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# Construction of polyhedron decorated MOF with unique network through the combination of two classic secondary building units

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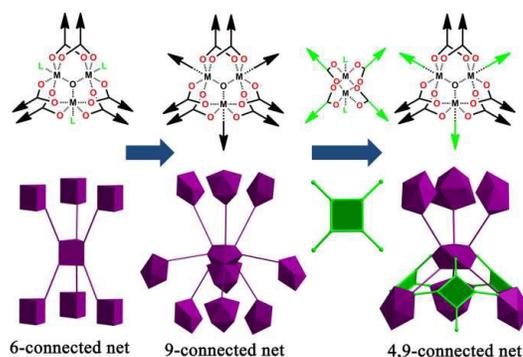
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A novel decorated metal-organic polyhedron (MOP) based metal-organic framework with unique 4,9-connected network is successfully constructed, which displays relatively strong interaction toward H<sub>2</sub> and CO<sub>2</sub> probably due to the existence of open metal sites in the secondary building units.

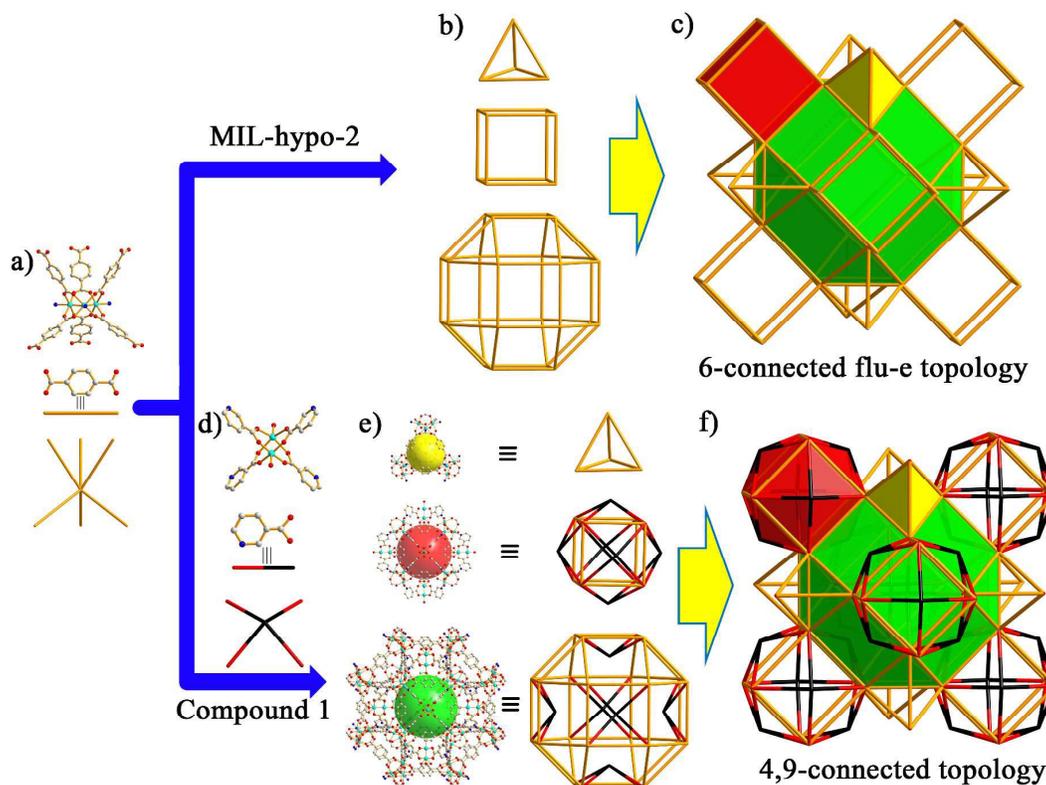
Metal-organic frameworks (MOFs) have been widely explored as one class of emerging porous materials due to their unique properties and potential applications in gas adsorption, molecule sensing, heterogeneous catalysis and so on.<sup>1,2</sup> Among the various kinds of MOFs, metal-organic polyhedron (MOP) based MOFs, with distinct structures and topologies have attracted much attention owing to their readily realized design and construction feature based on the rational combination of organic linkers with defined configurations and secondary building units (SBUs).<sup>3-4</sup> It has been found that the triangular  $\mu_3$ -oxo trimetallic M<sub>3</sub>O(O<sub>2</sub>CR)<sub>6</sub>L<sub>3</sub> (M = transition metal, R = linker groups, and L = axial ligand) (Scheme 1) SBUs could facilitate the construction of MOP-based MOFs with remarkable architectures and properties.<sup>5</sup> For example, Mellot-Draznieks and co-workers have designed and predicted two hybrid frameworks with high porosity, named MIL-hypo-1 and MIL-hypo-2, via the assembling of BDC<sup>2-</sup> (H<sub>2</sub>BDC = 1,4-benzenedicarboxylic acid) and the triangular M<sub>3</sub>O SBUs.<sup>6</sup> Shortly thereafter, Férey *et al.* reported the well-known MIL-101 built by 6-connected Cr<sub>3</sub>O MBB and BDC<sup>2-</sup>.<sup>7</sup> In addition, MOFs with dynamic breathing feature have been obtained by the assembly of M<sub>3</sub>O and linear dicarboxylate ligands.<sup>8</sup>

An important feature should be noted that the trimetallic SBUs commonly serve as classic 6-connected nodes in MOFs with only the carboxylate sites extended with linear spacers, while the axial sites are occupied by terminal molecules (Scheme 1 left). Then, by introducing proper ligands to extend the connections through the replacement of axial sites, more complicated MOFs could be obtained with the SBUs as high connected nodes (Scheme 1 middle). By judicious choice and combination of pyridine-carboxylate ligands and linear dicarboxylate ligands, the coordination configuration of M<sub>3</sub>O(O<sub>2</sub>CR)<sub>6</sub>L<sub>3</sub> was successfully modulated from 6-connected trigonal prism to 9-connected tricapped trigonal-prismatic geometry, and a series of highly connected MOFs with **ncb** topology were obtained.<sup>9,10</sup> These results indicate the connection flexibility of the SBU in the construction of MOFs.



**Scheme 1** Presentation of connection modes involved in  $\mu_3$ -oxo trimetallic SBUs, left: 6-connected net based on trigonal prism SBU, middle: 9-connected net based on tricapped trigonal prism SBU, right: 4,9-connected net in **1** based on paddle wheel and tricapped trigonal prism SBU (M = transition metal, O = oxygen, L = axial ligand, black arrow = linker group, green arrow = the same linker).

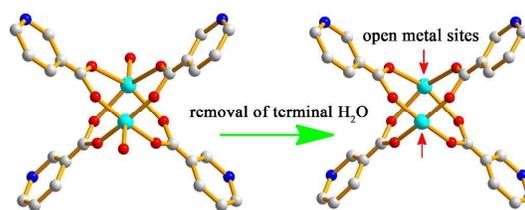
Motivated by the intriguing achievement mentioned above, we have focused on the investigation of unique MOFs based on M<sub>3</sub>O(O<sub>2</sub>CR)<sub>6</sub>L<sub>3</sub> SBU and linear dicarboxylate ligands through the introduction of ancillary pyridine-carboxylate ligand. As the connection conformation of the SBU is variable, we expect that the ancillary ligand could be utilized to modulate the conformation of SBU as well as the structure of the obtained MOFs. Based on this assumption, a MOP-based MOF, (Ni<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>)<sub>1.5</sub>(Ni<sub>3</sub>OH)<sub>2</sub>(BDC)<sub>6</sub>(NA)<sub>6</sub> (**1**) (HNA = nicotinic acid), is successfully constructed. In this MOF, the NA<sup>-</sup> ligand with bended linking mode not only extend the Ni<sub>3</sub>OH(O<sub>2</sub>CR)<sub>6</sub>L<sub>3</sub> SBU (**SBU1**) through the axial sites, but also introduce the classic paddle wheel Ni<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(O<sub>2</sub>CR)<sub>4</sub> (**SBU2**) (Scheme 1 right) into the MOF. On the basis of the modulated conformation of **SBU2**, the BDC-**SBU1** contained subnet reveals rare **flu-e** topology, which could be regarded as the packing of three kinds of MOPs. Then compound **1** could be described as a **SBU2** decorated MOP based MOF, which is a rare example as compared with the widely reported *in situ* ligands decoration of discrete MOPs.<sup>11</sup> Also, this MOF reveals unique topology in which **SBU1** and **SBU2** serve as 9- and 4-connected vertexes, respectively. To our knowledge, this is the first example of 4,9-connected topology in the MOP-based MOFs. Furthermore, the presence of open metal sites in **SBU2** makes **1** show relatively strong interaction toward H<sub>2</sub> and CO<sub>2</sub>.



**Fig. 1** a) The  $\mu_3$ -oxo trimetallic SBU involved in **1** (gray: C, red: O, blue: N, green: Ni, H atoms were omitted for clearness) and the topological simplification of the BDC<sup>2-</sup> ligand and SBU; b) Three kinds of MOPs involved in MIL-hypo-2<sup>6</sup> (the tetrahedron, hexahedron, and rhombicuboctahedron); c) the **flu-e** topology network; d) The paddle wheel SBU in **1**, and the topological simplification of the NA<sup>-</sup> ligand and SBU; e) Internal diameters of three kinds of cages (yellow: 9.6 Å, red: 14.4 Å, green: 14.6 Å) and the corresponding MOPs in **1**; f) The packing mode of MOPs in **1** and the topology of the framework.

Solvothermal reaction of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, H<sub>2</sub>BDC and HNA in *N,N'*-dimethylformamide (DMF) for 3 days gave the green crystals of **1** (please see ESI for more detail). X-ray single crystal structural determination reveals that **1** crystallizes in cubic space group *Fm-3m*. The asymmetric unit of **1** contains one NA<sup>-</sup>, a pair of half BDC<sup>2-</sup> and three Ni centers. As shown in Fig.1a, the Ni1 ions in **1** reveal six coordinated octahedral geometry, which is coordinated with four O atoms from four different BDC<sup>2-</sup>, one  $\mu_3$  OH<sup>-</sup> group, and one N atom from one NA<sup>-</sup> ligand. Through the linkage of six carboxylates of BDC<sup>2-</sup> and the central O atom, three Ni1 ions are banded to result in a Ni<sub>3</sub>OH(O<sub>2</sub>CR)<sub>6</sub>L<sub>3</sub> SBU (**SBU1**) with three N atoms of NA<sup>-</sup> ligands coordinated at the axial sites. It should be noted that the central OH<sup>-</sup> in this SBU could be confirmed by the consideration of charge balance and the rule of bond valence sum, since there should be a delocalized positive charge in each of the triangular SBU, according to the results of bond valence calculation and characterizations of X-ray photoelectron spectroscopy (XPS), magnetic data as well as theoretical calculations (see ESI for detail). On the other hand, four carboxylates of NA<sup>-</sup> chelate with a pair of Ni2 and Ni3 ions, giving a paddle wheel Ni<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(O<sub>2</sub>CR)<sub>4</sub> SBU (**SBU2**) with the O atoms from two coordinated H<sub>2</sub>O molecules occupied the terminal sites (Fig. 1d), which could serve as open metal sites to benefit gas sorption performances when the terminal H<sub>2</sub>O molecules were removed (Fig. 2). Each **SBU2** was connected to four different **SBU1** through the

linkage of NA<sup>-</sup> ligands, and every **SBU1** links six same **SBU1** by the connection of BDC<sup>2-</sup> ligands and three **SBU2** through the linkage of NA<sup>-</sup> ligands. Based on the connection between two kinds of SBUs, a complicated three dimensional porous framework was obtained.



**Fig. 2** The formation of open metal sites in the paddle wheel **SBU2**.

To better understand the structure of **1**, the framework was analyzed and simplified in the perspective of MOP. As shown in Fig.1e, there are three kinds of MOPs with **SBU1** and **SBU2** as vertexes. Six BDC<sup>2-</sup> ligands link four **SBU1**, resulting in a tetrahedron MOP (Fig.1e top). The triangle window of the MOP is about 3.8 Å, and the internal cavity is about 9.6 Å in diameter. Eight **SBU1** connect twelve BDC<sup>2-</sup> ligands, forming the hexahedron. On the other hand, a tetrakis hexahedral MOP is obtained with eight **SBU1** and six **SBU2** as vertexes (Fig.1e middle). Considering about the different linkages between the SBUs, this rare MOP could be described as a **SBU2** decorated **SBU1** based hexahedral MOP. To the best of our knowledge, this is the first decorated MOP in the

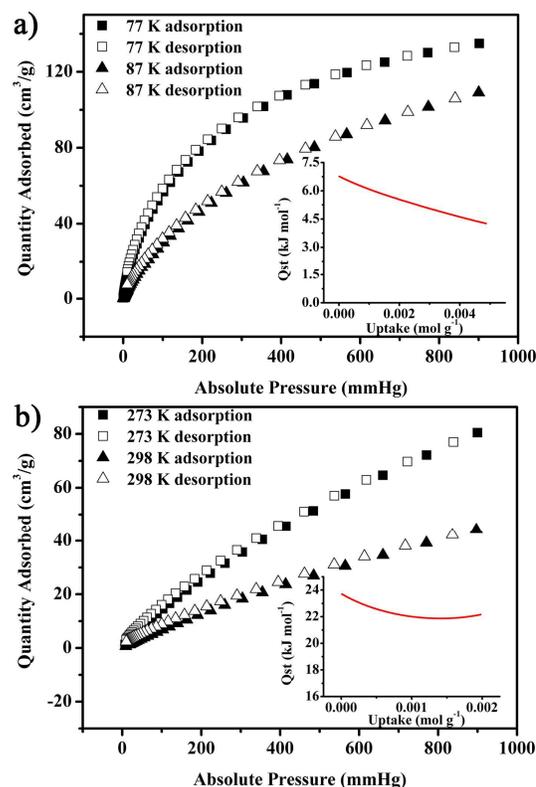
construction of MOFs. The diameter of the internal cavity in decorated polyhedron 1 is about 14.4 Å. Furthermore, when eight tetrahedrons and six tetrakis hexahedrons pack together by vertexes sharing, a rhombicuboctahedron MOP is formed (Fig. 1e bottom). A complicated architecture is built through the packing form of the above-mentioned three kinds of MOPs as shown in Fig. 1f. The diameter of the interior space is about 14.6 Å. Though the square windows of the rhombicuboctahedron MOP are partially decorated with **SBU2**, there are still three-dimensional channels with large aperture left in the framework of **1**. The free volume of **1** in fully desolvated condition is about 59.9% as calculated by PLATON.<sup>12</sup> When the framework was simplified topologically, **SBU2** and **SBU1** could be regarded as 4- and 9-connected node respectively, and the structure of **1** can be simplified as a unique binodal 4,9-connected topology with point symbol  $\{3^4.4^2\}_3\{3^9.4^9.5^{15}.6^3\}_4$  (Fig. S4). It should be noted that though MOFs with  $M_3O(O_2CR)_6L_3$  SBUs as 9-connected nodes are common,<sup>13</sup> the combination of that with other SBU is quite rare, and the topology of **1** should be the first 4,9-connected network reported in the MOP-based MOFs materials.

Interestingly, when the **SBU2** nodes are neglected in topology analysis, the remained framework of **1** based on **SBU1** and  $BDC^{2-}$  is the same to the MIL-hypo-2 as predicted by Mellot-Draznieks, and can be simplified as a uninodal 6-connected **flu-e** net composed of tetrahedron, hexahedron and rhombicuboctahedron (Fig. 1b and Fig. 1c).<sup>14</sup> Though MOFs with this kind of topology has been predicted,<sup>6,15</sup> no examples has been reported up to now. This might be due to the particular requirement of the configuration of the 6-connected nodes: to achieve the fundamental tetrahedral and hexahedral MOPs in **flu-e**, the angles between three of the linkages of the nodes should be 60°, while the angle between the other three should be 90°.

When structure of **1** is compared with those of the MIL-101 and MCF-19,<sup>7,9a</sup> it could be find that the introduction of  $NA^-$  as well as **SBU2** play a crucial role in the formation of **1** and the **flu-e** net. As shown in Fig.S5, the angle between adjacent two  $BDC^{2-}$  ligands in MIL-101 is 60° which is an essential factor for building the tetrahedral MOPs. When linear pyridylcarboxylate ligand is applied in MCF-19, three chelation sites of dicarboxylate ligand and three axial site of  $M_3OH(O_2CR)_6L_3$  are occupied, resulting in the change of angle between adjacent linkers (54.1°) and the formation of trigonal pyramid MOPs. Differ from that mentioned above, the well-defined square configuration of **SBU2** restricts the angles between three linkers of **SBU1** as 90°, which is required for the assembly of hexahedron MOPs, while the angle between the other three linkers maintain 60°, that allowed the assembly of tetrahedral MOPs simultaneously. Based on the structure analysis, the realization of hexahedron and tetrahedral MOPs based **flu-e** subnet in **1** should be due to the presence of  $NA^-$  ligands which is vital for the construction of **SBU2**. This hypothesis could be proved by the fact that the **flu-e** subnet compound cannot be obtained when  $NA^-$  is not present in the reaction system. Then, the rare 4,9-connected topology of **1** as well as the achievement of **flu-e** subnet further proved that the combination of SBUs could be an

efficient strategy for the fabrication of MOFs with unique structures.

Beside the attractive peculiarity of the framework structure, the high porosity of the framework also motivated us for the investigation of its gas adsorption properties. Before the measurements, X-ray powder diffraction (XRPD) (Fig. S6) and thermogravimetric analyses (TGA) (Fig. S7) were performed to confirm the stability of the compound. The  $N_2$  adsorption at 77 K was performed to estimate the porosity of **1**, and the classic type I isotherm obtained indicates the micropore character of this compound (Fig. S9). The upake amount was 310.9  $cm^3/g$  with the BET surface area 997.8  $m^2/g$  (Langmuir surface area 1323.8  $m^2/g$ ).



**Fig. 3** a)  $H_2$  adsorption isotherms of **1** (insert:  $H_2$  adsorption enthalpies depending on uptake), b)  $CO_2$  adsorption isotherms of **1** (insert:  $CO_2$  adsorption enthalpies depending on uptake).

Furthermore,  $H_2$  adsorption measurements were performed at 77 and 87 K to investigate the hydrogen adsorption capacity of **1**. At 1 atm, the uptake amounts reach 134.9  $cm^3/g$  and 109.0  $cm^3/g$  (STP) for 77 and 87 K, respectively, and the adsorption enthalpies ( $Q_{st}$ ) calculated with Virial equation is 6.7-4.2  $kJ mol^{-1}$ , depending on the  $H_2$  uptake (Fig. 3a). The relatively high  $Q_{st}$  should be attributed to the presence of open metal sites in the paddle-wheel **SBU2**, which could serve as adsorption sites of  $H_2$  molecules. Though the value of adsorption heat is relatively lower than that of the best MOFs, it is comparable with some reported MOFs containing open metal sites.<sup>17</sup> More important, the value of adsorption heat is comparable with that of MOFs with Cu paddle-wheel SBUs, such as HKUST-1 (6-7  $kJ mol^{-1}$ )<sup>18</sup>, and this result agree well with the expectation based on theory calculations that the Ni ion in paddle-wheel SBUs have relatively low interaction toward

H<sub>2</sub> when compared with Co and Zn ion, but comparable with that of Cu ion.<sup>19</sup> The CO<sub>2</sub> adsorption ability of compound **1** was also investigated. The maximum CO<sub>2</sub> capacities at 1 atm are 80.4 cm<sup>3</sup>/g at 273 K and 44.2 cm<sup>3</sup>/g at 298 K, respectively. The  $Q_{st}$  value of **1** for CO<sub>2</sub> is 23.7 kJ mol<sup>-1</sup> at zero loading (Fig. 3b), which is relatively lower than that of HKUST-1 isostructural series with unsaturated metal sites (25.6-36.8 kJ mol<sup>-1</sup>),<sup>20</sup> but higher than other reported results which do not contain open metal sites (20.2 and 21.3 kJ mol<sup>-1</sup>).<sup>21</sup> The relatively high  $Q_{st}$  values for H<sub>2</sub> and CO<sub>2</sub> indicates enhanced interactions between the adsorbed gas molecules and the framework structure owing to the presence of **SBU2** based open metal sites, which could benefit the gas adsorptions performances.

In conclusion, a porous MOF, which is the first example of 4,9-connected network, has been obtained through the approach of combining Ni<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(O<sub>2</sub>CR)<sub>4</sub> and Ni<sub>3</sub>OH(O<sub>2</sub>CR)<sub>6</sub>L<sub>3</sub> SBUs. The structure of **1** could be described as a rare SBUs decorated MOPs based framework. Also, the presence of Ni<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(O<sub>2</sub>CR)<sub>4</sub> in the framework restricts the geometrical configuration of Ni<sub>3</sub>OH(O<sub>2</sub>CR)<sub>6</sub>L<sub>3</sub> SBUs and results in the achievement of subnet with unique flu-e topology. Furthermore, this MOF reveals enhanced interactions between the adsorbed H<sub>2</sub>/CO<sub>2</sub> gas molecules and the porous framework, which might be utilized in the gas storage. The results suggest that the combination of SBUs could be an efficient approach to construct MOFs with unique structures and properties.

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## Notes and references

Crystal data for **1**: C<sub>84</sub>H<sub>48</sub>N<sub>6</sub>Ni<sub>9</sub>O<sub>41</sub>,  $M_r = 2325.49$ , Cubic, *Fm*-3*m*,  $a = b = c = 41.4694(4)$  Å,  $\alpha = \beta = \gamma = 90$  (4)°,  $V = 71315(2)$  Å<sup>3</sup>,  $Z = 16$ ,  $\rho_{calcd} = 0.886$  g cm<sup>-3</sup>,  $T = 100$  K,  $R_{int} = 0.0801$ ,  $R_1 = 0.1638$  ( $I > 2\sigma(I)$ ),  $wR_2 = 0.3793$  (all data), GOF = 1.218, CCDC No: 1032254;

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† Electronic Supplementary Information (ESI) available: [materials and general methods, adsorption measurements, crystal structure, bond valence sum, XPS spectrum, magnetic data, IR spectrum, PXRD, TGA, gas adsorption data]. See DOI: 10.1039/b000000x/

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