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A porous metal–organic framework with helical chain building units exhibiting facile transition from micro- to meso-porosity†

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A metal–organic framework (MOF) with helical channels has been constructed by bridging helical chain secondary building units with 2,6-di-*p*-carboxyphenyl-4,4′-bipyridine ligands. The activated MOF shows permanent porosity and gas adsorption selectivity. Remarkably, the MOF exhibits a facile transition from micro- to meso-porosity.

Metal–organic frameworks (MOFs) have been attracting a tremendous amount of interests due to their fascinating structural topologies[1] and potential applications[2] such as gas storage,[3] gas separation,[4] catalysis,[5] and sensing.[6] In particular, this new class of porous materials have been considered as promising sorbents for CO_2 capture[7,8] and H_2 storage.[9,10]

MOFs prepared with ligands of high symmetry have been well-studied because of synthetic and crystallographic considerations. However, linkers with reduced symmetry containing mixed carboxylate/pyridine coordinating groups are uncommon in MOF studies.[11] In this report, a ligand with one pyridyl and two carboxylate groups has been used to react with a Co(II) salt under solvothermal conditions to give a notable porous Co(II)-based MOF with one-dimensional (1D) helical chains acting as secondary building units.[12,13] While an individual crystal is enantio-pure, the bulk sample is racemic. The MOF also exhibits a facile transition from micro- to meso-porosity, which may pave a new way for the search of mesoporous MOFs.

The MOF $Co_3(OH)(OH_2)(OAc)_3(dcbp)$ (PCN-121, PCN represents porous coordination network) was synthesized by a reaction between 2,6-di-*p*-carboxyphenyl-4,4′-bipyridine (H_2dcbp) and $Co(NO_3)_2 \cdot 6H_2O$ in *N,N′*-dimethylacetamide (DMA) at 85 °C. The structure of PCN-121 was determined by single crystal X-ray diffraction. PCN-121 crystallizes in space group $P6_1$ (or $P6_5$). As shown in Fig. 1a, there exist three crystallographically independent Co(II) atoms, each of which is octahedrally coordinated. Co1 and Co2 are coordinated by
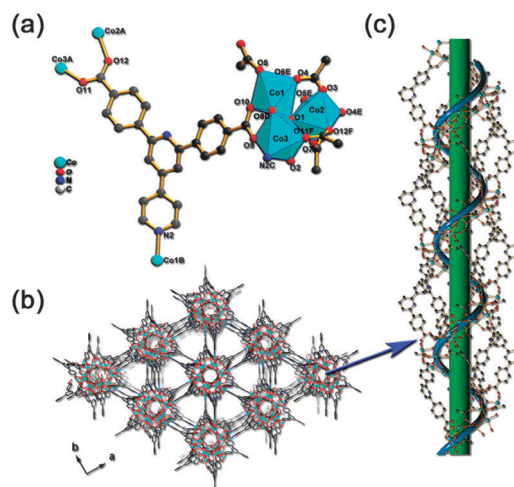
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† Electronic supplementary information (ESI) available: Experimental details, crystallographic data of PCN-121 and -122, TGA. IR and additional gas adsorption isotherms. CCDC 813603 and 813719. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc16261f

Fig. 1 Views of (a) the asymmetric unit of PCN-121 (symmetry code: (A) $Y, -X + Y, 0.83 + Y$; (B) $1 - Y, X - Y, 1/3 + Z$; (C) $1 - X + Y, 1 - X, Z - 1/3$; (D) $X - Y, X, 1/6 + Z$; (E) $Y, -X + Y, Z - 1/6$; (F) $X - Y, X, Z - 0.83$); (b) the channels of PCN-121, viewed through [0 0 1] direction; (c) the helical chains viewed through [1 1 0] direction.

four acetate O atoms, one carboxylate O atom of the $dcbp^{2-}$ ligand, and one O atom from a μ_3-OH group (the identity of the OH group was established through the pyramidal geometry of the Co_3O unit, the Co–OH distances and charge balance if the Co atoms are divalent, which is further confirmed by magnetic susceptibility measurements). Co3 is coordinated by one water O atom, two carboxylate O atoms of the two different $dcbp^{2-}$ molecules, one acetate O atom, one O atom from the μ_3-OH, and one N atom of the $dcbp^{2-}$ ligand. Three Co(II) atoms are thus connected to form a $Co_3(\mu_3$-OH) cluster, in which Co1 is connected to Co2 through O3, C1 and O4 of one acetate ligand. Co1 and Co2 share O8 of an acetate group. In addition, Co1 in one cluster is connected to Co2 of another cluster through two O atoms from two acetates. In this way, these $Co_3(\mu_3$-OH) clusters link with each other to form a 1D chain along a 6_1 axis (or 6_5 in its enantiomeric counterpart, Fig. 1c). Each organic ligand coordinates three different μ_3-OH centered clusters to form an overall three-dimensional (3D) structure with helical channels (Fig. 1b). The helical structure of this MOF arises from the non-planarity of the $dcbp^{2-}$ ligand.[13]

Another interesting point is that using a different Co(II) salt to react with this ligand resulted in a different MOF reported

recently by Chen and co-workers.[14] Octacobalt cluster based (3,12)-connected frameworks were obtained by the reaction of $CoSO_4$ and H_2dcbp under solvothermal conditions. Sulfate participated in the formation of a Co_8 cluster in this structure. Furthermore, a porous Cd(II) coordination polymer with the same ligand has also been reported recently.[15] It is clear that the formation of MOFs, even with the same ligand and metal ions, is highly susceptible to reaction conditions such as pH, temperature, solvents, and counterions.[16,17] For instance, in this work, although the PCN-121 structure contains an acetate as a secondary ligand generated *in situ*, when acetic acid was added intentionally to the reaction mixture in the synthesis, a new MOF was obtained (PCN-122) and structurally characterized with single crystal X-ray diffraction.‡ Interestingly, this new structure does not contain an acetate group (Fig. S3, ESI†). The addition of acetate to the reaction system, however, gave an uncharacterized powder. These demonstrate the complexity of the dynamic equilibriums among different components in a solvothermal reaction mixture. Evidently, the acetate must be provided at a suitable rate to ensure effective crystallization of PCN-121.

Thermal gravimetric analysis (TGA) revealed a loss of uncoordinated solvates in as-synthesized PCN-121 around 100 °C and the decomposition of the sample when the temperature is higher than 300 °C (Fig. S3, ESI†). The relatively high thermal stability of the sample and the 3D porous structure revealed by X-ray diffraction studies prompted us to test the gas adsorption performance of PCN-121.

The most salient feature of the adsorption properties of PCN-121 lies in its facile transition from microporosity to mesoporosity depending on the methods of activation.

After evacuation of solvates from a fresh sample at 60 °C for 10 h under reduced pressure, the N_2 adsorption isotherm at 77 K exhibits type I behavior revealing microporous nature of the MOF (Fig. 2), consistent with the observed microporosity from the crystal structure and the powder X-ray diffraction (PXRD) pattern. Langmuir and Brunauer–Emmett–Teller (BET) surface areas are 2618 $m^2 g^{-1}$ and 1839 $m^2 g^{-1}$, respectively, and the total pore volume is 0.93 $cm^3 g^{-1}$. However, when activated at 60 °C under vacuum after soaking in methanol and dichloromethane for three days, the activated PCN-121 exhibits a type IV isotherm for N_2 sorption at 77 K and no diffraction peaks in its PXRD pattern were found.
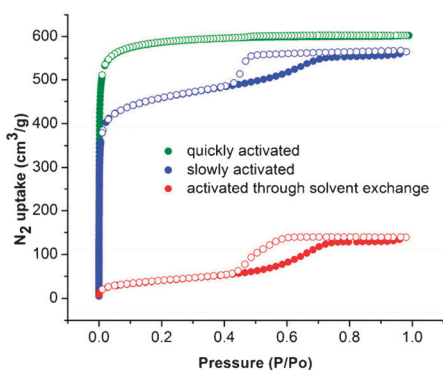
This implies a transition of PCN-121 from microporosity to mesoporosity and from crystalline to amorphous. When an as-synthesized sample was pumped under reduced pressure for 10 days at 60 °C, a type IV isotherm was observed (Fig. 2), albeit the total N_2 uptake of the sample is similar to that of the one with the type I isotherm. The PXRD pattern of the slowly activated sample exhibiting a type IV isotherm is different from those of the simulated based on single crystal data, the as-synthesized sample, and the quickly activated sample showing a type I isotherm (Fig. S1, ESI†). This implies a phase transition of PCN-121 from a microporous form to a mesoporous one in the solid state that maintains crystallinity. This type of transition normally takes days to complete. The removal of the aqua ligands may have promoted this transition. When activated quickly, the crystal structure of the as-synthesized sample was largely preserved due to the difficulty in aqua ligand removal and the slow pace of structural rearrangements in a solid phase. These rearrangements can be accelerated by solvent exchange. After the solvent exchange with methanol, the water ligands were most likely replaced by methanol ligands, which are easier to eliminate than aqua ligands. The faster phase transition destroys crystallinity and leads to an amorphous PCN-121. Experiments using time-resolved PXRD techniques with synchrotron X-ray sources are in progress collaborating with Argonne National Lab and the results will be published elsewhere.

Mesoporous MOFs are a sort-after target due to their vast potential in catalysis, sensing, and host–guest chemistry.[19] The discovery of the transition from micro- to meso-porosity by constructing MOFs containing labile terminal ligands, followed by slow removal of them to trigger the structural rearrangement, may pave a new way for the preparation of mesoporous MOFs. For gas storage and selective gas adsorption, however, microporosity is more desirable,[2] therefore the following discussion will be focused on the microporous PCN-121.

CO_2 and CH_4 adsorption isotherms were measured at different temperatures as shown in Fig. 3. The CO_2 isotherm at 195 K exhibited a rapid rise at low pressures to reach a maximum uptake of 420 $cm^3 g^{-1}$ at 1 bar. CH_4 uptake at the same temperature was 120 $cm^3 g^{-1}$. Both gas uptakes were not saturated even at 1 bar, and this unsaturation of CO_2 uptake is more pronounced at 273 and 295 K than that of CH_4. Similar to a lot of other MOFs, the selective adsorption of CO_2 over CH_4 of PCN-121 was observed at all three temperatures tested.

Fig. 2 The N_2 adsorption isotherms (77 K) of PCN-121 samples quickly activated (green, 10 h), slowly activated (blue, 10 days), and activated through solvent-exchange (red) (●: adsorption; ○: desorption).
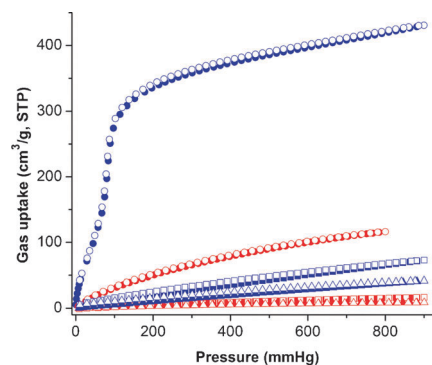

Fig. 3 The CO_2 (blue) and CH_4 (red) adsorption of PCN-121 (●: 195 K; ■: 273 K; ▲: 295 K. Filled markers for adsorption and open ones for desorption.).
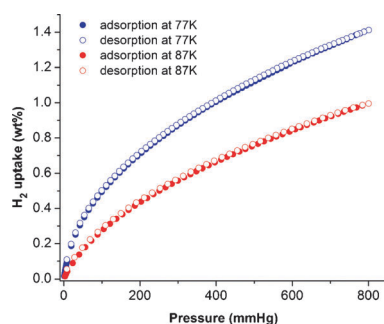
Fig. 4 The low pressure H_2 uptake in PCN-121 at 77 K and 87 K.

This relatively high CO_2 adsorption is a result of strong interaction between CO_2 (having a high quadruple moment) and pore surface of the MOF. Presumably, the non-coordinated N atoms (Lewis base site) of $dcbp^{2-}$ ligands in the wall may have played a role in these interactions.[18] The heats of adsorption of CO_2 and CH_4 were 23.0 and 15.1 kJ mol^{-1}, respectively.

H_2 adsorption isotherms at 77 and 87 K were also measured (Fig. 4). The uptakes of 1.4 wt% at 77 K and 1 wt% at 87 K led to a heat of hydrogen adsorption of 6.63 kJ mol^{-1}, consistent with literature values.[9]

To confirm the oxidation state of the Co atoms, magnetic susceptibility data were collected for crystalline sample of PCN-121. The data were not field dependent (Fig. S8, ESI†). The χT product at 300 K has a value of 6.4 cm^3 K mol^{-1}, in agreement with the expected for three Co(II) ions in a distorted octahedral coordination environment with strong spin–orbit coupling. In a magnetization *vs.* field plot at 2 K, each Co(II) ion behaves as an effective $S = 1/2$. The magnetization does not saturate, and it reaches a value of 2.5 at 5 T, indicating a non-zero spin ground state for the tricobalt repeating unit of PCN-121 with anisotropy and low lying excited states. This is in agreement with the structural parameters of PCN-121. PCN-121 consists of infinite chains of tricobalt units, where the three Co(II) ions are bridged by a μ_3-OH and various O atoms from the carboxylate groups.

In summary, a helical-chain Co(II)-based MOF has been synthesized. The structure of this MOF contains unusual M–O–M clusters in its helical chain building units, which are responsible for the observed magnetic properties. Selective adsorption of CO_2 over CH_4 was demonstrated using a quickly activated sample. Remarkably, PCN-121 exhibits a facile transition from micro- to meso-porosity depending on the methods of activation. Mechanistic studies using time-resolved PXRD techniques are currently under way.

Notes and references

‡ The space group of PCN-122 is $I4_1cd$ (a = 23.394 Å, c = 49.524 Å, V = 27102.9 $Å^3$). Co1 has an octahedral coordination geometry with mixed functional groups, one pyridyl N atom, four carboxylate oxygen atoms and one aqua ligand (Fig. S4, ESI†). Co1 is connected with Co1 in the other asymmetric unit through one aqua ligand and two carboxylates from two different ligands.

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