

# Highly-thermostable metal–organic frameworks (MOFs) of zinc and cadmium 4,4'-(hexafluoroisopropylidene)dipthalates with a unique fluorite topology†

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Two novel zinc and cadmium 4,4'-(hexafluoroisopropylidene)-dipthalate metal–organic frameworks have been synthesized and characterized using single crystal X-ray diffraction analysis, and exhibit a unique fluorite topology and high thermal stabilities.

Although the design and construction of novel metal–organic frameworks (MOFs) have recently attracted considerable attention for potential applications in connection with their promising properties,<sup>1</sup> it is still of primary importance to understand the structural aspects of such materials at a molecular or atomic resolution. Recent reviews on the network topologies and other geometrical characteristics of such crystalline solids illustrate this importance.<sup>2–5</sup> The topological types found in three-dimensional MOFs are commonly defined by the vertices (metal ions and/or ligands) and edges (links between vertices), among which three-, four-, and six-connected topologies are commonly observed.<sup>6</sup> However, examples of five-, seven-, and eight-connected MOFs remain scarce,<sup>7</sup> and are severely hampered by the number of available coordination sites at the metal centers and the sterically demanding nature of the organic ligands.<sup>7d</sup> In other ways, with the development of this topic, another valuable discovery is that the topological paradigms of some MOFs are consistent with those of natural minerals, such as diamond,  $\alpha$ -Po, boracite, CdSO<sub>4</sub>, CaB<sub>6</sub>, feldspar, NbO, perovskite, Pt<sub>3</sub>O<sub>4</sub>, PtS, pyrite, quartz, rutile, sodalite, SrSi<sub>2</sub>, tungsten bronze, CsCl, and so on,<sup>8</sup> and this will undoubtedly extend the applied area for these materials. Up to now, MOFs with higher or mixed connectivities are extremely rare; the only reported MOFs with 12-connected and (4,8)-connected topologies adopt clusters as nodes.<sup>8,9</sup> Considering the limited number of coordination sites at the metal centers, our strategy is to develop multidentate ligands as higher-connected vertices and metal ions as lower ones to construct 3-periodic mixed-connected MOFs. Herein, we present two highly-thermostable three-dimensional (3D) MOFs created from an 8-connected ligand, 4,4'-(hexafluoroisopropylidene)dipthalate (**L**), and 4-connected metal ions of Zn(II) or Cd(II). The resulting (4,8)-connected net presents a unique fluorite topology. Both complexes display high thermal

stability, which should be related to the compact nature of the crystalline lattices as well as the unusual network topology.

The hydrothermal reaction of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O or Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O with H<sub>4</sub>**L** gives, respectively, two kinds of colorless block crystals, [Zn<sub>2</sub>(**L**)] (**1**) and [Cd<sub>2</sub>(**L**)(H<sub>2</sub>O)<sub>2</sub>] (**2**). The bulk purities of the products were independently confirmed from elemental analyses and powder X-ray diffraction (PXRD) measurements. The experimental PXRD patterns perfectly match the simulated ones based on the single-crystal X-ray data (SI-1 and 2, see ESI†).‡

Complexes **1** and **2** are close to being isomorphous and isostructural; the only difference being the presence of a water molecule bonded to the Cd atom in the asymmetric unit of **2**. The two complexes both crystallize in the monoclinic space group *C2/c* and consist of **L** ligands coordinating to metal ions (Zn or Cd) in a 1 : 2 chemometrics ratio. It should be noted that in both structures the **L** ligand lies with its central carbon (C9) on a twofold axis. In **1**, each Zn(II) ion adopts a tetrahedral coordination mode to link four separate **L** ligands *via* uniform monodentate carboxylate groups (see Fig. 1, right), and each ligand possesses an 8-connected geometry to connect the Zn(II) ions (see Fig. 1, left). The Zn–O bonds fall in the normal range of 1.927–1.992 Å (SI-3†). The shortest Zn···Zn separation connected by the same carboxylate group is 3.777(2) Å, while the shortest one connected by the space unit of the **L** ligand is 11.887(2) Å. In **2**, each Cd(II) ion adopts a distorted octahedral coordination mode to link a water and four

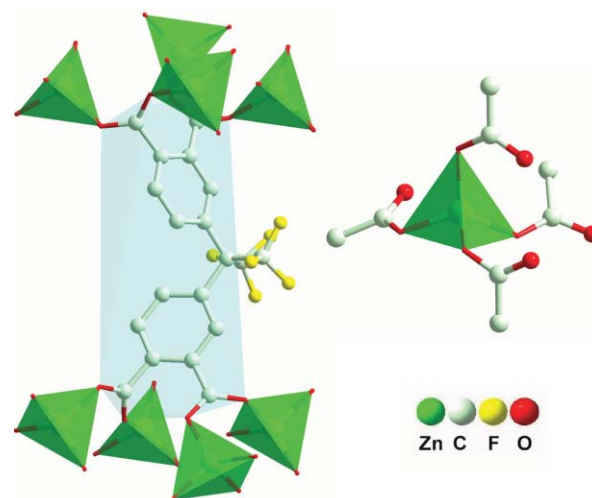


Fig. 1 A local view showing the 8-connected ligand (left) and the 4-connected Zn(II) ion (right) of **1**.

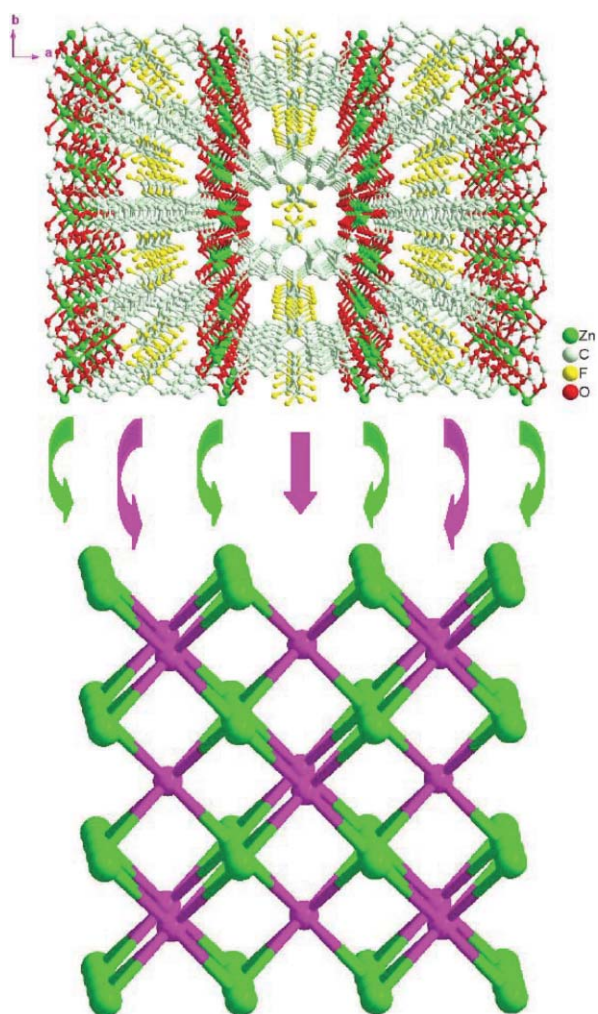
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separate **L** ligands *via* three monodentate and one chelating carboxylate groups, and each ligand has a similar 8-connected geometry to that of **1** (SI-4<sup>†</sup>). It should be noted that the Cd1–O4B bond length to the chelating carboxylate group in **2** (2.558(2) Å) is significantly longer than those of other Cd–O<sub>carboxylate</sub> (2.253–2.294 Å) and Cd–O<sub>water</sub> (2.339 Å) bonds (SI-5<sup>†</sup>). The shortest Cd···Cd separation connected by the same carboxylate group is 4.046(1) Å, while the shortest one connected by the space unit of the **L** ligand is 11.680(2) Å. As a consequence, the metal centers are interconnected by the ligands to generate a 3D coordination framework, as illustrated in Fig. 2 top.

It is interesting to note that each carboxylate oxygen atom of the ligand links only one metal ion and lacks a more complex connectivity. This leads to the formation of an unprecedented 8-connected building block, as confirmed from a CSD (Cambridge Structural Database) search.<sup>10</sup> The reason for such a coordination is unclear, but may be ascribed to the steric effect of the bulky ligand and the dense nature of the framework. To the best of our knowledge, this is the first case of an 8-connected organic ligand with a uniform coordination mode. Furthermore, up to now, there was only an example for a metal–organic replica of fluorite with (4,8)-connected topology in which, however, the 8-connected

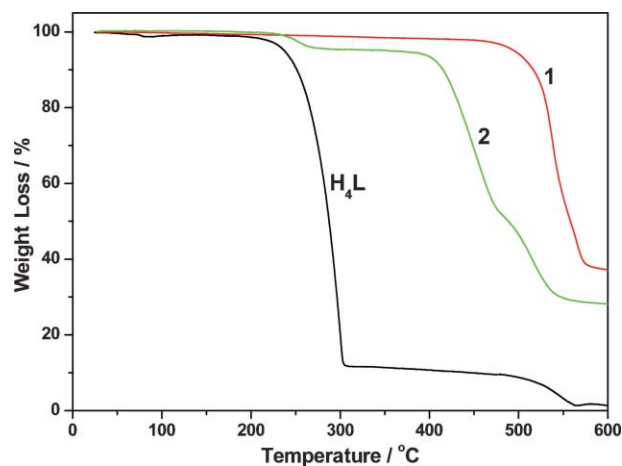


**Fig. 2** (Top) 3D coordination framework of **1** and (bottom) a schematic view of (4,8)-connected CaF<sub>2</sub> topology. Ca: purple; F: green.

vertex is simplified by a cadmium–carboxylate cluster.<sup>8</sup> To our surprise, complexes **1** and **2** are the first cases of metal–organic frameworks with the fluorite topology (see Fig. 2 bottom) in which the corresponding metal centers and ligands directly act as the vertices. Notably, the 8-connected geometry of the ligand is distorted, which results in the lack of the classic cubic geometry. In spite of the long organic linker, complexes **1** and **2** present non-interpenetrating compact structures with no accessible void space.<sup>11</sup>

Thermogravimetric analysis (TGA) experiments were conducted to determine the thermal stability of both complexes, which is an important aspect for metal–organic frameworks.<sup>12</sup> As shown in Fig. 3, for H<sub>4</sub>L, the rapid weight loss of *ca.* 90%, starting at 200 and ending at 300 °C (peaking position: 280 °C), implies the decomposition of the organic ligand. For **1**, the host framework is stable up to 470 °C and the one-step weight loss rapidly happens only from 470 to 580 °C (peaking position: 540 °C). For **2**, the TGA curve shows the weight loss of the coordinated water molecules (calculated: 4.88%; observed: 4.57%) in the temperature range of 230–270 °C (peak: 250 °C). The host framework starts to decompose beyond 400 °C, and ends at 570 °C (peak: 470 °C). It is interesting that the host framework of **2** remains in its crystalline phase after losing the coordinated water molecules, as indicated from the PXRD patterns. It is noteworthy that the PXRD pattern of rehydrated **2**, made by adding water to the dehydrated material, is in agreement with that of the original material (SI-2<sup>†</sup>). So the guest-free Lewis acidic sites are available in the dehydrated framework of **2**.

In general, degradation of the organic components of MOFs typically begins at moderate temperatures (200–350 °C),<sup>13–15</sup> resulting in decomposition of the synthesized materials. In rare instances, a MOF material may be stable above 350 °C,<sup>12,16–18</sup> but the reasons for this are still unspecified. It is widely believed that the flexibility of the organic linkers, as well as the included guest molecules, may be connected with the thermal stability of the metal–organic frameworks.<sup>12</sup> Herein, the zinc and cadmium complexes **1** and **2** are stable up to at least 400 °C. We presume that the strong metal–carboxylate interactions tighten the backbone of the ligand to enhance the resistance to pyrolysis (the free H<sub>4</sub>L ligand starts to degrade upon heating to 200 °C). Furthermore, the compact networks of the host frameworks also



**Fig. 3** TGA curves of H<sub>4</sub>L, **1** and **2**.

play a vital role in determining their thermal stabilities. The difference in thermal stabilities between **1** and **2** may be attributed to the stronger Zn–O interactions compared to the Cd–O ones, as well as the small structural discrepancy in their coordination geometries.

Complexes **1** and **2** also display strong solid-state fluorescent emissions at room temperature. Their emission maxima are at 610 nm with the excitation at 456 nm (SI-6<sup>†</sup>). To further explore the mechanism of the emission bands, the fluorescent property of the ligand was also investigated, which shows a very weak emission peak at 610 nm under the same conditions. Thus, we presume that these emissions originate from the intraligand transitions, and the significant enhancement of their intensities should be ascribed to the metal–carboxylate coordinative interactions.<sup>19</sup>

In conclusion, two unusual metal–organic framework materials have been hydrothermally prepared with high thermal stability. Remarkably, they represent the first fluorite network directly constructed from an 8-connected ligand and 4-connected metal nodes.

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## Notes and references

† Syntheses of **1** and **2**: 4,4'-(hexafluoroisopropylidene)diphthalic acid (H<sub>4</sub>L) (96 mg, 0.20 mmol), Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (124 mg, 0.42 mmol) or Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (130 mg, 0.42 mmol), and LiOH (10 mg, 0.42 mmol) were dissolved in H<sub>2</sub>O (10 mL), and the solution was heated in a screw-capped vial at 140 °C for 6 days. The colorless crystals of **1** and **2** formed were collected, washed with water and ethanol, and dried under a reduced pressure at room temperature (yield: **1**, 66 mg, 54%; and **2**, 68 mg, 46% based on H<sub>4</sub>L). Elemental analysis calcd (%) for **1**, [Zn<sub>2</sub>(L)]: C 37.60, H 1.00; found: C 36.76, H 0.65; **2**, [Cd<sub>2</sub>(L)(H<sub>2</sub>O)<sub>2</sub>]: C 30.96, H 1.37; found: C 30.72, H 1.05. IR (Al<sub>2</sub>O<sub>3</sub>, cm<sup>-1</sup>): **1**, 3109m, 2991w, 2356w, 1948m, 1884m, 1831m, 1715m, 1636s, 1610vs, 1582s, 1436s, 1392m, 1290m; **2**, 3245b, 3199m, 2965w, 2356m, 1925s, 1877s, 1823m, 1795m, 1631s, 1595vs, 1505s, 1490s, 1387m.

Single-crystal X-ray crystallography: the crystal data were collected on a R-Axis RAPID II diffractometer at room temperature with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å).<sup>20</sup> The structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL.<sup>21</sup> Metal atoms in each complex were located from the *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses, which were refined with anisotropic thermal parameters on *F*<sup>2</sup>. The hydrogen atoms of the ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The hydrogen atoms of the water molecules were located using the difference Fourier method and refined freely. Crystal data for **1**: C<sub>19</sub>H<sub>6</sub>F<sub>6</sub>O<sub>8</sub>Zn<sub>2</sub>, *M* = 606.98, monoclinic, space group *C2/c*, with *a* = 23.966(5), *b* = 7.6492(15), *c* = 10.627(2) Å,  $\beta$  = 94.63(3)°, *V* = 1941.9(7) Å<sup>3</sup>, *Z* = 4,  $\rho_{\text{calcd}}$  = 2.076 g cm<sup>-3</sup>, *T* = 293(2) K,  $\mu$  = 2.577 mm<sup>-1</sup>. Least-squares refinement based on 7037 reflections with *I* > 2 $\sigma$ (*I*) and 159 parameters, *R*<sub>int</sub> = 0.0410, led to convergence, with a final *R*1 = 0.0594, *wR*2 = 0.1712, and GOF = 1.120. Crystal data for **2**: C<sub>19</sub>H<sub>10</sub>Cd<sub>2</sub>F<sub>6</sub>O<sub>10</sub>, *M* = 737.07, monoclinic, space group *C2/c*, with *a* = 24.483(5), *b* = 7.7834(16), *c* = 10.488(2) Å,  $\beta$  = 90.73(3)°, *V* = 1998.4(7) Å<sup>3</sup>, *Z* = 4,  $\rho_{\text{calcd}}$  = 2.450 g cm<sup>-3</sup>, *T* = 293(2) K,  $\mu$  = 2.246 mm<sup>-1</sup>. Least-squares refinement based on 9339 reflections with *I* > 2 $\sigma$ (*I*) and 177 parameters, *R*<sub>int</sub> = 0.0662, led to convergence, with a final *R*1 = 0.0360, *wR*2 = 0.0909, and GOF = 1.051. CCDC 632140 (**1**) and CCDC 632141 (**2**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b701200d

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