2ndc, 1,3,5-benzenetricarboxylate, isophthalate, 4,4-oxybisbenzoicdicarboxylate, and terephthalate), bi-functional amine or imine ligands (4,4-bipyridine, *trans*-1,2-bis(4-pyridyl)ethylene, and pyrazine), and guest solvents (benzene, toluene, xylene, and naphthalene) all failed in producing the desired MOFs. Probably, the successful synthesis of such MOFs requires very stringent conditions for the dimensions of the host framework and guest molecule. Nevertheless, it is highly possible, with suitably selected reagents, to obtain MOFs with hydrophobic templates and thus specific adsorption properties for a variety of guest molecules. Recently, we have found an MOF system that can incorporate naphthalene as a guest.[17]

Conclusion

In conclusion, we have demonstrated a novel strategy to synthesize an MOF that forms with a benzene template from a hydrothermal reaction and shows specific sorption characteristics for benzene and cyclohexene over other ring compounds. Our synthetic strategy employing hydrophobic molecules in the synthesis of an otherwise undesirable multiply interpenetrated MOF can be adopted to other MOF systems to obtain novel MOFs with tailor-made pore structures and molecule-specific sorption properties. In general, the formation of two different MOFs depending on the solvent system in our study implies that even presently well-known MOF systems may have a new dimension of structural variability by simply modifying the solvent composition.

Experimental Section

General Methods: All chemicals purchased were of reagent grades and used without further purification. Elemental analyses (C, H, and N) were performed on an EA1110 elemental analyzer. Fourier-Transform infrared spectra were obtained with a Nicolet 1700 FT-IR spectrometer using KBr disks dispersed with sample powders in the 4000–400 cm^{-1} range. Thermal gravimetric analyses were conducted on a TA4000/SDT 2960 instrument in flowing N_2 with a heating rate of 10 °C min^{-1}. X-ray powder diffraction data were recorded on a Rigaku D/max-RC diffractometer at 30 kV, 40 mA for $Cu_{K\alpha}$, ($\lambda = 1.5406$ Å) with a scan speed of 2° min^{-1} and a step size of 0.02° in 2θ. The calculated XRPD patterns were produced by using the atoms program with the single crystal data.

Synthesis of $[Co_3(ndc)_3(bipyen)_{1.5}]{\cdot}H_2O$ (1): A mixture of $Co(NO_3)_2{\cdot}6H_2O$ (0.16 g), H_2ndc (0.12 g), bipyen (0.10 g), and H_2O (6 mL) in the mole ratio of 1:1:1:600 was heated in a 23 mL Teflon-lined autoclave at 180 °C for 2 days and then cooled to room temperature. The product was collected by filtration, washed with H_2O, ethanol, and acetone and then air-dried. IR (KBr): 3426 (br), 2924 (s), 1620 (s, C=O), 1406 (s, C=O), 1359 (s, C=O), 829 (s), 782 (s), 549 (s), 490 cm^{-1} (s); elemental analysis calcd for $C_{54}H_{32}O_{13}N_3Co_3$ ($M_r = 1107.62$): C 58.56, H 2.912, N 3.794; found: C 59.56, H 3.31, N 4.23.

Synthesis of $[Co_2(ndc)_2(bipyen)]{\cdot}C_6H_6{\cdot}H_2O$ (2): A mixture of $Co(NO_3)_2{\cdot}6H_2O$ (0.10 g), H_2ndc (0.074 g), bipyen (0.063 g), benzene (1.53 mL; precaution: benzene is a cancer suspect agent and flammable liquid), and H_2O (6 mL) in the mole ratio of 1:1:1:50:970 was heated in an autoclave at 180 °C for 2 days and then cooled to room temperature. Black crystals were obtained along with orange powdery materials of unknown nature. The crystals lose crystallinity in air due to the loss of benzene and so were kept in the mother liquor. IR (Nujol): 3422 (br), 1625 (s, C=O), 1408 (vs, C=O), 829 (m), 781 (vs), 547 (m), 489 cm^{-1} (m); elemental analysis calcd for $C_{42}H_{22}O_9N_2Co_2$ ($M_r = 816.48$): C 60.88, H 3.65, N 3.38; found: C 60.89, H 3.58, N 3.53.

X-ray crystallography

Crystal data of 1: $M_r = 1107.62$; triclinic; $P\bar{1}$, $a = 13.172(1)$, $b = 13.190(1)$, $c = 16.235(2)$ Å, $\alpha = 97.293(7)$, $\beta = 94.437(7)$, $\gamma = 90.523(5)°$, $V = 2788.8(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.319$ g cm^{-3}; $R_1/wR_2 = 0.0575/0.1518$ ($I > 2\sigma$) and 0.0840/0.1723 (all data); GOF = 1.019.

Crystal data of 2: $M_r = 816.48$; monoclinic, $C2/c$, $a = 16.900(3)$, $b = 20.189(3)$, $c = 12.128(2)$ Å, $\beta = 116.89(1)°$, $V = 3690.5(10)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.470$ g cm^{-3}; $R_1/wR_2 = 0.0370/0.0917$ ($I > 2\sigma$) and 0.0465/0.0987 (all data); GOF = 1.048.

A crystal of **1** glued on a glass fiber and a crystal of **2** sealed in a capillary tube to prevent benzene loss were used for the data collections. The data were collected at 293(2) K using a Siemens P4 four circle diffractometer. The crystal structures were solved with the direct methods (SHELXS-97, Sheldrick, 1990) and refined anisotropically with a full-matrix least-squares procedure on F_o^2 (SHELXL-97, Sheldrick, 1997). The hydrogen atom positions were program generated and refined with a riding model. The final-difference Fourier maps show the largest peak and hole as 1.137 and −0.736 e Å^{-3}, respectively, for **1** and the largest peak and hole as 0.968 and −0.401 e Å^{-3}, respectively, for **2**. CCDC-202099 (**1**) and CCDC-202100 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk).

N_2 adsorption measurement: The pore structures were determined by the adsorption of N_2 at 77 K using volumetric equipment (Micromeritics ASAP2020). The sample was evacuated at 373 K and 10^{-4} Pa for 2 h prior to the adsorption measurement. High purity N_2 gas (99.999 %) was used.

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