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## Introduction

Microporous metal–organic frameworks (MOFs) have attracted considerable attention in view of their structural diversity and adjustable porosity that allow almost unlimited ways to optimize their properties and functionality, making them very promising for a wide range of important applications, especially in capture and separation of small gases or hydro-carbons,<sup>1</sup> as well as luminescence.<sup>2</sup> More remarkably, these physical properties might be integrated into individual architectures to generate multifunctional MOFs.<sup>3</sup>

Among many ongoing efforts to manipulate high-performance MOF materials, one of the effective approaches to improve their affinity and gas selectivity is to build structures bearing open metal sites (OMSs) on the pore surfaces.<sup>4</sup> The OMSs serving as charge-dense binding sites could interact

# A highly stable multifunctional three-dimensional microporous framework: excellent selective sorption and visible photoluminescence<sup>†</sup>

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A Cd(II)-MOF [Cd(L)(DMF)] (1) (H<sub>2</sub>L = 5-(4-pyridyl)-isophthalic acid) featuring high thermal and chemical stability has been solvothermally synthesized and characterized. Complex 1 is a robust multifunctional three-dimensional (3D) microporous framework possessing an unusual (4,5)-connected topological net. Activated 1 shows high-efficiency for the selective capture of CO<sub>2</sub> over N<sub>2</sub> and CH<sub>4</sub> under ambient conditions, which ranks it among MOFs with the highest selectivity. In addition, desolvated 1 exhibits good separation ratios of H<sub>2</sub> over N<sub>2</sub> at lower temperature, as well as alcohols from water. In particular, desolvated 1 demonstrates significantly higher adsorption enthalpies for CO<sub>2</sub> and CH<sub>4</sub> gas molecules, which are in the range of the highest  $Q_{st}$  values reported to date. Furthermore, complex 1 displays visible photo-luminescence in the solid state under UV irradiation.

more strongly with the absorbed gas molecule, and moreover, could selectively separate certain gas mixtures due to their distinct polarizability and/or quadrupole moment. On the other hand, a ligand-based strategy to the design of new luminescent MOFs is commonly used,<sup>2</sup> arising from  $\pi$ -conjugated skeleton and rigidity of the organic molecules. In our effort to develop multifunctional MOFs combined with selective adsorption and strong luminescence, we incorporated the dianionic form of tripodal 5-(4-pyridyl)-isophthalic acid (H<sub>2</sub>L)<sup>5</sup> into a cadmium MOF based on the following considerations: (1) the relatively large Cd(II) cation may enhance the presence of OMSs via uptake of solvent molecules (e.g. H2O, DMF) as terminal ligands, which can be readily detached following desolvation at elevated temperatures and/or under vacuum; (2) the robust rigid organic moiety facilitates the preparation of highly stable porous materials; (3) the collaborative interaction between the  $d^{10}$  metal ion of Cd(II) and the rigid organic ligand is favorable for enhancing fluorescence of the resulting architecture.

Herein, we present a microporous framework, [Cd(L)(DMF)](1), which has been solvothermally synthesized and characterized. Complex 1 is a robust multifunctional three-dimensional (3D) microporous framework possessing an unusual (4,5)-connected topological net. The open Cd( $\pi$ ) metal sites and smallsized pores enable desolvated 1 to exhibit excellent selective capture of CO<sub>2</sub> over N<sub>2</sub> and CH<sub>4</sub> at 298 K, H<sub>2</sub> over N<sub>2</sub> at lower temperature, as well as alcohols from water. In addition, the desolvated form of 1 possesses high adsorption enthalpy for CO<sub>2</sub> and CH<sub>4</sub>. It is worth noting that complex 1 displays visible green-blue photoluminescence in the solid state under UV



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<sup>†</sup> Electronic supplementary information (ESI) available: X-ray crystallographic file (CIF), additional crystal figures, TGA data, PXRD patterns,  $Q_{\rm st}$  and  $\rm CO_2$  selectivity calculation details and decay lifetime fitting for complex 1. CCDC 971223. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt00230j

irradiation. So far, a combination of significantly stable, highly selective absorption of small molecules and intense visible fluorescence in Cd-MOF materials is uncommon in the literature.

### Experimental section

#### Materials and methods

All chemicals and solvents were commercially available and used as received. Elemental microanalyses (C, H and N) were carried out using a Perkin-Elmer 240 elemental analyzer. IR spectra were recorded on a Bruker Vector 22 spectrometer as dry KBr discs in the 400–4000 cm<sup>-1</sup> region. Thermogravimetric analyses (TGA) were measured on a Netzsch STA449C apparatus under a N<sub>2</sub> stream (heating rate of 10 °C min<sup>-1</sup>). All powder X-ray diffraction (PXRD) data were collected on a Siemens D5005 diffractometer using Cu K $\alpha$  radiation ( $\lambda$  = 1.5418 Å) and 2 $\theta$  ranging from 5 to 50°. Solid-state fluorescence spectra were recorded on an Edinburgh Analytical instrument FLS920.

Synthesis of [Cd(L)(DMF)] (1). A mixture of  $Cd(NO_3)_2 \cdot 6H_2O$ (30.8 mg, 0.10 mmol),  $H_2L(24.3$  mg, 0.10 mmol), 5-aminobenzene-1,2,3-tricarboxylic acid (22.5 mg, 0.10 mmol), and DMF (3 mL) was sealed in a parr Teflon-lined stainless steel vessel (25 cm<sup>3</sup>) and heated at 120 °C for 2 days. After slowly cooling to room temperature, light brown crystals of 1 were isolated (yield: 75% based on Cd). Anal. Calcd for  $C_{16}H_{14}CdN_2O_5$ : C, 45.04; H, 3.31; N, 6.57%; found: C, 45.08; H, 3.39; N, 6.51%. IR spectrum (cm<sup>-1</sup>): 3411m, 1658s, 1613s, 1566s, 1504w, 1443s, 1416s, 1368s, 1294w, 1102w, 1072w, 840w, 779m, 731s, 644m, 511w.

#### X-Ray crystallography study

The diffraction data for 1 were collected on a Bruker Smart Apex DUO CCD equipped with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 293(2) K. Data reductions and absorption corrections were respectively performed with the SAINT<sup>6</sup> and SADABS<sup>7</sup> software packages. The structure was solved by direct methods, and refined anisotropically on  $F^2$  by the full-matrix least-squares technique using the SHELXL-97<sup>8</sup> except for the disordered atoms. Disordered segments were subjected to geometric restraints during the refinements. The coordinated DMF is disordered over two positions with equal site occupancy factors, the C-N bonds of DMF were restrained by DFIX, and equal C15 and C15', C16 and C16' displacement parameters were obtained by EADP instructions. Crystallographic data and refinement information for complex 1 are provided in Table S1.<sup>†</sup> Relevant selected parameters are given in Table S2.†

#### Sorption measurements

All gases used are of 99.999% purity throughout the gas sorption measurements. Low-pressure nitrogen  $(N_2)$ , carbon dioxide  $(CO_2)$ , methane  $(CH_4)$ , hydrogen  $(H_2)$ , water and alcohol sorption experiments (up to 1 bar) were performed on

a Quantachrome  $IQ_2$  system. A solvent-exchanged sample was obtained by soaking the as-made sample in methanol for 3 days with methanol, refreshing every 8 h. A completely desolvated sample (about 100 mg) was afforded by heating the solvent-exchanged bulk at 473 K under vacuum overnight. Before the gas/vapor measurement, the samples were evacuated again by using the "degas" function of the surface area analyzer for 10 h at 473 K.

## **Results and discussion**

Each asymmetric unit of complex 1 includes one crystallographically independent Cd(n) atom, one  $L^{2-}$  anion and one coordinated DMF molecule. As displayed in Fig. 1a, Cd(n)exhibits distorted pentagonal bipyramidal character, the equatorial positions being occupied by two chelating carboxylate groups and one  $L^{2-}$  nitrogen atom. The axial positions are coordinated by a monodentate carboxylate group and a terminal DMF. The Cd–O<sub>DMF</sub> bond distance is 2.369 Å and somewhat shorter than the average Cd–O<sub>carboxylate</sub> bond length (2.415 Å) in 1, thereby implying stronger interaction between DMF molecules and the central Cd(n) ions. Obviously, the unsaturated



Fig. 1 (a) The coordination environment of Cd1 atom with hydrogen atoms for clarity of 1 with ellipsoids drawn at the 30% probability level. (b) 3D structure of 1 with microporous cavity. (c) Schematic representation of the (4,5)-connected 2-nodal 3D network of 1 with  $(3.6^5)(3^2.4.6^7)$  topology: purple, L<sup>2-</sup> ligand; black, Cd1.

metal binding sites are accessible upon removal of coordinated solvent molecules.

In 1, each  $L^{2-}$  ligand links four Cd(II) atoms via two carboxylate groups respectively adopting  $\mu^1 - \eta^1: \eta^1$  and  $\mu^2 - \eta^1: \eta^2$  coordination modes, as well as one pyridyl donor, while each Cd(II)connects four  $L^{2-}$  anions (Fig. S1<sup>†</sup>), giving rise to a non-interpenetrated three-dimensional (3D) porous structure. Viewed along the *a* axis in **1**, there exist micropore windows of approximately  $6.0 \times 4.0$  Å<sup>2</sup>, taking into account van der Waals distances (Fig. 1b). The solvent accessible volume per unit cell for 1 is calculated to be *ca.* 24.0% (472  $Å^3$ ) using *PLATON* program,<sup>9</sup> where the ligated DMF molecules were excluded from the framework. From a topological point of view,<sup>10</sup> for the structure of 1, each  $L^{2-}$  ligand connects four Cd(II) atoms to serve as a 4-connected node, whereas each Cd(II) center in turn links four  $L^{2-}$  and another Cd(II) atom to act as a 5-connected node (Fig. S1<sup>†</sup>). Therefore, the overall structure of 1 can be simplified as quite a rare binodal (4,5)-connected tcj/hc net with the Schläfli symbol  $(3.6^5)(3^2.4.6^7)$  (Fig. 1c). The topology of the network is identified by the transformation symbol<sup>11</sup> tcj/hc;  $P6_3/mmc-P2_1/c$  (a – b, c, -2a; 1/2, 0, 0); bond sets: 5,6,7,9,14:tcj in the TOPOS binodal database. This symbol suggests that the net is derived from the binodal net tcj/hc by decreasing its space-group symmetry from  $P6_3/mmc$  to  $P2_1/c$ with transformation of the unit cell by (a - b, c, -2a; 1/2, 0, 0)vector.

Although the crystal data of complex **1** has also been reported by other groups,<sup>12</sup> the unsaturated metal binding sites and micropore windows of the compound responsible for the potential selective adsorption were not detected and mentioned completely in the literature.

It is interesting to note that 5-amino-benzene-1,2,3-tricarboxylic acid may have a template effect in the preparation of 1, although it is not incorporated into the final network structure. In the absence of 5-amino-benzene-1,2,3-tricarboxylic acid, only undetermined polycrystalline samples were attained.

The thermal stability and bulk identity of **1** were verified by PXRD and TGA. As revealed in Fig. S2,† the TGA curve of **1** at 298–443 K shows a 17.45% weight loss, which corresponds well to the release of one coordinated DMF molecule (calcd 17.13%) per formula unit. The absence of a plateau after 673 K suggests that the organic ligands start to decompose. Additionally, activated sample **1** exhibits a similar TGA curve as that of the as-synthesized compound (Fig. S2†), indicative of the good thermal stability of the architecture after evacuation of coordinated DMF molecules.

In situ temperature-dependent PXRD studies were recorded for the as-synthesized sample of **1** under a  $N_2$  atmosphere from room temperature to 673 K (Fig. 2). The peak positions of the as-synthesized sample at ambient temperature agree well with the simulated PXRD profiles, indicating the phase purity of the products (Fig. S3†). Notably, there is no significant change of the peak positions except only a slight broadening of some diffraction peaks when the sample is heated up to 673 K, further suggesting that the framework is robust upon removal of coordinating DMF molecules. Generally, the



Fig. 2 In situ temperature-dependent PXRD profiles for complex 1. Simulated spectrum was calculated from the single crystal data.



Fig. 3  $N_2$  (77 K) and CO<sub>2</sub> (195 K) sorption isotherms for desolvated 1, where filled and open shapes represent adsorption and desorption, respectively.

decomposition of MOFs typically occurs at moderate temperature (423–573 K). Currently, only limited MOFs have been reported to be stable beyond 673 K.<sup>13</sup>

The similarity of simulated PXRD forms of as-synthesized, methanol-exchanged, and activated 1 means that the activated sample maintains the same structure as that of 1. In addition, complex 1 is air-stable even after several months (Fig. S4†). This excellent stability is primarily assigned to the strongly coordinated nitrogen atoms from  $L^{2-}$  rather than purely coordinated oxygen atoms of carboxylate, which is believed to be fragile with respect to water molecules.<sup>14</sup> Further, the chemical stability of 1 is attested by suspending crystal samples of 1 in boiling toluene, ethanol, DMF and water for 24 h. The resembling PXRD patterns (Fig. S5†) confirm that the solid samples retain structural integrity after the treatments.

The porosity as well as highly thermal and chemical stability makes complex **1** a very promising potential gas storage material. The desolvated **1** only exhibits external surface adsorption of N<sub>2</sub> at 77 K. In contrast, CO<sub>2</sub> adsorption of activated **1** measured at 195 K and 1 bar shows a fully reversible type-I isotherm with an adsorption amount of 76.7 cm<sup>3</sup> g<sup>-1</sup>, thus indicating that **1** possesses permanent porosity (Fig. 3).<sup>15</sup> Fitting the CO<sub>2</sub> adsorption isotherm gives an apparent BET (Brunauer–Emmett–Teller) surface area of 231.31 m<sup>2</sup> g<sup>-1</sup>. More importantly, the gas sorption and surface area of complex **1** after boiling it in different solvents were examined (Fig. S6†).





**Fig. 4** (a) Sorption isotherms for  $CO_2$ ,  $CH_4$ , and  $N_2$  at 273 and 298 K of desolvated **1** (adsorption and desorption branches are shown with filled and empty shapes, respectively). (b) The isosteric heats of  $CO_2$  and  $CH_4$  adsorption ( $Q_{st}$ ) for desolvated **1**.

Obviously, the  $CO_2$  adsorption isotherms at 195 K/1 bar before and after treatment are almost the same, and the estimated apparent BET surface area is 224.4 m<sup>2</sup> g<sup>-1</sup> (after treatment), very close to that of as-made samples, which again strongly corroborates the high stability of **1**.

Type-I CO<sub>2</sub> isotherms of the desolvated 1 are also probed at 273 and 298 K (1 bar), both of which are completely reversible and exhibit a steep rise at the low-pressure region. Compound 1 shows a maximum CO<sub>2</sub> uptake of 46.9 cm<sup>3</sup> g<sup>-1</sup> (2.09 mmol  $g^{-1}$ , 9.21%) at 273 K and 32.5 cm<sup>3</sup>  $g^{-1}$  (1.45 mmol  $g^{-1}$ , 6.38%) at 298 K, respectively. This value is moderately high, comparable to that of earlier reported MOFs.<sup>16,17</sup> Comparatively, the  $N_2$  uptake is only 3.8  $\mbox{cm}^3\mbox{ g}^{-1}$  (0.17 mmol  $\mbox{g}^{-1},$  0.48%) and 1.6 cm<sup>3</sup> g<sup>-1</sup> (0.071 mmol g<sup>-1</sup>, 0.2%) at 273 and 298 K (1 bar), respectively. Furthermore, the low-pressure CH<sub>4</sub> absorptions on evacuated 1 are also examined. As seen from the isotherm data (Fig. 4a), the desolvated 1 has a maximum CH<sub>4</sub> uptake of 19.7 cm<sup>3</sup> g<sup>-1</sup> (0.879 mmol g<sup>-1</sup>, 1.41%) and 10.1 cm<sup>3</sup> g<sup>-1</sup>  $(0.879 \text{ mmol g}^{-1}, 0.72\%)$  at 273 and 298 K (1 bar). Clearly, CH<sub>4</sub> sorption isotherms under ambient conditions show higher uptakes than that for  $N_2$ , but much less compared to  $CO_2$ .

To better understand these observations, the adsorption enthalpies ( $Q_{st}$ ) were calculated by a virial method.<sup>18</sup> Notably, compound 1 exhibits a strong binding affinity for CO<sub>2</sub> (44.5 kJ mol<sup>-1</sup>) at zero coverage (Fig. 4b), placing it at the third highest record of MOFs with accessible metal sites so far, despite a surface area of only 202 m<sup>2</sup> g<sup>-1</sup>. The value is just lower than

Table 1 CO<sub>2</sub> enthalpy of adsorption for selected MOFs and 1

MOF	$Q_{\rm st}$ (CO <sub>2</sub> ) (kJ mol <sup>-1</sup> )	Reference
1	44.5	This work
MIL-100(Cr)	62	19
MIL-101(Cr)	44	19
Mg-MOF-74	47	20
Ni-MOF-74	42	21
HKUST-1	35	22
CuBTTri	21	14 <i>a</i>

that of MIL-100(Cr),<sup>19</sup> quite close to those found for representative compounds bearing open metal sites, such as MIL-101-(Cr), Mg-MOF-74 and Ni-MOF-74,<sup>19–22</sup> but considerably higher than those determined for well-studied compounds featuring open metal sites, such as HKUST-1 and CuBTTri (Table 1). The  $Q_{\rm st}$  decreased to ~33.7 kJ mol<sup>-1</sup> at the maximum measured loading. Here, a relatively high initial adsorption enthalpy of CH<sub>4</sub> for **1** of 29.03 kJ mol<sup>-1</sup> has been achieved (Fig. 4b), comparable to that of SUN-50' (26.8 kJ mol<sup>-1</sup>),<sup>23</sup> which is among the best values reported thus far for MOF materials.<sup>24</sup> It should be pointed out that the high enthalpy of CO<sub>2</sub> and CH<sub>4</sub> adsorption of **1** stems principally from the presence of exposed metal Cd( $\pi$ ) sites on the pore surface, which is easily polarized due to the relatively large ionic radius and therefore could interact strongly with the absorbed gas molecules.

The uptake capacities at approximate pressures of 0.15 bar for CO2 and 0.75 bar for N2 have been used to effectively perform the selectivity calculation for CO2 over N2, which is more favorable compared to the value based on the adsorbed amounts of both CO<sub>2</sub> and N<sub>2</sub> at 1 bar. The latter substantially overestimates the fraction of CO<sub>2</sub> in post-combustion flue gas and the entire pressure of the binary mixture system.<sup>1d</sup> At 298 K, the uptake amount of CO<sub>2</sub> is 13.19 cm<sup>3</sup> g<sup>-1</sup> (2.59 wt%) at 0.15 bar, which outperforms those of well-known MOFs with open metal sites under similar conditions, such as PCN-68 (0.8 wt%) and SNU-21S (2.25 wt%).<sup>25</sup> In contrast, its N<sub>2</sub> adsorption is 1.6 cm<sup>3</sup> g<sup>-1</sup> (0.2 wt%) at 298 K and 0.75 bar. Therefore, the selectivity of CO<sub>2</sub>/N<sub>2</sub> is 54 at 298 K, which is evaluated from the pure-component isotherms according to eqn (S1) (ESI<sup>†</sup>). As far as we know, such a high selectivity of CO<sub>2</sub>/N<sub>2</sub> has only been reported for several most promising MOFs,<sup>26</sup> apparently illustrating that **1** may be a feasible candidate for the post-combustion capture of CO<sub>2</sub>. Also, the selectivities were calculated using Henry's law constants<sup>27</sup> from the adsorption isotherms in the linear low pressure regime (<0.1 bar) and the Ideal Adsorbed Solution Theory (IAST)<sup>28</sup> for the CO<sub>2</sub>/N<sub>2</sub> mixture in the ratio of 0.15/0.85 and the equimolar CO<sub>2</sub>/CH<sub>4</sub> mixture. Therefore, the ratios for the initial slopes of CO2, N2 and CH4 adsorption isotherms were also used to estimate the adsorption selectivity for CO2 over N2 and CH4 (Fig. S8a<sup>†</sup>).<sup>29</sup> From these data, the calculated  $CO_2/N_2$  and  $CO_2/N_2$ CH<sub>4</sub> Henry's selectivity is 45:1 and 15:1 at 298 K, respectively, which are close to the superior values of MOFs with significant sorption affinity for CO<sub>2</sub> over N<sub>2</sub> and CH<sub>4</sub>, such as ZIF-78<sup>29</sup> (CO<sub>2</sub>/N<sub>2</sub>, 50.1; CO<sub>2</sub>/CH<sub>4</sub>, 10.6), Mg-MOF-74<sup>30</sup> (CO<sub>2</sub>/N<sub>2</sub>, 49),

en-Cu-BTTri<sup>31</sup> (CO<sub>2</sub>/N<sub>2</sub>, 44) and NJU-Bai8<sup>32</sup> (CO<sub>2</sub>/N<sub>2</sub>, 58.3; CO<sub>2</sub>/ CH<sub>4</sub>, 15.9). However, the CO<sub>2</sub>/N<sub>2</sub> selectivity is apparently lower than that of bio-MOF-11, which features the highest selectivity value (75:1) under the same conditions.<sup>33</sup> Additionally, as illustrated in Fig. S8b,† the IAST selectivity of CO<sub>2</sub> relative to N<sub>2</sub> is very sensitive to loading and demonstrates two steps in the change of selectivity: a sharp decrease of CO<sub>2</sub> selectivity at the lower pressure region, and a slow increase at higher pressures (77.3–116.3). The predicted IAST value of CO<sub>2</sub> over CH<sub>4</sub> reaches 10.9–34.4 in the region of 0–1 bar at 298 K.

The significant CO<sub>2</sub> sorption selectivity over CH<sub>4</sub> and N<sub>2</sub> under ambient conditions 1 can primarily be related to the open metal cation sites, which function as charge-dense binding sites and interact more strongly with CO<sub>2</sub> because of its greater quadrupole moment (CO<sub>2</sub>,  $13.4 \times 10^{-40}$  C m<sup>2</sup>; N<sub>2</sub>,  $4.7 \times 10^{-40}$  C m<sup>2</sup>) and polarizability (CO<sub>2</sub>, 29.1 × 10<sup>-25</sup> cm<sup>-3</sup>;  $CH_4$ , 25.9 × 10<sup>-25</sup> cm<sup>-3</sup>; N<sub>2</sub>, 17.4 × 10<sup>-25</sup> cm<sup>-3</sup>) compared with CH4 and N2. In addition, the kinetic sieving effect may be responsible for the high selectivity, where the small windows  $(6.0 \times 4.0 \text{ Å}^2)$  limit the diffusion of larger N<sub>2</sub> (3.64 Å) and CH<sub>4</sub> (3.8 Å) molecules into pores, consequently resulting in relatively lower adsorption, whereas smaller  $CO_2$  molecules (3.3 Å) are allowed to enter into the pore under the given conditions. Taking into consideration that CH4 and N2 molecules are close in size, the distinct uptakes of CH4 and N2 could not be simply ascribed to the size-sieving effect. In fact, the different polarizability of CH<sub>4</sub> and N<sub>2</sub> could be the reason why CH<sub>4</sub> could interact with the polar void more significantly.

Low-pressure H<sub>2</sub> sorption isotherms were recorded at 77 and 87 K as well to evaluate its H<sub>2</sub> adsorption performance, which were also both sharp in the low-pressure regime and completely reversible, as shown in Fig. 5. A moderate  $H_2$ -uptake of 0.73 and 0.66 wt% (81.6 and 73.5 cm<sup>3</sup> g<sup>-1</sup>) was achieved at 77 and 87 K (1 bar) for 1, respectively. At zero loading, Qst of H2 adsorption was calculated to be ~8.25 kJ mol<sup>-1</sup>, which is significantly greater than those of "benchmark MOFs" with both larger surface area and exposed metal cation sites (Table 2).<sup>23,34-41</sup> In addition, the value surpasses the average value (ca. 7.8 kJ mol<sup>-1</sup>) of isosteric heats of H<sub>2</sub> adsorption for MOFs with vacant metal sites reported hitherto. The  $H_2$  adsorption enthalpy of complex 1 is also higher than the typical van der Waals-type interactions (4-6 kJ mol<sup>-1</sup>).<sup>42</sup> The  $Q_{st}$  decreased slowly with increasing  $H_2$  loading as expected and reached ~6.88 kJ mol<sup>-1</sup> at the maximum coverage. Obviously, this high adsorption enthalpy unveiled a significant interaction between H2 molecules and the framework, which is possibly associated with the presence of accessible open metal sites and narrow pores (6.0 Å) since an optimal pore size of just slightly over twice the kinetic diameter of the  $H_2$  molecules (2.9 Å) strengthens the interactions between hydrogen molecules and pore walls.43 In our case, the preferential adsorption of H2 over N2 might be due to the size-exclusion effect.

The systematic sorption studies clearly reveal that the desolvated 1 exhibits excellent selective adsorption of  $CO_2$  over  $N_2$  and  $CH_4$  under ambient conditions. In addition, the



Fig. 5 (a) Sorption isotherms for  $H_2$  at 77 and 87 K of desolvated 1, where filled and open shapes represent adsorption and desorption, respectively. (b) Isosteric heats of  $H_2$  adsorption ( $Q_{st}$ ) for 1.

 Table 2
 H<sub>2</sub> enthalpy of adsorption for selected MOFs and 1

MOF	$Q_{\rm st}$ (H <sub>2</sub> ) (kJ mol <sup>-1</sup> )	Reference
1	8.25	This work
NOTT series	5.68-6.70	34
SNU-21S	6.65	35
SNU-50'	7.1	23
UMCM-150	6.3	36
MIL-100	6.3	37
MIL-102	6.0	38
PCN-6'	6.0	39
PCN-46	6.36	40
soc-MOF	6.5	41

framework displays preferential adsorption of  $H_2$  over  $N_2$  at lower temperature. Apparently, **1** may be applied in capturing  $CO_2$  from flue gases, natural gas purification, and hydrogen enrichment of the  $H_2/N_2$  exhaust in ammonia synthesis.

In order to further evaluate the porosity and adsorption capacity of **1**, we have also carried out vapor adsorption measurements comparing water, methanol, ethanol, and i-propanol at 298 K (Fig. 6). For **1**, the isotherms of water, methanol and ethanol show typical type-I adsorption. In addition, in the low pressure region, the adsorptions of methanol and ethanol reached saturation quickly, thereby demonstrating strong host–guest interactions. The adsorption isotherms of water and light alcohols exhibit obvious hysteresis loops, indicating that desorption of water and alcohol molecules from the micropores is difficult. This is presumably related to the hydroxyl groups of water and alcohol molecules binding at the open Cd( $\pi$ ) sites and forming H-bonds with the L<sup>2–</sup> ligand.



Fig. 6 Water and alcohol vapor adsorption-desorption isotherms of the desolvated 1: water, methanol, ethanol and i-propanol at 298 K, where filled and open shapes represent adsorption and desorption, respectively.



Fig. 7 The solid-state fluorescent spectra of 1 and free ligand L at room temperature. The inset displays visible photoluminescence manifested by 1 under UV irradiation.

The adsorption isotherms also suggest that the saturated uptake amount decreases with increasing kinetic diameter of water and alcohol molecules (water: 2.64–2.9 Å; methanol: 3.626–4.0 Å; ethanol: 4.3–4.53 Å; i-propanol: 4.7 Å). The maximum uptake of water into the pores was approximately 188 cm<sup>3</sup> g<sup>-1</sup>, 74 cm<sup>3</sup> g<sup>-1</sup> for methanol, 38 cm<sup>3</sup> g<sup>-1</sup> for ethanol, and 10 cm<sup>3</sup> g<sup>-1</sup> for i-propanol, which indicates the possibility of selective separation of alcohols from water.

The solid state photoluminescent properties of the as-synthesized 1 were explored at room temperature (Fig. 7). Upon excitation by a UV lamp at 360 nm, 1 shows intense green-blue luminescence (observed by naked eyes) with a maximum at 500 nm, whereas the free organic ligand exhibits a weaker emission at 452 nm. Indeed, owing to the formation of the network structure, an apparent fluorescent enhancement along with a red-shift for 1 compared with that of organic linkers has been observed. Obviously, the overall 3D architecture has endowed the rigidity of the aromatic backbones and maximized the intramolecular/intermolecular interactions among the organic moieties for energy transfer, and hence effectively reduced the intraligand HOMO-LUMO energy gap. Moreover, the emission decay lifetimes of compound 1 were monitored and the curves have been best fitted by biexponentials in the solid.44 The emission decay lifetime of compound **1** is as follows:  $\tau_1$  = 4.961 ns (25.35%) and  $\tau_2$  = 1.450 ns (8.11%) (Fig. S9<sup>†</sup>).

## Conclusions

We have synthesized and structurally characterized a robust multifunctional 3D microporous framework [Cd(L)(DMF)] (1) with high thermal and chemical stability, and carried out a systematic study to investigate and understand the effect of open Cd(II) metal sites and small-sized pores on the selective small adsorption of the compound. The activated 1 showed high-efficiency for the selective capture of small molecules of CO<sub>2</sub> over N<sub>2</sub> and CH<sub>4</sub> under ambient conditions, which ranks it among MOFs with the highest reported values of selectivity. In addition, the desolvated 1 exhibits good separation ratios of H<sub>2</sub> over N<sub>2</sub> at lower temperature, as well as alcohols from water. In particular, the desolvated 1 demonstrates significantly higher adsorption enthalpy for CO2 and CH4 gas molecules, which are in the range of the highest  $Q_{st}$  value reported to date. More interesting, complex 1 displays intense greenblue photoluminescence in the solid state under UV irradiation at room temperature, which mainly originates from the collaborative interaction between the  $d^{10}$  metal ion of Cd(II) and the rigid organic ligand. The permanent porosity and collaborative luminescent properties of complex 1 are particularly useful to exploit potential luminescent detecting materials.

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## Notes and references

- 1 (a) S. D. Burd, S. Q. Ma, J. A. Perman, B. J. Sikora, R. Q. Snurr, P. K. Thallapally, J. Tian, L. Wojtas and M. J. Zaworotko, J. Am. Chem. Soc., 2012, 134, 3663-3666; (b) P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Q. Ma, B. Space, L. Wojtas, M. Eddaoudi and M. J. Zaworotko, Nature, 2013, 495, 80-84; (c) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. H. Bae and J. R. Long, Chem. Rev., 2012, 112, 724-781; (d) J. R. Li, J. Sculley and H. C. Zhou, Chem. Rev., 2012, 112, 869-932; S. H. Yang, X. Lin, W. Lewis, M. Suyetin, (*e*) E. Bichoutskaia, J. E. Parker, C. C. Tang, D. R. Allan, P. J. Rizkallah, P. Hubberstey, N. R. Champness, K. M. Thomas, A. J. Blake and M. Schröder, Nat. Mater., 2012, 11, 710-716; (f) H. B. T. Jeazet, C. Staudt and C. Janiak, Chem. Commun., 2012, 15, 2140-2142.
- 2 (a) S. Pramanik, C. Zheng, X. Zhang, T. J. Emge and J. Li,
   J. Am. Chem. Soc., 2011, 133, 4153-4155; (b) Y. J. Cui,

Y. F. Yue, G. D. Qian and B. L. Chen, *Chem. Rev.*, 2012, 112, 1126–1162; (c) D. Tanaka, S. Horike, S. Kitagawa, M. Ohba, M. Hasegawa, Y. Ozawac and K. Toriumi, *Chem. Commun.*, 2007, 3142–3144; (d) J. H. Cui, Z. Z. Lu, Y. Z. Li, Z. J. Guo and H. G. Zheng, *Chem. Commun.*, 2012, 48, 7967–7969; (e) A. L. Lan, K. H. Li, H. H. Wu, D. H. Olson, T. J. Emge, W. Ki, M. C. Hong and J. Li, *Angew. Chem., Int. Ed.*, 2009, 48, 2334–2338.

- 3 (a) H. L. Jiang, Y. Tatsu, Z. H. Lu and Q. Xu, J. Am. Chem. 2010, 132, 5586-5587; (b) Y. Takashima, Soc., V. M. Martínez, S. Furukawa, M. Kondo, S. Shimomura, H. Uehara, M. Nakahama, K. Sugimoto and S. Kitagawa, Nat. Commun., 2011, 2, 168; (c) B. L. Chen, Y. Yang, F. Zapata, G. Lin, G. D. Qian and E. B. Lobkovsky, Adv. Mater., 2007, 19, 1693-1696; (d) B. L. Chen, L. B. Wang, Y. Q. Xiao, F. R. Fronczek, M. Xue, Y. J. Cui and G. D. Qian, Chem., Int. Ed., 2009, 48, 500-503; Angew. (e) B. V. Harbuzaru, A. Corma, F. Rey, P. Atienzar, J. L. Jordá, H. García, D. Ananias, L. D. Carlos and J. Rocha, Angew. Chem., Int. Ed., 2008, 47, 1080-1083.
- 4 (a) M. P. Suh, H. J. Park, T. K. Prasad and D. W. Lim, *Chem. Rev.*, 2012, 112, 782–835; (b) Z. J. Zhang, Y. G. Zhao, Q. H. Gong, Z. Li and J. Li, *Chem. Commun.*, 2013, 49, 653–661; (c) T. A. Makal, J. R. Li, W. G. Lu and H. C. Zhou, *Chem. Soc. Rev.*, 2012, 41, 7761–7779; (d) J. G. Duan, M. Higuchi, S. Horike, M. L. Foo, K. P. Rao, Y. Inubushi, T. Fukushima and S. Kitagawa, *Adv. Funct. Mater.*, 2013, 23, 3525–3530.
- 5 (a) H. H. Li, W. Shi, K. N. Zhao, Z. Niu, X. T. Chen and P. Cheng, *Chem.-Eur. J.*, 2012, **18**, 5715-5723; (b) X. Tan, J. X. Zhan, J. Y. Zhang, L. Jiang, M. Pan and C. Y. Su, *Cryst-EngComm*, 2012, **14**, 63-66; (c) J. H. Jia, H. S. Athwal, A. J. Blake, N. R. Champness, P. Hubberstey and M. Schröder, *Dalton Trans.*, 2011, **40**, 12342-12349; (d) S. J. Liu, L. Xue, T. L. Hu and X. H. Bu, *Dalton Trans.*, 2012, **41**, 6813-6819; (e) S. L. Xiang, J. Huang, L. Li, J. Y. Zhang, L. Jiang, X. J. Kuang and C. Y. Su, *Inorg. Chem.*, 2011, **50**, 1743-1748.
- 6 SAINT, version 6.2, Bruker AXS, Inc., Madison, WI, 2001.
- 7 G. M. Sheldrick, *SADABS*, University of Göttingen, Göttingen, Germany, 1997.
- 8 G. M. Sheldrick, *SHELXTL, version 6.10*, Bruker Analytical X-ray Systems, Madison, WI, 2001.
- 9 A. L. Spek, J. Appl. Crystallogr., 2003, 36, 7-13.
- 10 A. T. Balaban, From Chemical Topology to Three-Dimensional Geometry, Plenum Press, New York, 1997.
- 11 (a) V. A. Blatov, TOPOS, A Multipurpose Crystallochemical Analysis with the Program Package, Russia, 2004;
  (b) V. A. Blatov and D. M. Proserpio, Acta Crystallogr., Sect. A: Found. Crystallogr., 2009, 63, 329–343.
- 12 (a) C. Hou, Y. Zhao, T.-a. Okmura, P. Wang and W. Y. Sun, J. Coord. Chem., 2012, 65, 4409–4418; (b) F. Wang, X. M. Jing, B. Zheng, G. H. Li, G. Zeng, Q. S. Huo and Y. L. Liu, Cryst. Growth Des., 2013, 13, 3522–3527.
- 13 (a) M. Gustafsson, A. Bartoszewicz, B. Martín-Matute, J. L. Sun, J. Grins, T. Zhao, Z. Y. Li, G. S. Zhu and X. D. Zou,

*Chem. Mater.*, 2010, 22, 3316–3322; (*b*) S. Q. Ma, X. S. Wang, D. Q. Yuan and H. C. Zhou, *Angew. Chem., Int. Ed.*, 2008, 47, 4130–4133; (*c*) V. Colombo, S. Galli, H. J. Choi, G. D. Han, A. Maspero, G. Palmisano, N. Masciocchi and J. R. Long, *Chem. Sci.*, 2011, 2, 1311–1319.

- 14 (a) A. Demessence, D. M. D'Alessandro, M. L. Foo and J. R. Long, J. Am. Chem. Soc., 2009, 131, 8784–8786;
  (b) H. J. Choi, M. Dinca, A. Dailly and J. R. Long, Energy Environ. Sci., 2010, 3, 117–123; (c) K. A. Cychosz and A. J. Matzger, Langmuir, 2010, 26, 17198–17102.
- 15 (a) M. S. Chen, M. Chen, S. Takamizawa, T.-a. Okamura, J. Fan and W. Y. Sun, *Chem. Commun.*, 2011, 47, 3787–3789;
  (b) M. S. Chen, M. Chen, T.-a. Okamura, W. Y. Sun and N. Ueyama, *Microporous Mesoporous Mater.*, 2011, 139, 25–30.
- 16 (a) R. R. Yun, J. G. Duan, J. F. Bai and Y. Z. Li, Cryst. Growth Des., 2013, 13, 24–26; (b) L. Hou, L. N. Jia, W. J. Shi, Y. Y. Wang, B. Liu and Q. Z. Shi, Dalton Trans., 2013, 42, 3653–3659.
- 17 (a) C. Hou, Q. Liu, T.-a. Okamura, P. Wang and W. Y. Sun, *CrystEngComm*, 2012, 14, 8569–8576; (b) Y. P. He, Y. X. Tan and J. Zhang, *Cryst. Growth Des.*, 2013, 13, 6–9.
- 18 J. L. C. Rowsell and O. M. Yaghi, J. Am. Chem. Soc., 2006, 128, 1304–1315.
- 19 P. L. Llewellyn, S. Bourrelly, C. Serre, A. Vimont, M. Daturi, L. Hamon, G. D. Weireld, J.-S. Chang, D.-Y. Hong, Y. K. Hwang, S. H. Jhung and G. Férey, *Langmuir*, 2008, 24, 7245–7250.
- 20 S. R. Caskey, A. G. Wong-Foy and A. J. Matzger, J. Am. Chem. Soc., 2008, 130, 10870–10871.
- P. D. C. Dietzel, R. E. Johnsen, H. Fjellvag, S. Bordiga, E. Groppo, S. Chavan and R. Blom, *Chem. Commun.*, 2008, 5125–5127.
- 22 Q. M. Wang, D. Shen, M. Bülow, M. L. Lau, S. Deng, F. R. Fitch, N. O. Lemcoff and J. Semanscin, *Microporous Mesoporous Mater.*, 2002, 55, 217–230.
- 23 T. K. Prasad, D. H. Hong and M. P. Suh, *Chem.-Eur. J.*, 2010, **16**, 14043–14050.
- 24 (a) S. Q. Ma, D. F. Sun, J. M. Simmons, C. D. Collier, D. Q. Yuan and H. C. Zhou, *J. Am. Chem. Soc.*, 2008, 130, 1012–1016; (b) Y. Peng, V. Krungleviciute, I. Eryazici, J. T. Hupp, O. K. Farha and T. Yildirim, *J. Am. Chem. Soc.*, 2013, 135, 11887–11894.
- 25 (a) D. Q. Yuan, D. Zhao, D. F. Sun and H. C. Zhou, Angew. Chem., Int. Ed., 2010, 49, 5357–5361; (b) T. K. Kim and M. P. Suh, Chem. Commun., 2011, 47, 4258–4260.
- 26 (a) J. A. Mason, K. Sumida, Z. R. Herm, R. Krishna and J. R. Long, *Energy Environ. Sci.*, 2011, 4, 3030–3040;
  (b) P. Aprea, D. Caputo, N. Gargiulo, F. Iucolano and F. J. Pepe, *Chem. Eng. Data*, 2010, 55, 3655–3661;
  (c) T. M. McDonald, D. M. D'Alessandro, R. Krishna and J. R. Long, *Chem. Sci.*, 2011, 2, 2022–2028.
- 27 (a) A. L. Myers and J. M. Prausnitz, *AIChE J.*, 1965, 11, 121–127; (b) Y.-S. Bae, O. K. Farha, A. M. Spokoyny, C. A. Mirkin, J. T. Hupp and R. Q. Snurr, *Chem. Commun.*,

2008, 4135–4137; (*c*) Y.-S. Bae, O. K. Farha, J. T. Hupp and R. Q. Snurr, *J. Mater. Chem.*, 2009, **19**, 2131–2134.

- 28 (a) H. A. Patel, S. H. Je, J. Park, D. P. Chen, Y. Jung, C. T. Yavuz and A. Coskun, *Nat. Commun.*, 2013, 4, 1357;
  (b) J. G. Duan, Y. Zhen, J. F. Bai, B. S. Zheng, Y. Z. Li and S. H. Li, *Chem. Commun.*, 2012, 48, 3058–3060.
- 29 R. Banerjee, H. Furukawa, D. Britt, C. Knobler, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2009, **131**, 3875– 3877.
- 30 (a) S. R. Caskey, A. G. Wong-Foy and A. J. Matzger, J. Am. Chem. Soc., 2008, 130, 10870–10871; (b) H. H. Wu, R. S. Reali, D. A. Smith, M. C. Trachtenberg and J. Li, Chem.-Eur. J., 2010, 16, 13951–13954.
- 31 K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724–781.
- 32 L. T. Du, Z. Y. Lu, K. Y. Zheng, J. Y. Wang, X. Zheng, Y. Pan, X. Z. You and J. F. Bai, *J. Am. Chem. Soc.*, 2013, 135, 562– 565.
- 33 J. An, S. J. Geib and N. L. Rosi, J. Am. Chem. Soc., 2010, 132, 38–39.
- 34 X. Lin, I. Telepeni, A. J. Blake, A. Dailly, C. M. Brown, J. M. Simmons, M. Zoppi, G. S. Walker, K. M. Thomas, T. J. Mays, P. Hubberstey, N. R. Champness and M. Schröder, *J. Am. Chem. Soc.*, 2009, **131**, 2159–2171.
- 35 T. K. Kim and M. P. Suh, *Chem. Commun.*, 2011, 47, 4258-4260.
- 36 A. G. Wong-Foy, O. Lebel and A. J. Matzger, J. Am. Chem. Soc., 2007, 129, 15740–15741.

- 37 M. Latroche, S. Suble, C. Serre, C. Mellot-Draznieks, P. L. Llewellyn, J.-H. Lee, J.-S. Chang, S. H. Jhung and G. Férey, *Angew. Chem., Int. Ed.*, 2006, 45, 8227–8231.
- 38 S. Surblé, F. Millange, C. Serre, T. Düren, M. Latroche, S. Bourrelly, P. L. Llewellyn and G. Férey, *J. Am. Chem. Soc.*, 2006, **128**, 14889–14896.
- 39 H.-C. Zhou, S. Q. Ma, D. F. Sun, M. Ambrogio, J. A. Fillinger and S. Parkin, J. Am. Chem. Soc., 2007, 129, 1858–1859.
- 40 D. Zhao, D. Q. Yuan, A. Yakovenko and H.-C. Zhou, *Chem. Commun.*, 2010, 46, 4196–4198.
- 41 Y. Liu, J. F. Eubank, A. J. Cairns, J. Eckert, V. C. Kravtsov, R. Luebke and M. Eddaoudi, *Angew. Chem., Int. Ed.*, 2007, 46, 3278–3283.
- 42 (a) W. Zhou, H. Wu, M. R. Hartman and T. Yildirim, J. Phys. Chem. C, 2007, 111, 16131–16137; (b) A. G. Wong-Foy, O. Lebel and A. J. Matzger, J. Am. Chem. Soc., 2007, 129, 15740–15741.
- 43 (a) J. Luo, H. Xu, Y. Liu, Y. Zhao, L. L. Daemen, C. Brown, T. V. Timofeeva, S. Ma and H.-C. Zhou, *J. Am. Chem. Soc.*, 2008, 130, 9626–9627; (b) S. Barman, H. Furukawa, O. Blacque, K. Venkatesan, O. M. Yaghi and H. Berke, *Chem. Commun.*, 2010, 46, 7981–7983; (c) B. Chen, X. Zhao, A. Putkham, K. Hong, E. B. Lobkovsky, E. J. Hurtado, A. J. Fletcher and K. M. Thomas, *J. Am. Chem. Soc.*, 2008, 130, 6411–6423.
- 44 (a) X. Li, H. L. Sun, X. S. Wu, X. Qiu and M. Du, *Inorg. Chem.*, 2010, 49, 1865–1871; (b) J. S. Hu, L. F. Huang, X. Q. Yao, L. Qin, Y. Z. Li, Z. J. Guo, H. G. Zheng and Z. L. Xue, *Inorg. Chem.*, 2011, 50, 2404–2414.