A robust microporous metal–organic framework constructed from a flexible organic linker for highly selective sorption of methanol over ethanol and water†

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A microporous metal–organic framework MOF 1 [Zn(L)2(methanol)2] (H2L = (1R,3S)-1,2,2-trimethyl-3-(pyridin-4-ylcarbamoyl)cyclopentanecarboxylic acid) constructed from a flexible Zn²⁺ node and a flexible organic linker L was obtained by solvothermal reaction of diamond topology, and exhibits highly selective sorption of methanol over ethanol and water.

1. Introduction

It took almost one decade to realize a few porous coordination polymers (PCPs) and/or metal–organic frameworks (MOFs) whose gas/vapor sorption isotherms were established during the 1990s. This is mainly because “Nature abhors the vacuum”, thus the as-synthesized coordination polymers are easily collapsed to form condensed ones once the solvent molecules have been removed during thermal and/or vacuum activation. The establishment of permanent porosities in many porous MOFs during the 2000s has indicated that the rigid metal-containing clusters (typically termed as secondary building units (SBUs)) and highly conjugated rigid organic linkers have played crucial roles to stabilize the framework structures and thus to sustain the permanent porosities. Since then, tremendous research has been carried out to incorporate suitable rigid SBUs and organic linkers for the construction of porous MOFs and thus for their important applications in gas storage, separation, heterogeneous catalysis, sensing and drug delivery.

Among the diverse porous MOFs, those with small pores of less than 4 Å are particularly useful for gas/vapor separation. In this regard, framework interpenetration has been demonstrated as a very powerful methodology to tune the small pores within porous MOFs to direct their highly selective gas/vapor separation. However, framework interpenetration is typically not the default choice when we assemble rigid SBUs and organic linkers into their framework structures, mainly because the spatial arrangements of these SBUs and organic linkers have enabled them to construct porous MOFs with moderate pore spaces which cannot provide enough empty space to hold the second framework. Although framework interpenetration does occur in some cases, most of such interpenetrated frameworks tend to have condensed structures because of multiple framework interpenetration. The importance of porous MOFs with small pores has motivated the community to explore more methodologies to synthesize such porous MOFs with small pores for their highly selective gas/vapor separation. One of the questions posted to the community might be: whether or not the isolated single metal nodes and flexible less conjugated organic linkers will also have the capacity to construct porous MOFs with small pores and thus to direct their highly selective gas/vapor separation. We define such less conjugated organic linkers as flexible ones because they can easily have conformational changes, leading to contracted and expanded pores of the frameworks, which cannot provide enough empty space to hold the second framework.

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2. Experimental section

2.1 Materials and methods

All the chemicals were commercially available and used without further purification. Infrared spectra (IR) were recorded on a Thermo Fisher Nicolet iS10 spectrometer using KBr pellets. Elemental analyses for C, H, and N were performed on an EA1112 microelemental analyzer. Powder X-ray diffraction (PXRD) patterns were collected in the 2θ = 5–60° range on an X’Pert PRO diffractometer with Cu-Kα radiation at room temperature. Thermogravimetric analyses (TGA) were carried out on a TA Instruments SDT Q600 with a heating rate of 10 °C min⁻¹ in N₂ atmosphere. Luminescence spectra for the solid samples were recorded with a Hitachi F4500 fluorescence spectrometer. The photomultiplier tube voltage was 700 V and the scan speed was 240 nm min⁻¹. The slit widths were both 2.5 nm for excitation and emission spectra.

2.2 Synthesis of H₂L

To a suspension of PCl₅ (8.32 g, 40 mmol) in petroleum ether at 0 °C was added n-camphoric acid (4.74 g, 20 mmol) in portions at 0 °C for 5 h. The solvent was evaporated under reduced pressure to give the crude product as a pale yellow oil (2). A suspension of 3-pyridinamine (7.52 g, 80 mmol) in CH₂Cl₂ at 0 °C was added in portions. The solution was allowed to stir at 0 °C for 5 h and then warmed to room temperature and allowed to stir overnight. Then the precipitate was filtered off, the solvent in filtrate was removed in vacuo and the residue was purified by silica gel column chromatography using ethyl acetate as the eluent to afford a pure white solid (3). ¹H NMR (CDCl₃): δ 8.24(s, 1H), 8.21(s, 1H), 7.27(t, 1H), 7.15(t, 1H), 2.82(t, 1H), 2.03(m, 1H), 1.93(m, 1H), 1.90(m, 2H), 1.16(s, 3H), 1.04(s, 3H), 0.94(s, 3H). A mixture of 3 and triethylamine was stirred at 50 °C for 24 h. Then the precipitate was filtered off and the solvent was removed in vacuo to give the product (1R,3S)-1,2,2-trimethyl-3-(pyridin-4-ylcarbamoyl)cyclopentanecarboxylic acid (H₂L) as a white solid (80% yield). ¹H NMR (DMSO): δ 10.06(s, 1H), 8.41(d, 2H), 7.59(d, 2H), 2.92(t, 1H), 2.46(m, 1H), 2.04(m, 1H), 1.76(m, 1H), 1.42(m, 1H), 1.19(s, 6H), 0.78(s, 3H). ¹³C NMR (DMSO): 179.748, 173.589, 144.045, 141.305, 136.551, 126.424, 123.842, 56.709, 55.074, 46.361, 34.115, 24.501, 23.606, 22.856, 21.841. MS (ESI), exact mass calcd for C₁₅H₂₀N₂O₃ [M + H]⁺, 277.2. Found 277.1; [M – H]⁻, 275.2, Found 275.0. HRMS (ESI); exact mass calcd for C₁₅H₂₀N₂O₃ [M + H]⁺, 277.1547. Found: 277.1540.

2.3 Synthesis of MOF 1

A mixture of Zn(NO₃)₂·6H₂O (0.119 g, 0.4 mmol), H₂L (0.0552 g, 0.2 mmol), methanol (3 mL) and water (0.5 mL) was sealed into a 20 mL Teflon cup. The vessel was heated at 100 °C for 2 days. After the mixture was slowly cooled to room temperature, colorless block crystals were obtained in 60% yield. Elemental analysis (%). Calcd for C₃₂H₄₆N₄O₈Zn: C, 56.51; H, 6.82; N, 13.82. Found: C, 56.60; H, 6.32; N, 8.11. IR (KBr, cm⁻¹): 3413(s), 2964(s), 1671(s), 1610(w), 1584(s), 1479(w), 1429(s), 1396(w), 1358 (s), 1282(w), 1305(w), 1275(s), 1197(s), 1175(s), 1130(s), 1040(s), 821(s), 699(s), 647(w).

2.4 Single-crystal X-ray crystallography

Crystal structure analyses: Diffraction data were collected on an Oxford Xcalibur Gemini Ultra diffractometer with an Atlas detector using graphite monochromatic Mo-Kα radiation (λ = 0.71073 Å) at 293 K. The structures of MOF 1 were solved by direct methods and refined with full-matrix least-squares on F² with the SHELXL-97 program package. Crystal data for MOF 1: molecular formula: C₁₅H₂₄N₄O₈Zn, formula weight: 680.10, tetragonal, P4₃2₁2₁, a = 14.3035(3) Å, b = 14.3035(3) Å, c = 15.9627(6) Å, V = 3265.8(2) Å³, Z = 4, T = 293(2), crystal size = 0.32 × 0.29 × 0.21 mm³. D_c = 1.383 g cm⁻³, F(000) = 438, 14844 reflections collected, 2989 independent reflections (R_int = 0.0543) which were used in all the calculations. After the refinement cycles, reliability factors were R₁ = 0.0616, wR₂ = 0.1256 for [I > 2σ(I)], and R₁ = 0.0648, wR₂ = 0.1270 for all 2989 data. CCDC 676452 and 870505.

3. Results and discussion

3.1 Synthesis

The free organic linker H₂L can be straightforwardly synthesized from the precursor n-camphoric acid in three steps as shown in Scheme 1. The as-synthesized MOF 1 can be readily obtained by solvothermal reaction of Zn(NO₃)₂·6H₂O and L in a methanol/water mixture at 100 °C for 48 h as colourless crystals. It was formulated as [Zn(L)₃(MeOH)]₂ by elemental analysis and single-crystal X-ray diffraction studies, and the phase purity of the bulk material was independently confirmed by powder X-ray diffraction (PXRD).

3.2 Crystal structure descriptions

The X-ray single crystal structure of MOF 1 features a three-dimensional framework structure in which each Zn²⁺ is tetrahedrally coordinated by four organic linker L whose pyridyl nitrogen and carboxylate oxygen are involved in the coordination (Fig. 1a). The overall structure is a three-dimensional framework exhibiting irregular cages of 3.194 × 11.811 × 7.182 Å. The void space accounts approximately 15.3% of the whole crystal volume calculated by PLATON analysis.

3.3 Thermal properties and powder X-ray diffraction studies

To investigate the thermal stability of the framework of 1, thermogravimetric analyses (TGA) were carried out. As shown...
in Fig. S1,+ TGA analysis indicates that methanol molecules can be readily released in the temperature range of 25–160 °C to form guest-free phase MOF 1a, which is stable up to 260 °C.

Rietveld structural refinement indicates that the activated MOF 1a keeps the basic framework structure with slight shrinking from the original unit cell volume of 3265.8 Å³ in MOF 1 to 3232.9 Å³ in MOF 1a, and all the methanol molecules have been completely removed from the pores during the activation. Once the methanol is re-adsorbed into the activated MOF 1a, the structure is recovered into the original MOF 1 (see ESI† for the details). These studies indicate that the framework is robust and the adsorption of MOF 1a for methanol is reversible. A small amount of secondary impurity phase(s) was observed after activation (see ESI†), however, the impurity phase has little effect on the structure restoration from MOF 1a to MOF 1 after re-adsorption of methanol and on the solvent selectivity of this new MOF material.

### 3.4 Luminescent and adsorption properties

Upon excitation at 276 nm, MOF 1 exhibits intensive blue luminescence centered at \( \lambda_{\text{max}} \) of 321 nm (Fig. 2(upper), red) which is significantly stronger than the free organic linker H2L in the solid state (black) and in dilute solution of ethanol (blue). Such luminescence enhancement might be due to the coordination of the organic linker L to the Zn²⁺, which increases the rigidity of the ligand and thus reduces the loss of energy by radiationless decay.

The most important and interesting feature of MOF 1 is the highly selective sorption of methanol over ethanol and water. As shown in Fig. 2(bottom), the activated MOF 1a (the as-synthesized MOF 1 was thermally activated at 120 °C under high vacuum overnight to generate activated MOF 1a) takes up significantly different saturated amounts of methanol, ethanol and water of 101, 2 and 7 cm³ g⁻¹, respectively, at 298 K. This is really remarkable, highlighting this new MOF as a potentially useful microporous material for the separation of methanol over ethanol and water. Separation of methanol over water might be of more practical importance among these two potential applications, and can be utilized to generate high purity methanol by releasing the adsorbed methanol molecules from MOF materials. Such highly exclusive sorption of methanol over ethanol and water might be attributed to matching of methanol molecules into the small cages within MOF 1a which has enhanced the much stronger interactions between host porous structures and guest methanol molecules.

The robustness of this framework constructed from a flexible single metal ion node and flexible organic linker is very unusual. It highlights the potential to make use of these flexible building blocks to construct robust porous MOF materials with small pores and thus for their highly selective gas/vapor separation. Robust MOFs are those whose structures remain the same after thermal/vacuum activation (generally can be established by single and/or powder X-ray diffraction studies) and the activated ones can take up gas/vapor molecules.

It needs to be mentioned that most of the MOFs generated from flexible units are easily collapsed and thus non-porous as exemplified in one of the first such MOFs, Cu(i)[4,4',4'',4'''-tetracyanotetraphenylmethané]·BF4·xCH3OH.¹⁸ The very few examples of robust MOFs from such flexible metal ion nodes and organic linkers are [CuSiF6(4,4'-bipyridine)]·8H2O (single Cu²⁺ as the flexible node with rigid organic linker 4,4'-Bipy)¹⁹ and CuG(4,4'-bipyridine)₉₅ (G = glutarate; rigid paddle-wheel...
Cu$_2$(COO)$_4$ node with rigid organic linker 4,4′-Bipy and flexible organic linker glutarate). Close structure examination indicates that the multiple hydrogen bonding and van der Waals interactions among the organic linkers have played important roles in stabilizing the framework. This accidental discovery in this reported MOF might motivate more comprehensive research endeavors on the construction of robust porous MOFs from a variety of flexible metal ion nodes and organic linkers, and then on their applications for highly selective gas/vapor separation in the near future.

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Notes and references


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