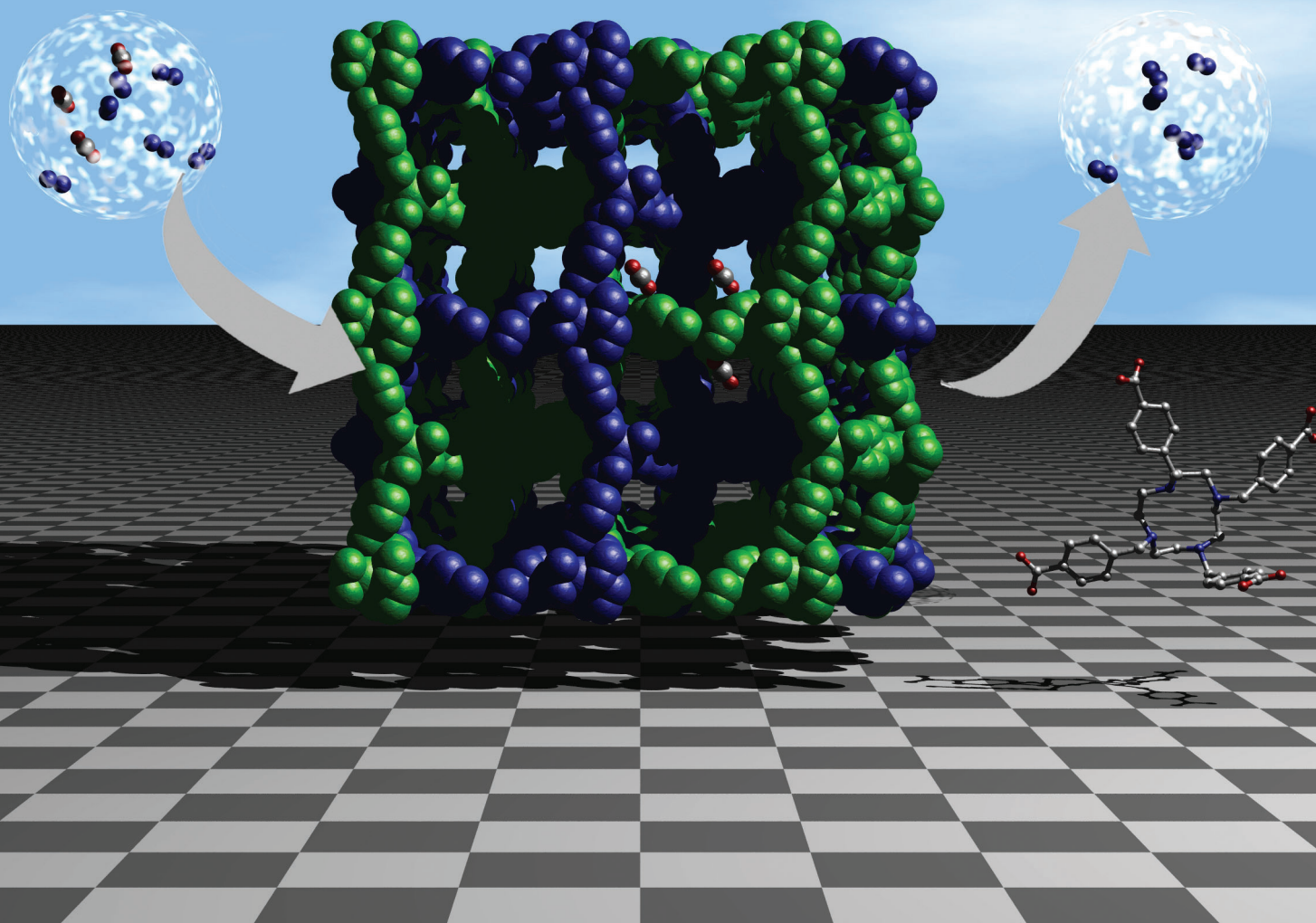


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## Porous metal–organic framework based on a macrocyclic tetracarboxylate ligand exhibiting selective CO<sub>2</sub> uptake†

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A two-fold interpenetrating microporous metal–organic framework, MMCF-1, has been constructed *via* the self-assembly of a custom-designed macrocyclic tetracarboxylate ligand and Cd(II), and it exhibits interesting selective uptake of CO<sub>2</sub> over N<sub>2</sub>.

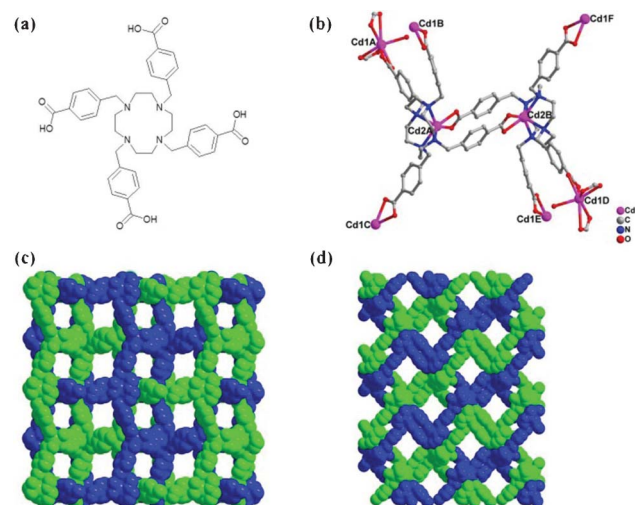
By virtue of high porosity, tunable pore size and large internal surface area,<sup>1</sup> metal–organic frameworks (MOFs)<sup>2</sup> have been highlighted as promising candidates with potential for applications in gas storage,<sup>3</sup> separation,<sup>4</sup> heterocatalysis,<sup>5</sup> sensors<sup>6</sup> and other areas.<sup>7</sup> Over the past decade considerable attention has been attracted to constructing microporous MOFs *via* self-assembly of multifunctional organic ligands and metal ions or clusters.<sup>8</sup> Carboxylate-based linkers have been predominantly employed for the construction of MOFs and many of them have been developed into prototypal platforms, such as HKUST-1,<sup>9</sup> MOF-5,<sup>10</sup> MOF-74,<sup>11</sup> MOF-505,<sup>12</sup> and *rht*-MOF-1<sup>13</sup> *etc.* Under the concept of “reticular synthesis”,<sup>14</sup> the properties of prototypal MOF platforms can be targeted *via* functionalizing the organic linkers. Meanwhile, the versatile coordination feature of a carboxylate donor group can afford diverse structures, as particularly observed for MOFs based upon flexible ligands.<sup>15</sup>

Azamacrocycle-based ligands represent a type of flexible ligands, and their intriguing properties afford them wide applications for activation of small molecules,<sup>16</sup> ion recognition and capture<sup>17</sup> in supramolecular chemistry. This could also provide an opportunity to establish a new type of functional MOFs accompanied with the ascendancy of macrocycles in host–guest chemistry, although flexible macrocycle ligands have rarely been explored for MOFs.<sup>18</sup>

To combine the coordination diversity of a carboxylate group and the merits of a flexible macrocycle, in this contribution, we designed an azamacrocyclic tetracarboxylate ligand 1,4,7,10-tetrazacyclododecane-*N,N',N'',N'''*-tetra-*p*-methylbenzoic acid

(*tactmb*) (Fig. 1a). The self-assembly of the *tactmb* ligand with Cd(II) under solvothermal conditions gave rise to a microporous MOF, termed MMCF-1 (MMCF denotes Metal-Macrocyclic Framework) which possesses a three dimensional (3D) structure with two-fold interpenetration, as well as exhibiting interesting selective uptake of CO<sub>2</sub> over N<sub>2</sub>.

The colorless block crystals of MMCF-1 were obtained by reacting the *tactmb* ligand with Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O in *N,N*-dimethylformamide (DMF) for 48 h. Single-crystal X-ray crystallographic studies conducted using synchrotron radiation at the Advanced Photon Source, Argonne National Laboratory, revealed that MMCF-1 crystallizes in the space group *P*<sub>2</sub><sub>1</sub>/*c*.† The asymmetric unit of MMCF-1 contains two Cd(II) ions, one *tactmb* ligand and one coordinated water molecule. The seven-coordinated Cd atom (Cd1) connects with six oxygen atoms of three carboxylate groups from three different *tactmb* ligands and



**Fig. 1** (a) The *tactmb* ligand; (b) the coordination unit of MMCF-1; (c) the two-fold interpenetrating structure viewed from the *b* direction; (d) the two-fold interpenetrating structure viewed from the *c* direction.

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† Electronic supplementary information (ESI) available: Experimental procedures for the synthesis of the ligand and MMCF-1, TGA plots, heat of adsorption of CO<sub>2</sub>, IAST calculation, and crystal data of MMCF-1. CCDC reference number 874284. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ce25484k

† X-ray crystal data for MMCF-1: C<sub>40</sub>H<sub>40</sub>N<sub>4</sub>O<sub>9</sub>Cd<sub>2</sub>, *f*<sub>w</sub> = 945.56, monoclinic, *P*<sub>2</sub><sub>1</sub>/*c*, *a* = 17.8372(19) Å, *b* = 21.164(2) Å, *c* = 21.721(2) Å, *V* = 8199.7(15) Å<sup>3</sup>, *Z* = 4, *T* = 100 K, ρ<sub>c</sub> = 0.766 g cm<sup>-3</sup>, *R*<sub>1</sub> (*I* > 2σ(*I*)) = 0.0725, *wR*<sub>2</sub> (all data) = 0.2019.

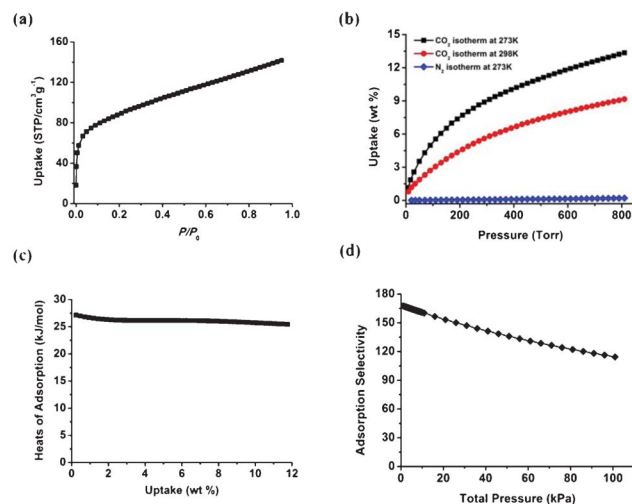
one oxygen atom from the coordinated water. The other Cd atom (Cd2) is located in the center of the macrocycle of the tactmb ligand, and it is coordinated with four nitrogen atoms of the macrocycle and two oxygen atoms of one carboxylate group from another tactmb ligand. Each tactmb macrocycle ligand links with three seven-coordinated Cd atoms (Cd1) and one six-coordinated Cd atom (Cd2) that is located in the macrocycle center of another tactmb ligand through four carboxylate groups to form an overall 3D structure of MMCF-1.

Topologically, MMCF-1 can be described as a two-fold interpenetrating (6,3) network, in which two tactmb ligands that are bridged together by two methylbenzoate moieties through Cd2 within the macrocycle can be regarded as an overall 6-connected node while Cd1 itself serves as the 3-connected node to link with three independent carboxylate groups (Fig. 1b). MMCF-1 is porous and has a solvent accessible volume of 63% calculated using PLATON.<sup>19</sup> MMCF-1 possesses two types of rectangular channels with sizes of 4.8 Å × 6.8 Å and 7.5 Å × 8.2 Å (atom to atom distance) along the crystallographic *b* and *c* axis respectively (Fig. 1c, d).

Thermogravimetric analysis (TGA) (Fig. S1, ESI†) of the fresh MMCF-1 sample reveals a weight loss of ~38% from 30 to ~200 °C corresponding to the loss of guest DMF solvent molecules trapped in the channels and coordinated water molecules. The plot is followed by a steady plateau from 200 to 320 °C before complete decomposition of the framework. The thermal stability was confirmed by the TGA studies on the solvent-free MMCF-1 sample (Fig. S1, ESI†), highlighting the robustness of its framework.

To evaluate the permanent porosity of MMCF-1, gas adsorption studies were performed on the activated sample. As shown in Fig. 2(a), the CO<sub>2</sub> adsorption isotherm collected at 195 K reveals that MMCF-1 exhibits an uptake capacity of 140 cm<sup>3</sup> g<sup>-1</sup> at 1 atmosphere pressure with typical type-I adsorption behavior, as expected for microporous materials. Derived from CO<sub>2</sub> adsorption data at 195 K, MMCF-1 possesses a Brunauer–Emmett–Teller (BET) surface area of ~500 m<sup>2</sup> g<sup>-1</sup> ( $P/P_0 = 0.01$ – $0.15$ ), corresponding to a Langmuir surface area of ~600 m<sup>2</sup> g<sup>-1</sup> ( $P/P_0 = 0.9$ ). To our knowledge, MMCF-1 represents the first example of a permanently porous MOF based upon a flexible tetraazamacrocyclic ligand, while there have been reported several MOF structures constructed from other azamacrocyclic ligands.<sup>18</sup>

It has been well-documented that grafting primary, secondary, or tertiary amine groups into porous MOFs can significantly increase the CO<sub>2</sub> binding affinity although sometimes at the expense of sacrificing the uptake CO<sub>2</sub> capacity due to the decreased surface area.<sup>20</sup> The azamacrocyclic of the tactmb ligand features four tertiary amines and this prompts us to investigate the CO<sub>2</sub> uptake performances of MMCF-1. As shown in Fig. 2(b), MMCF-1 can adsorb substantial amounts of CO<sub>2</sub> with the uptake capacities of 13.1 wt.% at 273 K and 9.0 wt.% at 298 K under 1 atm of pressure. These values are comparable to the best performing ZIF material (ZIF-20, 13.7 wt.% cm<sup>3</sup> g<sup>-1</sup> at 273 K, 1 atm)<sup>21</sup> but are moderate compared to some highly porous MOFs due to the much lower surface area of MMCF-1.<sup>22</sup> However, it's worth noting that the shape of the CO<sub>2</sub> adsorption isotherms is an indication of relatively strong interactions between the MMCF-1 framework and CO<sub>2</sub> gas molecules. We calculated the heats of adsorption ( $Q_{st}$ ) of CO<sub>2</sub> for MMCF-1 based upon the CO<sub>2</sub>



**Fig. 2** (a) CO<sub>2</sub> adsorption isotherm of MMCF-1 at 195 K; (b) Gas adsorption isotherms of MMCF-1 (black, CO<sub>2</sub> at 273 K; red, CO<sub>2</sub> at 298 K; blue, N<sub>2</sub> at 273 K); (c) heats of adsorption of CO<sub>2</sub> for MMCF-1; (d) IAST-predicted selectivity of the mixture of CO<sub>2</sub> and N<sub>2</sub> for MMCF-1.

adsorption isotherms at 273 K and 298 K using the virial method (Fig. S2, ESI†).<sup>23</sup> As shown in Fig. 2(c), MMCF-1 exhibits a constant  $Q_{st}$  of ~26 kJ mol<sup>-1</sup> at all loadings, distinguishing it from other MOFs with open metal sites or decorated with primary amine groups, whose  $Q_{st}$  usually decreases abruptly to 20–22 kJ mol<sup>-1</sup> with the increase of CO<sub>2</sub> loading despite their high initial  $Q_{st}$ .<sup>20a,24</sup> We tentatively attribute this to the existence of tertiary amines from the azamacrocyclics that are incorporated into the framework of MMCF-1.

We also evaluated MMCF-1 for selective adsorption of CO<sub>2</sub> over N<sub>2</sub> which is related to the post-combustion CO<sub>2</sub> capture application. The N<sub>2</sub> adsorption isotherm at 273 K indicates that MMCF-1 can adsorb a very small amount of N<sub>2</sub> (0.18 wt.% at 1 bar), meaning a selective capacity of 73 for CO<sub>2</sub>/N<sub>2</sub> at 273 K and 1 bar. Given that our attempts to measure the low-pressure N<sub>2</sub> adsorption isotherms at 298 K could not generate meaningful data points because of the extremely low N<sub>2</sub> uptake capacity,<sup>25</sup> we decided to use the adsorption isotherms at 273 K to assess the potential of MMCF-1 for possible post-combustion CO<sub>2</sub> capture application. The Ideal Adsorption Solution Theory (IAST),<sup>26</sup> has been proved to be valid to calculate the adsorption selectivity of MOFs,<sup>27</sup> was employed to estimate the gas selectivity of MMCF-1 for CO<sub>2</sub>/N<sub>2</sub> (typically composed of 15/85%) in post-combustion flue-gas streams. The selectivity  $S_{A/B}$  in a binary mixture of component A and B is defined as  $(x_A/y_A)/(x_B/y_B)$ , where  $x_i$  and  $y_i$  are the mole fractions of component *i* (*i* = A, B) in the adsorbed and bulk phases respectively. As shown in Fig. 2(d), the adsorption selectivity of MMCF-1 is calculated to be 114 for CO<sub>2</sub> over N<sub>2</sub> at 273 K and 1 bar. To the best of our knowledge, both the selective uptake capacity observed experimentally and the adsorption selectivity estimated from IAST of MMCF-1 for CO<sub>2</sub> over N<sub>2</sub> are the highest yet reported for MOFs based upon tetraazamacrocyclic ligands, and are also among the highest for porous MOFs without open metal sites. The high selective uptake of CO<sub>2</sub> over N<sub>2</sub> for MMCF-1 could be attributed to the large quadrupole moment of CO<sub>2</sub> compared to N<sub>2</sub> as well as the tertiary amines



azamacrocycles, which could afford higher affinities for CO<sub>2</sub> compared to N<sub>2</sub> as illustrated in recent studies.<sup>28</sup>

In summary, a two-fold interpenetrating porous MOF, MMCF-1, has been constructed based upon the custom-designed flexible tactmb ligand which features azamacrocyclic and tetracarboxylate groups. MMCF-1 exhibits permanent porosity with a Langmuir surface area of 600 m<sup>2</sup> g<sup>-1</sup>, and demonstrates interesting selective uptake of CO<sub>2</sub> over N<sub>2</sub>. The strategy of employing a flexible azamacrocyclic-based ligand represents a promising way to construct new types of functional porous MOFs for various applications, particularly gas storage and CO<sub>2</sub> capture. Ongoing work in our laboratories includes the custom-design of new variants of azamacrocyclic-based ligands for the construction of functional MMCF materials and exploring them for applications in sensor, catalysis, and CO<sub>2</sub> capture.

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