

A metal–organic framework based on an unprecedented nonanuclear cluster as a secondary building unit: structure and gas sorption behavior†

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A 3D chiral microporous metal–organic framework containing a nonanuclear cluster as a secondary building unit was prepared using a bent and rigid dicarboxylic ligand, 2,7-naphthalene dicarboxylic acid, and the zinc ion, where a nonanuclear cluster with potential exposed metal sites is in the form of a corner-sharing cyclic trimer of a tetrahedral Zn_4O motif.

Metal–organic frameworks (MOFs) have received much attention because of their fascinating structures and intriguing potential applications in gas storage,¹ separation,² and catalysis.³ Secondary building units (SBUs) with well-established and rigid geometry have often been utilized for achieving stable open frameworks.⁴ It is well known that $[M_4O(COO)_6]$ tetrahedron⁵ and $[M_2(COO)_4]$ paddle-wheel motifs⁶ can be generated as SBUs of porous MOFs from the solvothermal reaction of an M^{2+} ion and carboxylic acid. In particular, MOFs retaining structural integrity and porosity upon removal of guest and/or ligating solvent molecules are important for applications in gas storage/separation. It is particularly the exposed metal sites in the open frameworks that are very important in hydrogen storage because the H_2 molecules can interact strongly with the exposed metal sites in the pore.⁷ However, only a few MOFs with exposed metal sites are known⁸ and the structural information on the exposed sites is limited, probably due to their inherent instability with exposed metal centers.

Here we report on the synthesis, structure, and gas sorption behavior of a 3D MOF having an unprecedented nonanuclear SBU with potential exposed metal sites. The solvothermal reaction of $Zn(NO_3)_2 \cdot 6H_2O$ with 2,7-naphthalene dicarboxylic acid (2,7- H_2ndc) at 120 °C in the presence of dimethylformamide (dmf) afforded a 3D MOF, $[Zn_9O_3(2,7-ndc)_6(dmf)_3]$ (**1**).†

Single crystal X-ray analysis revealed that **1** in a chiral space group $R32$ was a 3D MOF, $[Zn_9O_3(2,7-ndc)_6(dmf)_3] \cdot 7dmf \cdot 1.5H_2O$, having a homochiral 3D channel (Fig. 1 and S1†).‡ The asymmetric unit of **1** consists of two zinc atom sites, one 2,7- ndc^{2-} unit, a μ_4-O^{2-} group in the crystallographic C_2 axis, and a disordered dmf molecule coordinated to a zinc ion. Three $[Zn_4O(COO)_4]$ tetrahedra are fused to form a cyclic C_3 symmetric chiral nonanuclear SBU, $[Zn_9O_3(COO)_{12}]$, by

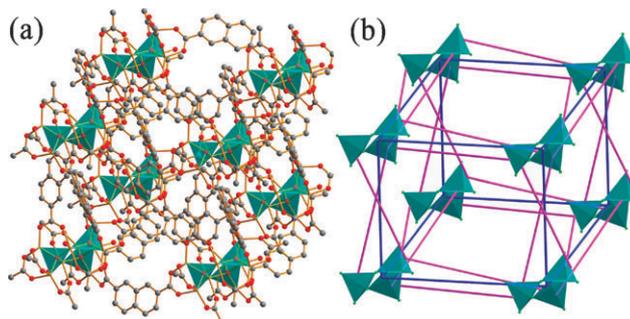


Fig. 1 (a) A packing diagram of **1**, where the $[M_4O(COO)_4]$ units are presented using polyhedron models. (b) A schematic drawing of **1** showing one unit of a cube, where the double linkages are represented in pink rods and the double connectivity is further simplified using a single blue rod.

corner-sharing the Zn atoms (Fig. 2a). The $[Zn_4O(COO)_4(dmf)]$ tetrahedron that consists of four Zn atoms, a μ_4-O , four carboxylates, and the solvent dmf is a hybrid form of a square paddle wheel, $[Zn_2(COO)_4]$, and a typical tetrahedral Zn cluster, $[Zn_4O(COO)_6]$. Contrary to the six bridging carboxylates between the metal ions at the six edges of the tetrahedron in a typical $[Zn_4O(COO)_6]$ tetrahedral SBU, in the hybrid tetranuclear cluster $[Zn_4O(COO)_4]$ one edge is doubly bridged by two carboxylate groups like a part of paddle-wheel unit, while two edges are connected by two singly bridging carboxylate groups, respectively, and no carboxylate group is involved in the bridging in the remaining three edges (Fig. 2b). The Zn atoms involved in the single carboxylate bridging mode are involved in the corner-sharing of the metal ions to form a cyclic trimer and are of a pentacoordinate trigonal bipyramidal geometry, where two μ_4-O^{2-} groups from the two adjacent tetrahedrons and an oxygen atom of the ligated dmf molecule form the basal plane of the trigonal bipyramid, and the remaining two apical positions are occupied by two bridging

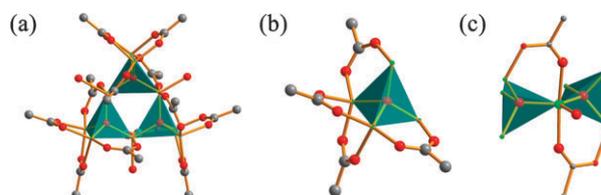


Fig. 2 (a) A nonanuclear SBU, $[Zn_9O_3(2,7-ndc)_{12}(dmf)_3]$, where three tetranuclear cluster units are interconnected in a cyclic manner via corner sharing of the two zinc atoms. (b) A tetranuclear unit, $[M_4O(COO)_4]$, as a hybrid form of a paddle-wheel unit, $[M_2(COO)_2]$, and a typical tetranuclear unit of octahedral nodality, $[M_4O(COO)_6]$. (c) Trigonal bipyramidal geometry of the corner-sharing zinc atom with the ligated dmf molecule at one corner of the trigonal basal plane. Key: Zn (green), O (red), C (gray).

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carboxylate oxygen atoms (Fig. 2c). This corner-sharing metal center is a potential exposed metal site if the ligated solvent molecule can be removed without distortion of the coordination geometry of the metal center with the remaining donor atoms.

Although the nonanuclear SBU is a dodecatopic node, the SBU is doubly linked to six adjacent nonanuclear SBUs *via* twelve bent ditopic ligand units to form a 3D MOF of a doubly bridged simple cubic network topology (Fig. 1a and 1b). This type of network topology leads to a complicated homochiral 3D channel of varying aperture shapes, with the narrowest around ~ 3.5 Å in diameter (Fig. S1c and S1d†). The volume occupied by the lattice solvent molecules in network **1** is 3638 \AA^3 per unit cell, which is $\sim 41\%$ of the total crystal volume (calculated by the program PLATON).⁹

The powder X-ray diffraction (PXRD) pattern of bulk crystals is very similar to that simulated from single crystal X-ray data of **1** (Fig. 3). The variable temperature PXRD shows that the framework is stable up to at least 400 °C (Fig. S4†). However, careful examination of the PXRD data indicates that structural distortion occurs when the sample is heated to above 200 °C. Some peaks start to shift above about 200 °C. This can be interpreted as a distortion of the framework caused by the removal of the ligated dmf molecules from the trigonal bipyramidal Zn(II) centers. A single crystal study of the desolvated crystal prepared by soaking **1** in methylene dichloride for a day and heating to about 190 °C under vacuum overnight confirmed a slight change in the unit cell parameters. This was probably caused by a distortion of the SBU in the framework. § Despite several attempts to solve the structure, even using single crystal data from high flux synchrotron radiation, the data quality was not good enough to reveal an interpretable electron density map for structure analysis. The PXRD pattern of **1a**, prepared by soaking **1** in methylene dichloride for a day and heating to about 100 °C under vacuum overnight, showed no significant peak shift, which suggests that the framework is stable and undistorted (Fig. 3). The IR spectrum of **1a** also confirmed that the ligated dmf at the metal center was intact (Fig. S5†). However, the significant peak shifts in the PXRD of **1b**, prepared by soaking **1** in methylene dichloride for a day and heating to about 250 °C under vacuum overnight, indicated that a framework distortion had occurred. The absence of an amide peak around

1656 cm^{-1} in the IR spectrum of **1b** suggested that the ligated dmf molecules were completely removed. When **1b** was re-immersed in dmf the PXRD pattern of **1** was recovered, which indicates that the structural transformation caused by the ligation and unligation of the dmf molecule at the metal center is reversible.

In order to assess the effect of exposed metal sites on the gas sorption properties, sorption experiments were carried out under two different activation conditions, based on PXRD and TGA analysis (see the ESI†), one with and the other without the ligated solvent molecules at the metal centers. The N_2 sorption on **1a** showed a typical type I behavior as a microporous material (Fig. 4). The BET and Langmuir surface areas of **1a** were calculated to be $834 \text{ m}^2 \text{ g}^{-1}$ and $1146 \text{ m}^2 \text{ g}^{-1}$, respectively. The measured pore volume from the N_2 sorption, $0.409 \text{ cm}^3 \text{ g}^{-1}$, was slightly larger than that estimated from the single crystal structure, $0.352 \text{ cm}^3 \text{ g}^{-1}$, which indicated that the nitrogen in the pore was compressed to a greater extent than in the liquid nitrogen at 77 K . The H_2 adsorption isotherm at 77 K revealed an uptake of $141 \text{ cm}^3 \text{ g}^{-1}$ ($1.26 \text{ wt}\%$, Fig. 4) at 1 bar . The hydrogen uptake of $213 \text{ cm}^3 \text{ g}^{-1}$ ($1.95 \text{ wt}\%$) at 20 bar (inset in Fig. 4) was very close to the predicted value, $1.92 \text{ wt}\%$, from a fit of the Langmuir–Freundlich equation to the data (Fig. S6 and S7†).¹⁰ The H_2 storage capacity was in the range expected from the BET surface area.¹¹ By fitting a second H_2 adsorption isotherm at 87 K , the enthalpy change of adsorption was calculated using a modified version of the Clausius–Clapeyron equation;¹² it ranged from -6.8 to -5.5 kJ mol^{-1} (Fig. S8†). These values are in the range of the H_2 adsorption enthalpies reported for non-interpenetrated MOFs with no exposed metal centers.¹³ The N_2 sorption on **1b** also showed the same type I behavior (Fig. 4), and small increases in both the BET and Langmuir surface areas ($901 \text{ m}^2 \text{ g}^{-1}$ and $1281 \text{ m}^2 \text{ g}^{-1}$) were observed. The measured pore volume from the N_2 sorption, $0.458 \text{ cm}^3 \text{ g}^{-1}$, was slightly smaller than that estimated from the single crystal structure from which solvent had been removed, including the ligated dmf molecules, and assuming no structural rearrangement of the framework, $0.499 \text{ cm}^3 \text{ g}^{-1}$. This, in addition to the IR spectrum supporting the removal of the ligated dmf at the metal center (Fig. S5†), indicated that most of the ligated dmf molecules in the trigonal bipyramidal Zn(II) centers had been

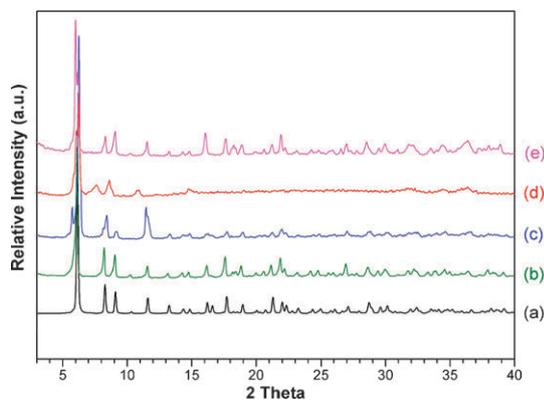


Fig. 3 PXRD patterns of **1**: (a) simulated from the single crystal structure of **1**, (b) **1**, as-synthesized, (c) **1a**, activated at 100 °C, (d) **1b**, activated at 250 °C, and (e) **1b** re-immersed in dmf.

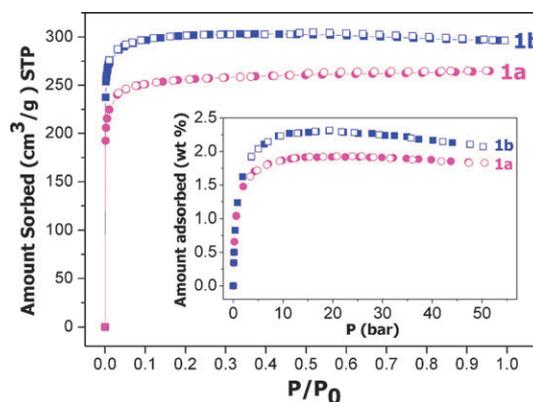


Fig. 4 Gas sorption isotherms of N_2 and H_2 (inset) on **1a** and **1b** at 77 K , respectively.

removed from the framework. An H₂ sorption experiment at 77 and 87 K on **1b** revealed only a small increase in the isosteric heat of adsorption (Fig. S8†). This was reflected in a small increase in H₂ sorption capacity at 77 K, from 1.26 wt% to 1.33 wt% at 1 bar, and from 1.92 to 2.30 wt% at 20 bar. We speculate that the negligible increase in the initial enthalpy change of adsorption and the small increase of the H₂ sorption capacity in **1b** are due to a change in the Zn(II) coordination geometry from trigonal bipyramid to tetrahedron having a nonexposed metal site rather than a seesaw-shaped 4-coordinate geometry having an exposed metal center after the removal of the ligated solvent dmf molecule at the metal center.¹⁴ The change in the coordination geometry probably led to a structural rearrangement of the SBU and a subsequent overall distortion of the framework with no exposed metal centers.

The adsorption amounts of CH₄ and CO₂ on **1b** at 298 K were 106 v/v at 50 bar and 171 v/v at 40 bar, respectively (Fig. S9†). The methane storage capacity was lower than that of the best MOF, pcn-14 (230 v/v),^{1e} which is consistent with the smaller surface area of **1b**. Similarly, the amount of CO₂ adsorbed on **1b** at 298 K and 40 bar was far lower than that of the best MOFs (MIL-101c: 390 v/v at 50 bar and 304 K¹⁵; MOF-177: 320 v/v at 42 bar and 298 K^{1a}). However, the volume adsorbed per volume of sample at ambient temperature and pressure reached 27 v/v, which is even higher than that of ZIF-100 (16 v/v).¹⁶

In conclusion, we prepared a 3D chiral microporous MOF having an unprecedented nonanuclear cluster as an SBU *via* a bent and rigid dicarboxylic ligand and the Zn²⁺ metal ion. The SBU consists of three tetrahedral Zn₄O motifs arranged to form a cyclic nonanuclear structure by corner-sharing the metal ions, where a solvent dmf molecule is ligated at a basal position of trigonal bipyramidal coordination geometry of the corner-sharing metal ion. The reduction of the coordination number of the corner-sharing metal center from five to four, achieved by removing the ligated solvent molecules in the nonanuclear cluster, resulted in an increase in the surface area and the pore volume of the MOF, with no exposed metal sites. The adsorption capacities of **1b** for gas molecules such as H₂, CO₂ and CH₄ showed no exposed metal center effect, probably due to the rearrangement of the coordination geometry of the potential exposed Zn(II) site to a tetrahedral geometry, with no exposed metal effect.

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Notes and references

† Crystal data for **1**: (C₁₀₂H₁₀₉N₁₀O_{38.5}Zn₉): *M* = 2679.32, rhombohedral, space group *R*32, *a* = *b* = 21.4718(18), *c* = 22.420(4) Å, *V* = 8951.7(18) Å³, *T* = 173(2) K, *Z* = 3, μ(Mo-Kα, λ = 0.71073 Å) = 1.858 mm⁻¹, ρ = 1.491 g cm⁻³, *F*(000) = 4107, GOF = 1079. Of 41 726 total reflections collected, 4924 were unique (*R*_{int} = 0.0661). *R*1(*wR*2) = 0.0339 (0.0996) for 4275 reflections [*I* > 2σ(*I*)], *R*1(*wR*2) = 0.0398 (0.0106) for all 4924 reflections. Flack parameter is -0.002(16). Although each crystal is enantiopure, bulk crystals are mixtures of both chiralities. We could structurally identify both right-handed **1R** and left-handed **1L** from different crystals of the same batch, demonstrating a racemic mixture of chiral crystals.

§ We could observe changes in the unit cell parameters of the desolvated crystal (rhombohedral, space group *R*32, *a* = *b* = 20.917(4), *c* = 24.272(7) Å) from those of the crystal **1**.

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