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## Two microporous metal-organic frameworks constructed from trinuclear cobalt(II) and cadmium(II) cluster subunits

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**Two novel microporous metal-organic frameworks were obtained by combination of a tetratopic linker and linear trinuclear cobalt(II) and cadmium(II) cluster subunits. The complexes exhibit unprecedented topological features and unique properties in magnetism and photoluminescence.**

Metal-organic frameworks (MOFs) have recently emerged as a new type of nanoporous materials with tailorable structures and have been attracting intense research interest due to their broad range of possible applications such as gas storage and separation, molecular magnetism, drug delivery, explosive detection, ion exchange, proton conduction, catalysis and nonlinear optics.<sup>1-8</sup> One of the most important properties of MOFs for the above applications is their high porosity and high specific surface area.<sup>9</sup> The simplest way to obtain MOFs with ultrahigh porosities is to expand the used organic linkers. However, there are two difficulties arising for such MOFs. The first one is that expanded ligands often yield fragile frameworks which tend to collapse upon gas sorption. The second difficulty derives from self-interpenetration which precludes high porosity for these MOFs. To overcome the two difficulties, Yaghi and co-workers developed a most efficient strategy for the construction of highly porous frameworks with the use of secondary building units (SBUs). The SBUs serve as large vertices that can be joined by rigid organic links to produce extended frameworks with high stability and without a tendency to interpenetrate. The best example of SBUs is the famous octahedral  $Zn_4O(CO_2)_6$  building unit from which a series of MOFs with exceptional porosities and gas uptake capacities have been constructed, such as MOF-5, MOF-177, MOF-180 and UMCM-2.<sup>10</sup> Over the last few years, a large number of porous MOFs have been synthesized by using

the SBUs strategy. For example, Zhou et al. reported a mesoporous MOF PCN-53 with stepwise adsorption properties by using the well-known trigonal prism  $[Fe_3O(O_2CR)_6]$  SBU.<sup>11</sup> Bu et al. constructed many microporous MOFs using multiple metal cluster SBUs for gas adsorption.<sup>12</sup> Recently, our group prepared a series of highly porous MOFs derived from different carboxylate ligands and zinc-based SBUs which exhibit excellent gas sorption capacities.<sup>13</sup>

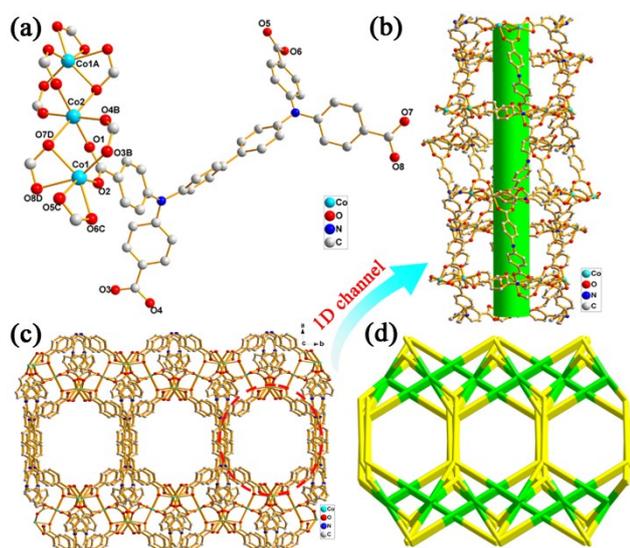
So far, the tetracarboxylate ligands have been successfully used for the construction of porous MOFs.<sup>14</sup> For example, Eddaoudi et al. synthesized a series of highly porous and stable aluminum-based *soc*-MOFs for  $CH_4$ ,  $O_2$  and  $CO_2$  storage by utilizing a tetratopic ligand 3,3',5,5'-tetrakis(4-carboxyphenyl)-p-terphenyl ( $H_4TCPT$ ).<sup>14a</sup> Ma et al. reported an nbo topology MOF platform MOF-505 constructed with a custom-designed azamacrocyclic tetracarboxylate ligand. This MOF demonstrates high catalytic activity for the chemical fixation of  $CO_2$  into cyclic carbonates at room temperature.<sup>14b</sup> Among the various tetracarboxylate ligands,  $H_4TCPBDA$  ( $N,N,N',N'$ -tetrakis(4-carboxyphenyl)-biphenyl-4,4'-diamine) was found to be an ideal molecular block for construction of porous MOFs.<sup>15</sup> In this work, two novel microporous MOFs, namely  $(MeNH_3)_2[Co_3(TCPBDA)_2] \cdot DMF \cdot 16H_2O$  (**1**) and  $(MeNH_3)_2[Cd_3(TCPBDA)_2] \cdot 2DMF \cdot 25H_2O$  (**2**), have been synthesized by  $H_4TCPBDA$  and trinuclear  $[M_3(COO)_8]$  ( $M = Co^{2+}$  and  $Cd^{2+}$ ) SBUs. Their structures and properties in magnetism and photoluminescence are presented.

Orange prism crystals of complex **1** were obtained by a solvothermal reaction between a tetracarboxylate ligand  $H_4TCPBDA$  and  $Co(ClO_4)_2 \cdot 6H_2O$  in  $N,N'$ -dimethylformamide (DMF) with an additional HAc at 100 °C for 2 days (see ESI† for details). The phase purity of above prism product has been confirmed by powder X-ray diffraction (PXRD) (Fig. S8, ESI†). X-Ray crystallography reveals that complex **1** crystallizes in the monoclinic system with space group  $C2/c$ . The asymmetrical unit of complex **1** contains one-and-a-half independent  $Co^{2+}$  ions, one fully deprotonated  $TCPBDA^{4-}$  ligand and one  $MeNH_3^+$  cation as counterion (Fig. 1a). In this structure, we assume that the distorted  $MeNH_3^+$  cations lie inside the accessible void which is the byproduct of *in situ* decomposition of the DMF solvent, thus leading to the charge equilibrium.<sup>16</sup> The central

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<sup>b</sup> University of the Chinese Academy of Sciences, Beijing, 100049, China Electronic Supplementary Information (ESI) available: Synthesis, crystallographic information, supplementary figures, PXRD, TGA and magnetic properties of complexes **1** and **2**. CCDC 1435242 and 1435244. For ESI and crystallographic data in CIF or other electronic format See DOI: 10.1039/x0xx00000x

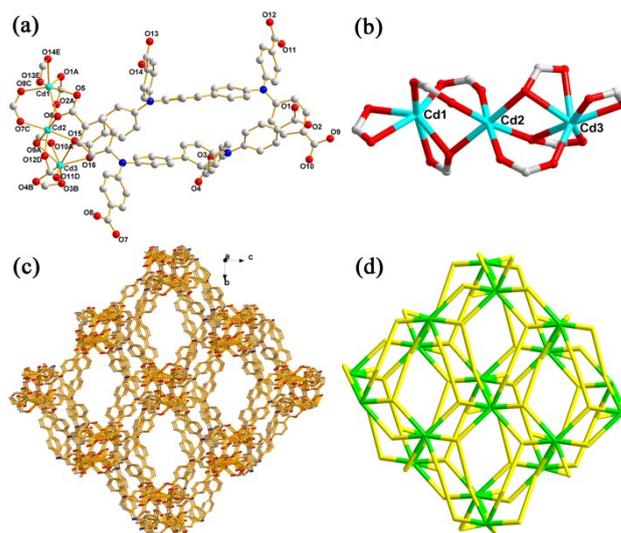
cobalt ion (Co2) lies on an inversion centre in an octahedral coordination sphere made of six oxygen atoms from six TCPBDA<sup>4-</sup> ions. The bond distances of Co2-O are in the range of 2.091(1)-2.287(1) Å. The bond angles of O-Co2-O vary from 87.21(4) to 92.79(4)°, which deviate slightly from an ideal octahedral geometry. The two peripheral cobalt ions [Co1 and Co1A] adopt a highly distorted bipyramidal geometry with a [CoO<sub>5</sub>] environment connected by five oxygen atoms from four TCPBDA<sup>4-</sup> ligands. The Co1-O bond lengths are in the range of 2.074(1)-2.381(1) Å (Table S2, ESI†). Each TCPBDA<sup>4-</sup> ligand coordinates to seven metal ions. Three carboxylate anions of the ligand (O1, O2, O3, O4 and O7, O8) are in the  $\mu_2(\eta_1, \eta_2)$  coordination mode and remaining one (O5, O6) is in the  $\mu_2(\eta_1, \eta_1)$  mode (Fig. S1, ESI†). It is noteworthy that the two central phenyl rings in each ligand are not coplanar with a dihedral angle of 33.56°. Structurally speaking, complex **1** presents a three-dimensional network constructed from the linear trinuclear [Co<sub>3</sub>(COO)<sub>8</sub>] SBUs linked together by the tetracarboxylate ligands with one-dimensional cylindrical channels along the *c*-axis (Fig. 1b and 1c). We will have a better insight into the nature of this intricate architecture by topological analysis. Regarding the structural features of complex **1**, the [Co<sub>3</sub>(COO)<sub>8</sub>] SBUs can be regarded as 8-connected nodes, and the TCPBDA<sup>4-</sup> ligands as two 2-connected nodes. As a result, the over-all structure of complex **1** can be simplified to a 3, 3, 8-c 3-nodal topological network with a point symbol of  $\{4.6^2\}_2\{4^2.6^{12}.8^{11}.10^3\}\{6^3\}_2$  (Fig. 1d). In the literature, as we know, much effort has been paid to the exploration of high nuclear cobalt based coordination polymers and their applications.<sup>17</sup> However, there is still limited research focused on the linear trinuclear cobalt based complexes, which might exhibit unique magnetic properties.<sup>18</sup>



**Fig. 1** Description of complex **1**: (a) The coordination environment of cobalt(II) atoms in complex **1**; symmetry code: A  $1.5 - x, 1.5 - y, 1 - z$ ; B  $1 - x, -0.5 + z$ ; C  $0.5 + x, -0.5 + y, z$ ; D  $0.5 + x, 0.5 + y, z$ . (b) The 1D cylindrical channels viewed along the *c*-axis. (c) The 3D framework of complex **1**. (d) The (3,3,8)-c 3-nodal topology of complex **1**.

Single crystals of complex **2** were produced by a solvothermal reaction with H<sub>4</sub>TCPBDA and CdCl<sub>2</sub>·2.5H<sub>2</sub>O in DMF with an additional HAc at 120 °C for 3 days (see ESI† for

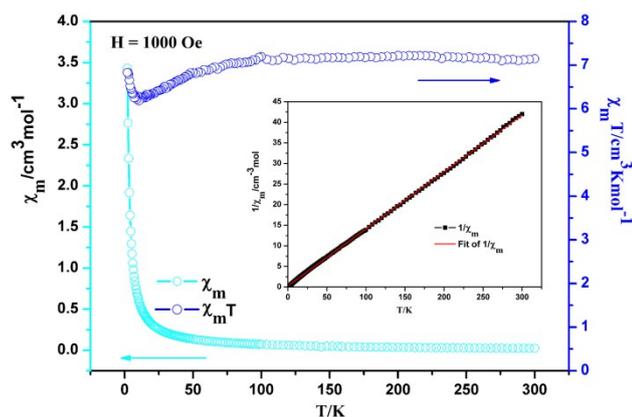
details). The phase purity of the block crystals has been confirmed by powder X-ray diffraction (PXRD) (Fig. S8, ESI†). Complex **2** crystallizes in the monoclinic space group *P2<sub>1</sub>/c*. Its asymmetric unit consists of three Cd<sup>2+</sup> cations, two TCPBDA<sup>4-</sup> ligands and two MeNH<sub>3</sub><sup>+</sup> cations (Fig. 2a). Similarly, complex **2** contains a linear trimetallic unit. However, the three Cd<sup>2+</sup> atoms adopt different coordinated geometries from each other (Fig. 2b). The independent Cd1 center has a distorted octahedral geometry coordinated by six carboxylate oxygen atoms from four fully deprotonated TCPBDA<sup>4-</sup> ligands. The Cd1-O bond distances are in the range of 2.202(5)-2.372(5) Å (Table S3, ESI†). The bond angles of O-Cd1-O vary from 56.39(2) to 113.22(2)°, which deviate substantially from an ideal octahedral geometry. The central cadmium ion (Cd2) adopts an octahedral coordination sphere made of six oxygen atoms from six TCPBDA<sup>4-</sup> ions where the observed Cd2-O bond lengths are in the range of 2.218(5)-2.311(5) Å. Whereas, the Cd3 center is linked by seven oxygen atoms from four TCPBDA<sup>4-</sup> ligands, generating a distorted pentagonal bipyramidal [CdO<sub>7</sub>] coordination geometry. The Cd3-O bonds range from 2.364(7) Å to 2.511(6) Å. Every TCPBDA<sup>4-</sup> ligand links to seven Cd<sup>2+</sup> centers through three pairs of  $\mu_2$ -bidentate COO<sup>-</sup> groups and one  $\mu_2$ -bridging monodentate COO<sup>-</sup> group (Fig. S5, ESI†). The trinuclear [Cd<sub>3</sub>(COO)<sub>8</sub>] SBUs are bridged by the carboxylate groups of TCPBDA<sup>4-</sup> to form a three-dimensional (3D) microporous framework with 1D rhombic channels along the *a*-axis (Fig. 2c). Topologically, if the [Cd<sub>3</sub>(COO)<sub>8</sub>] SBUs are viewed as 8-connected nodes and the TCPBDA<sup>4-</sup> ligands are regarded as two 2-connected nodes, the overall motif of complex **2** will be a 3, 8-c 2-nodal network with a point symbol of  $\{4.6^2\}_4\{4^4.6^6.7^{10}.8^4.9^2.10^2\}$  (Fig. 2d).



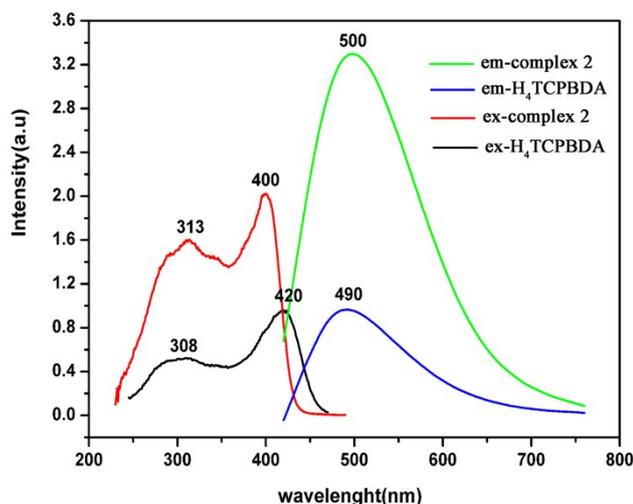
**Fig. 2** Description of complex **2**: (a) The coordination environment of cadmium(II) atoms in complex **2**; symmetry code: A  $x, 0.5 - y, -0.5 + z$ ; B  $1 - x, -0.5 + y, 0.5 - z$ ; C  $x, -0.5 - y, -0.5 + z$ ; D  $x, -1 + y, z$ ; E  $-x, -y, -z$ . (b) The structural motif of the linear trinuclear [Cd<sub>3</sub>(COO)<sub>8</sub>] SBU in complex **2**. (c) The 3D framework of complex **2**. (d) The (3,8)-c 2-nodal topology of complex **2**.

The temperature-dependent magnetic susceptibility was measured on crystalline samples of complex **1** at 1000 Oe in the range of 2-300 K. The  $g_m T$  and  $g_m$  versus T plots of complex **1** are shown in Fig. 3. At room temperature, the  $g_m T$  value is 7.15

$\text{cm}^3 \text{mol}^{-1} \text{K}$  for complex **1**, which is higher than the spin-only value ( $5.625 \text{ cm}^3 \text{mol}^{-1} \text{K}$ ) for three isolated HS  $\text{Co}^{2+}$  metal ions, indicating spin-orbital couplings present. As the temperature decreases to 10.4 K, the  $g_m T$  value slightly decreases to a minimum of  $6.18 \text{ cm}^3 \text{mol}^{-1} \text{K}$ , suggesting an appreciable antiferromagnetic coupling between the neighbouring  $\text{Co}^{2+}$  ions, and then increases to  $6.83 \text{ cm}^3 \text{mol}^{-1} \text{K}$  at 2 K. The magnetic susceptibility between 2–300 K conforms to the Curie-Weiss law, giving the Curie constant  $C = 7.23 \text{ emu mol}^{-1} \text{K}$  and the Weiss temperature  $\theta = -2.16 \text{ K}$  (Fig. 3 and Fig. S11, ESI†). The negative Weiss temperature shows that the neighbouring magnetic  $\text{Co}^{2+}$  ions are coupled with an antiferromagnetic interaction exchanges.<sup>19</sup>



**Fig. 3** The temperature dependence of  $\chi_m$  and  $\chi_m T$  for complex **1**. The inset shows the plot of  $1/\chi_m$  versus  $T$ . The solid line corresponds to the best theoretical fit.



**Fig. 4** Solid-state emission and excitation spectra of the free ligand  $\text{H}_4\text{TCPBDA}$  and complex **2** collected at room temperature.

The photoluminescence of  $d^{10}$  metal complexes has attracted long-standing interest, owing to the extensive utilizations of these observations for molecular recognition, chemosensing, photochemistry, optoelectronic applications, and so on.<sup>20</sup> Hence, in this work, the photoluminescent properties of the free ligand and complex **2** have been investigated in the solid state at room temperature. The emission and excitation spectra are shown in Fig. 4. The free ligand  $\text{H}_4\text{TCPBDA}$  exhibits a cyan emission centered at 490 nm upon excitation at 420 nm or 308 nm, which

may be attributed to the  $\pi^* \rightarrow n$  or  $\pi^* \rightarrow \pi$  transition.<sup>21</sup> In contrast, intense green emission is observed for complex **2** with a maximum at 500 nm upon excitation at 400 nm or 313 nm, which presents a red shift of 10 nm compared to that of the free ligand. Considering the similarities of the excitation and emission spectra of complex **2** and that of the free ligand, the photoluminescence of complex **2** should be attributed to disturbed ligand based emission.<sup>22</sup> It is worth noting that the emission intensity of complex **2** increases remarkably and is approximately 3.5 times higher than that of the free ligand, which may be attributed to the ligation of the ligand to the metal center. The coordination enhances the “rigidity” of the ligand and thus reduces the loss of energy through a radiationless pathway.<sup>23</sup>

## Conclusion

In conclusion, two novel microporous metal-organic frameworks have been synthesized and structurally characterized. In the presented MOFs, the linear trinuclear  $[\text{M}_3(\text{COO})_8]$  ( $\text{M} = \text{Co}^{2+}$  and  $\text{Cd}^{2+}$ ) subunits are linked by the tetracarboxylate ligands to form two porous frameworks with unprecedented topological features. The temperature-dependent magnetic susceptibility of complex **1** exhibits an antiferromagnetic coupling between the neighbouring  $\text{Co}^{2+}$  centers. Complex **2** displays an intense green emission in solid state at room temperature, where the emission intensity is 3.5 times higher than that of the free ligand. It is expected that this work might motivate more extensive research on the multinuclear metal cluster complexes and their unique properties.

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## Notes and references

Crystal data for complex **1** (CCDC 1435242):  $\text{C}_{80}\text{O}_{16}\text{H}_{48}\text{N}_4\text{Co}_3$ ,  $M = 1498.01$ , monoclinic, space group  $C2/c$ ,  $a = 40.267(1)$ ,  $b = 12.903(5)$ ,  $c = 25.995(9)$  Å,  $\beta = 104.20^\circ$ ,  $V = 14108(8)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 0.705 \text{ g/cm}^3$ ,  $F_{000} = 3060$ ,  $\text{CuK}\alpha$  radiation,  $\lambda = 1.54184$  Å,  $T = 100(2)$  K,  $2\theta_{\text{max}} = 70.5^\circ$ , 28579 reflections collected, 14179 unique ( $R_{\text{int}} = 0.034$ ). Final  $\text{Goof} = 1.023$ ,  $R_1 = 0.0393$ ,  $wR_2 = 0.0887$ ,  $R$  indices based on 8471 reflections with  $I > 2\sigma(I)$  (refinement on  $F^2$ ). Crystal data for complex **2** (CCDC 1435244):  $\text{C}_{80}\text{O}_{16}\text{H}_{48}\text{N}_4\text{Cd}_3$ ,  $M = 1658.42$ , monoclinic, space group  $P2_1/c$ ,  $a = 26.936(7)$ ,  $b = 22.123(4)$ ,  $c = 26.046(8)$  Å,  $\beta = 109.74^\circ$ ,  $V = 14609(6)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 0.754 \text{ g/cm}^3$ ,  $F_{000} = 3312$ ,  $\text{CuK}\alpha$  radiation,  $\lambda = 1.54184$  Å,  $T = 100(2)$  K,  $2\theta_{\text{max}} = 73.3^\circ$ , 27696 reflections collected, 14244 unique ( $R_{\text{int}} = 0.051$ ). Final  $\text{Goof} = 1.057$ ,  $R_1 = 0.0826$ ,  $wR_2 = 0.2709$ ,  $R$  indices based on 15755 reflections with  $I > 2\sigma(I)$  (refinement on  $F^2$ ). The diffraction data for complexes **1** and **2** were treated by the “*SQUEEZE*” method as implemented in PLATON to remove diffuse electron density associated with the badly disordered solvent molecules. The final formula of **1** and **2** were determined by combining with thermogravimetric analysis (TGA) and elemental analyses.

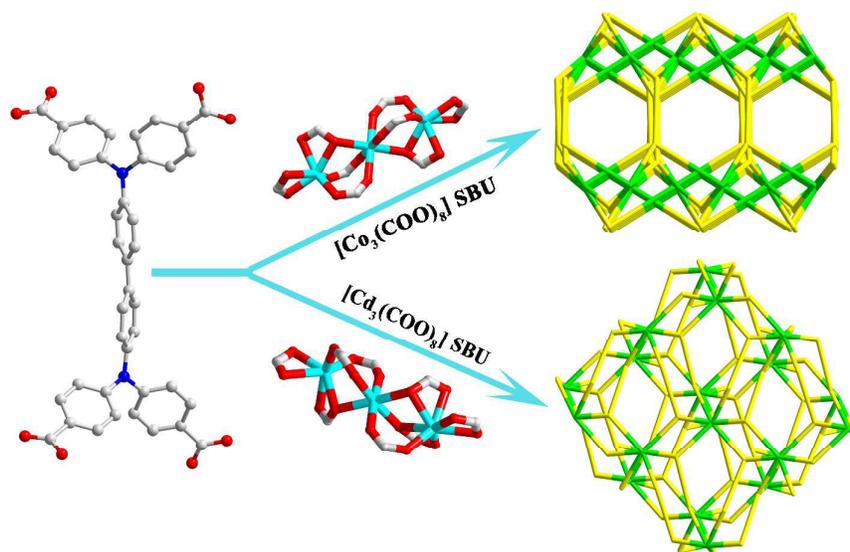
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## Table of Contents Synopsis

### Two microporous metal-organic frameworks constructed from trinuclear cobalt(II) and cadmium(II) cluster subunits

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This work presents two novel microporous metal-organic frameworks which are constructed from a tetracarboxylate ligand and trinuclear cobalt(II) and cadmium(II) cluster subunits.