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Porous layer built from connecting of orthorhombic cages with accessible metal centers shows high selectivity for CO$_2$ over CH$_4$. 
Microporous Metal-Organic Layer Built from Pentanuclear Tetrahedral Units: Gas Sorption and Magnetism

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Presented here is a porous layer motif 1 built from pentanuclear tetrahedral Ni-clusters with accessible metal centers. Activated 1 exhibits a high selectivity of 19.8 under 273 K and 1 bar for the separation of CO2 over CH4. Magnetic measurement shows the overall antiferromagnetic coupling between Ni(II) ions for 1. Metal-organic frameworks (MOFs) as a class of new porous materials with fascinating architectures and desirable topologies are widely applied especially in the areas of gas sorption/separation, heterogeneous catalysis and magnetism because of their diversified building units, large surface area and modifiable hole-wall. Among these functionalities, the capture of CO2 and H2 is one of the most important aspects. One promising point for MOF adsorbent with strong affinity for binding CO2 and H2 is the presence of active metal centers in the pores. For example, the high H2 and CO2 capacities of the well-known HKUST-1 and MOF-74 was due to the well defined accessible active metal centers exposed to the inner surface. To give birth to accessible active metal centers, one of the most effective approach is to construct secondary building blocks (SBUs) with potential unsaturated coordination sites, typically like the paddle-wheel Cu2(COO)4(H2O)2 unit, whose terminal solvent molecules can be remove by using thermal treatment or other methods.

Compared to these simple metallic-carboxylic SBUs, the tetrahedral units with polynuclear metal remain rarely known in the formation of MOFs with promising gas separation properties. As a tetrahedral cluster with accessible active metal centers, [Ni6(btz)4(NO3)4(H2O)2], has been proven to construct porous cluster-based MOFs through the substitution reaction of NO3-. For example, via a step-by-step assembly strategy, Tao and coworkers assembled two pentanuclear clusters [{CO2(btz)4(NO3)4(H2O)2} and {Ni5(btz)4(NO3)4(H2O)2}] synthesized as SBUs with TCNQ (7,7,8,8-tetracyano-p-quinodimethane) to construct 3D diamond-like networks by taking advantage of substitutable sites NO3 in the tetrahedral clusters. Subsequently, Wang’s groups successfully produced three microporous interpenetrated frameworks by using a predesigned tetrahedral metal cluster [Zn6(btz)4(NO3)4(H2O)2] and linear dicarboxylic acid. As another kind of common organic ligands, pyridine carboxylate acids with different functional groups and different donor atoms, such as O and N atoms, have been used to build many MOFs. However, little experimental effort has focused on determining the MOFs based

Figure 1. a) coordination environment of the Ni(II) centers in 1; b) an orthorhombic cage composed of eight pentanuclear tetrahedral units; c) a novel 6-connected net with Schlafli symbol (3,4)6(5,6); d) the packing arrangement viewed along the b axis in compound 1.
The reaction of HBtz, HIna and Ni(NO3)2·6H2O in a solution of DMA/MeOH (2:1, v/v) at 120 °C for 5 days afforded the blue crystals of 1. Single-crystal X-ray diffraction analysis revealed that 1 crystallized in monoclinic space group P21/c. In the structure of 1 shown in Figure 1a, the anticipated pentanuclear cluster, which is composed of a tetrahedral arrangement of four six-coordinated Ni(II) ions centered on the fifth one, is similar to previous reported pentanuclear clusters also synthesized under the mixed dissolvent system of DMA and MeOH. Each of the six μ3-Btz ligands straddles an edge of the tetrahedron and is bound to the central metal through the nitrogen atom in the 2-position. Six nitrogen atoms from six Btz ligands therefore complete the coordination sphere of the central Ni5 atom, while the remaining four Ni(II) atoms on the apical positions are all coordinated by three nitrogen atoms from three Btz ligands (Figure S1, ESI). The rest coordinated sites of Ni1, Ni2, Ni3, Ni4 are occupied by two oxygen atoms from a chelating carboxylate group of Ina ligand as well as one nitrogen atom from Ina ligand; two third of terminal MeOH molecule, one third of chelating NO3 group and one oxygen atoms from two third of carboxylate group of acetic acid derived from the decompose of DMA; two oxygen atoms from a chelating carboxylate group of Ina ligand as well as one terminal DMA molecule; one terminal H2O molecule as well as one nitrogen atom from Ina ligand, respectively. Interestingly, as shown in Figure 1b, eight adjacent penta-nuclear [Ni5(Btz)6] clusters as SBUs are linked by Ina ligands to form an orthorhombic cage, leaving an irregular void with size of about 14.2×14.3 Å (Ni5-to-Ni5 distance). Each such orthorhombic cage as super SBU further connects to other eight adjacent cages via sharing the penta-nuclear [Ni5(Btz)6] cluster as vertex along the ac plan, generating a porous layer motif Figure S2, ESI). In the structure of 1, the acetate group and MeOH molecule as dangling ligands occupy two coordination sites of each Ni2 center, and then prevent the extension of framework in a direction to control the dimensionality of framework of 1 (Figure 1c). From the viewpoint of topology, the layer of 1 can be described as a novel 6-connected net with Schlafl symbol (3^3·4^10·5·6) by reducing each [Ni5(Btz)6] cluster as the 6-connected node (Figure 1c). There is weak C–H–O hydrogen-bond interaction between adjacent infinite layers (Figure S3, ESI), which further stack into a 3D supramolecular architecture in an ABAB fashion, leaving 1D channels with window size of about 5×12 Å along b directions (Figure 1d). The solvent-accessible volume of 1 without all dissociative and terminal solvent molecules is approximately 3191.1 Å3 per unit cell (8145.8 Å3), being equal to about 39.2% of the total crystal volume estimated by PLATON. The dissociative and terminal solvent molecules in the free spaces are evidenced by thermal gravimetric analysis (TGA).

In order to examine the stability of the framework, TGA, X-ray powder diffraction (XRPD), and desorption experiments were carried out. TGA curve of 1 reveals a weight loss of 20.80% at 120 °C, corresponding to the release of all terminal coordinating solvent ligands as well as two dissociative DMA molecules, one disorder MeOH and one disorder H2O (Figure S4a, ESI) (calc. 20.2%). For gas adsorption studies, 1 was soaked at MeOH for one week and then dipped in CH2Cl2 for another week. It seems that these dissociative and coordinative DMA molecules is easily replaced MeOH and CH2Cl2 during the solvent-exchange process (Figure S4b, ESI). By The CH2Cl2-exchanged sample was activated at 80 °C for 12 h under high vacuum to form the desolvated solid (1-h). Further powder XRD experiments are carried out to verify the framework stability of 1-h. Compared to 1, the PXRD patterns of 1-h have appeared obvious change.
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Figure 5. Temperature dependence of magnetic susceptibilities in
the form of $\chi M T$ at an applied field of 1000 Oe (red part for the least-square fitting at 2–300 K) and $\chi M T$ vs. $T$ plot (red part for the Curie–Weiss fitting) for 1.

(Figure S5, ESI). It may be due to the slippage of layers after the removal of guest molecules.

The permanent porosity of 1-hf was established by reversible gas sorption experiments using N$_2$ at 77 K, which shows a typical type I behavior characterized by a plateau reached at low relative pressure, indicating the presence of permanent micropores in 1-hf (Figure 2a). The maximum N$_2$ uptake at 1 bar for 1-hf is 62.9 cm$^3$/g, giving a BET and Langmuir surface areas of 180.5 and 254.9 m$^2$/g, respectively (Figure S6, ESI). Pore size distribution based on Horvath–Kawazoe (H–K) model gives a pore diameter of 7.6 Å (Figure S7, ESI). In the adsorption data of 1-hf, a single data point at pressure of 0.98 bar gives a micropore volume of 0.097 cm$^3$/g, which is more than the theoretical value of 0.357 cm$^3$/g calculated from crystallographic data because of the slippage of layers after activation.

The CO$_2$ uptake of 1-hf at 273 and 298 K can reach 49.2 and 32.5 cm$^3$/g, respectively (Figure 2b and 2c). The enthalpies of CO$_2$ adsorption for 1-hf were calculated by the virial equation from the adsorption isotherms measured at 273 and 298 K (Figure S8 and S10b, ESI). At zero coverage, the CO$_2$ isosteric heat of 28.1 kJ/mol for 1-hf is comparable to those of MOFs with organic ammonium ions in the pores for strong CO$_2$ binding and indicates the strong interaction between CO$_2$ molecules and the host framework. We speculate that such behavior is a result of the increased sorbate–sorbent interactions as the gas molecules access the pore region around the unsaturated metal sites. Although the CO$_2$ uptake ability for 1-hf is at a moderate level compared to some currently reported MOFs, it shows high CO$_2$/CH$_4$ adsorption selectivity at ambient conditions. In contrast, CH$_4$ was hardly adsorbed by 1-hf under the conditions of 273 K (just 10.8 cm$^3$/g) (Figure 2d). The experimental data are fits of the dual-site Langmuir–Freundlich mode (Figure S11, ESI) and the adsorption selectivity for equimolar mixture adsorption of CO$_2$ with respect to CH$_4$ are calculated using ideal solution adsorbed theory (IAST). The selectivity of CO$_2$ component with respect to CH$_4$ at 273 K is in excess of 14.5 for a range of pressures to 100 kPa (Figure 3). Notably, the high selective separation of CO$_2$/CH$_4$ suggests that 1-hf may be a good candidate material for purification of natural gas.

Low-pressure H$_2$ adsorption isotherms collected for the sample of 1-hf indicates that the framework has a strong affinity for binding H$_2$ (Figure 4). At 77 K and 1.06 bar (800 Torr), it has a fully reversible H$_2$ uptake of 101.5 cm$^3$/g (0.91 wt%), a value surpassing that of the most favorable zeolite ZSM-5 (0.7 wt%) and closing to those of recently reported MOFs. As a further test, a second H$_2$ adsorption isotherm was measured at 87 K, and two data sets were used to determine the isosteric heat of H$_2$ adsorption using the virial equation to understand the affinity of 1-hf toward H$_2$ (Figure S9 and S10a, ESI), giving an isosteric heat of 7.2 kJ/mol under zero coverage.

The solid-state magnetic susceptibility of 1 was measured in the 2–300 K range at a field of 1000 Oe by using a SQUID magnetometer. The magnetic properties in the form of $\chi M T$ vs. $T$ plots are shown in Figure 5. At 300 K, the $\chi M T$ value of 1 is 4.45 cm$^3$/Kmol$^{-1}$, which is similar to the value that was previously reported for five uncoupled tetrahedral Ni-clusters. However, it is smaller than that of three Ni5 clusters employing the 2-pyridylcyano oxide ligand because of the distinct magnetic-exchange pathway. As the temperature decreases, the value of $\chi M T$ slowly decreases down to a minimum value of 0.58 cm$^3$/Kmol$^{-1}$ for 1 at 2 K. The data in the range of 40 – 300 K obeys the Curie–Weiss law with $C = 5.14$ cm$^3$/Kmol$^{-1}$, $\theta = -49.69$ K for 1. The negative values of $\theta$ and the gradient of $\chi M T$ vs. $T$ plots should be due to the overall antiferromagnetic coupling between Ni(II) ions for 1. The magnetic susceptibilities of 1 is fitted with a highly symmetric model to give $J_1 = -9.8$, $J_2 = -23.5$, $J_3 = -16.7$, $J_4 = -8.6$ and $g = 2.0$ for 1. The large negative values of $J$ further indicate that strong antiferromagnetic interaction exists among the Ni(II) centers.

In summary, by employing Ina ligands to assemble pentanuclear tetrahedral Ni-clusters, a new microporous layer 1 with exposed metal sites is successfully synthesized and features a porous layer motif with unusual 6-connected topology. Moreover, the desolvated solid 1-hf not only exhibits a high H$_2$ uptake of 101.5 cm$^3$/g, but also separates CO$_2$ over CH$_4$ with selectivity of 19.8 under 273 K and 1 bar. Magnetic measurement shows the overall antiferromagnetic coupling between Ni(II) ions for 1.

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Synthesis of [Ni$_2$(Btz)$_2$(Ina)$_3$(H$_2$O)$_2$(CH$_3$COO)$_2$]xG (1). HBTz (0.130 g, 1 mmol), HIna (0.062 g, 0.5 mmol), Ni(NO$_3$)$_2$·6H$_2$O (0.295 g, 1 mmol), 3 mL N,N-dimethylacetamide (DMA) and 1.5 mL methanol (MeOH) was sealed in a 20 mL vial and heated in an oven at 120 °C for 6 days. The vial was taken out and naturally cooled to room temperature. After washed with fresh methanol, blue block crystals were obtained in pure phase.

Notes and references

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Electronic Supplementary Information (ESI) available: [Experimental details, addition figures, TGA, powder X-ray patterns, adsorption isotherms and CIF file (CCDC-1022281)]. See DOI: 10.1039/b000000x.


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