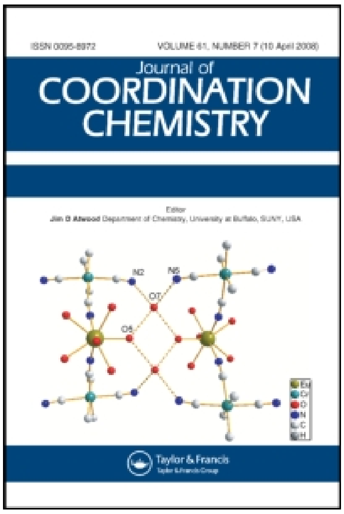

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Two new metal-organic frameworks possessing binodal high-connected topologies based on Cd_4-clusters and organic ligands

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To cite this Article Cui, Ruihai , Xu, Guangjuan and Jiang, Zhaohua(2011) 'Two new metal-organic frameworks possessing binodal high-connected topologies based on Cd_4-clusters and organic ligands', Journal of Coordination Chemistry, 64: 2, 222 — 231, First published on: 23 December 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958972.2010.541905

URL: http://dx.doi.org/10.1080/00958972.2010.541905

Journal of Coordination Chemistry
Vol. 64, No. 2, 20 January 2011, 222–231

Two new metal-organic frameworks possessing binodal high-connected topologies based on Cd_4-clusters and organic ligands

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(*Received 14 June 2010; in final form 22 October 2010*)

Two new compounds, $[Cd_2(bptc)(bpimb)(H_2O)]\cdot 2H_2O$ (**1**) and $[Cd_2(bptc)(bpib)]\cdot 4H_2O$ (**2**) (where H_4bptc = biphenyl-3,3′,4,4′-tetracarboxylic acid, bpimb = 1,3-bis((2-(pyridin-2-yl)-1*H*-imidazol-1-yl)methyl)benzene, bpib = 1,4-bis(2-(pyridin-2-yl)-1*H*-imidazol-1-yl)butane), were synthesized by reactions of the corresponding metal salts with H_4bptc and N-containing auxiliary ligands and their structures have been determined by single-crystal X-ray diffraction. Compound **1** is built by Cd_4-clusters which further construct a 3-D (3,8)-connected framework with *tfz-d* notation; **2**, also built by Cd_4-clusters, is a 3-D (4,8)-connected framework with $(3^2\cdot 4^2\cdot 5^2)(3^4\cdot 4^8\cdot 5^{12}\cdot 6^4)$ topology. In addition, the elemental analyses, infrared spectra, fluorescence, and thermogravimetric analyses for **1** and **2** are discussed.

Keywords: Metal-organic framework; Topology; Crystal structure; Photoluminescent property

1. Introduction

Metal-organic frameworks (MOFs) have been developed because of their fascinating structures and potential applications as functional materials, in adsorption [1], ion exchange [2], chirality [3], catalysis [4], luminescence [5], and magnetism [6]. Many 3-D MOFs have been prepared and characterized. Among them, a variety of binodal network topologies based on boracite, pyrite, rutile, and Pt_3O_4 topologies have been realized [7]. However, due to the limits of coordination numbers of metal centers and the steric hindrance of commonly used organic ligands, there is a lack of binodal high-connected structures, such as (3,8)-, (4,8)-, (3,9)-, and (3,10)-connected frameworks [8]. Polynuclear metal clusters as building blocks to construct high-connected frameworks have proved feasible. Multicarboxylate ligands may induce core aggregation, and it should be feasible to link discrete clusters into an extended high-connected network [9]. In this article, we report two new MOFs, $[Cd_2(bptc)(bpimb)(H_2O)]\cdot 2H_2O$ (**1**) and $[Cd_2(bptc)(bpib)]\cdot 4H_2O$ (**2**), synthesized by reactions of the corresponding cadmium

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2011 Taylor & Francis
DOI: 10.1080/00958972.2010.541905

salts with biphenyl-3,3′,4,4′-tetracarboxylic acid (H_4bptc) and N-containing auxiliary ligands.

2. Experimental

2.1. *General information and materials*

All chemicals were commercially available and used as received; bpimb and bpib were synthesized by the procedure reported [10]. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C elemental analyzer. Fourier transform-infrared (FT-IR) spectra were recorded from KBr pellets from 4000 to 400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Solid-state luminescence spectra were measured on a Cary Eclipse spectrofluorimeter (Varian) equipped with a xenon lamp and quartz carrier at room temperature. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TG-7 analyzer from 40°C to 600°C under nitrogen.

2.2. *Synthesis of [Cd_2(bptc)(bpimb)(H_2O)] · $2H_2O$ (1)*

A mixture of $Cd(CH_3COO)_2 \cdot 2H_2O$ (0.055 g, 0.20 mmol), H_4bptc (0.033 g, 0.10 mmol), bpimb (0.039 g, 0.10 mmol), and NaOH (0.16 g, 0.40 mmol) in H_2O (14 mL) was sealed in a 25 mL Teflon-lined stainless steel container, which was heated at 150°C for 3 days and then cooled to room temperature at 10°C h^{-1}. Colorless crystals of **1** were collected and washed with distilled water and dried in air. Yield: 54 mg (about 53% based on Cd). Elemental analyses Calcd (%) for $C_{40}H_{34}N_6O_{12}Cd_2$ (1015.53): C, 47.31; H, 3.38; N, 8.30. Found: C, 47.34; H, 3.36; N, 8.32. IR (KBr pellet, cm^{-1}): 3429(w), 3116(w), 1586(s), 1538(s), 1476(s), 1396(s), 1357(s), 1285(m), 1151(m), 1093(w), 824(w), 794(m), 705(m), 628(w) (figure S1a).

2.3. *Synthesis of [Cd_2(bptc)(bpib)] · $4H_2O$ (2)*

The procedure was the same as that for **1** except that bpimb was replaced by bpib (0.034 g, 0.1 mmol). Yield: 45 mg (about 46% based on Cd). Elemental analyses Calcd (%) for $C_{36}H_{34}N_6O_{12}Cd_2$ (967.49): C, 42.21; H, 3.55; N, 8.69. Found: C, 42.23; H, 3.54; N, 8.71. IR (KBr pellet, cm^{-1}): 3436(w), 1563(s), 1547 (s), 1523(s), 1416(s), 1097(m), 872(m), 837(m), 777(s), 704(m), 670(w), 599(w) (figure S1b).

2.4. *X-ray crystallography study*

Data collections of **1** and **2** were performed on a Bruker Smart Apex II CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. All absorption corrections were performed using the SADABS program. The crystal structure was solved by direct methods and refined with full-matrix least-squares (SHELXTL-97) with atomic coordinates and anisotropic thermal parameters for all nonhydrogen atoms. The hydrogens of aromatic rings were included in the structure factor calculation at idealized positions using a riding model.

Table 1. Crystal data and structure refinement for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{40}H_{34}N_6O_{12}Cd_2$	$C_{36}H_{34}N_6O_{12}Cd_2$
Formula weight	1015.53	967.49
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	P-1
Unit cell dimensions (Å, °)		
a	17.607(6)	12.148(3)
b	10.258(3)	13.123(6)
c	21.879(7)	13.980(7)
α	90	75.633(4)
β	101.049(5)	64.450(6)
γ	90	67.616(2)
Volume (Å^3), Z	3878(2), 4	1849.8(13), 2
Calculated density (g cm^{-3})	1.739	1.737
Absorption coefficient (mm^{-1})	1.170	1.222
Observed reflection	19056	11098
Independent reflection	6829 [R(int) = 0.0457]	8100 [R(int) = 0.0532]
Goodness-of-fit on F^2	1.075	1.016
$R_1{}^a$ $[I > 2\sigma(I)]$, $wR_2{}^b$ (all data)	$R_1 = 0.0233$, $wR_2 = 0.0586$	$R_1 = 0.0798$, $wR_2 = 0.1846$

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $^bwR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

Crystallographic data and structure refinement parameters are summarized in table 1. Selected bond lengths and angles for **1** and **2** are given in table S1.

3. Results and discussion

3.1. *Crystal structures of 1 and 2*

3.1.1. [Cd_2(bptc)(bpimb)(H_2O)]·$2H_2O$ (1). Single-crystal X-ray analysis reveals that **1** crystallizes in the monoclinic space group $P2_1/n$ with the asymmetric unit consisting of two kinds of crystallographically independent Cd^{II}'s, one bptc, one bpimb, one coordinated water molecule, and two lattice water molecules. As shown in figure 1, each Cd1^{II} is coordinated by two carboxylate oxygens (Cd1–O1 2.302(2) Å, Cd1–O7D 2.239(2) Å) from two bptc ligands, four nitrogens (Cd1–N1 2.521(2) Å, Cd1–N2 2.307(2) Å, Cd1–N4B 2.608(3) Å, Cd1–N5B 2.305(2) Å) from two bpimb ligands in a distorted octahedral coordination geometry; while each Cd2^{II} is ligated with six carboxylate oxygens (Cd2–O2 2.343(4) Å, Cd2–O4 2.407(3) Å, Cd2–O3A 2.425(2) Å, Cd2–O4A 2.385(1) Å, Cd2–O5C 2.236(2) Å, Cd2–O6C 2.606(2) Å) from three bptc ligands and one coordinated water molecule (Cd2–O9 2.242(2) Å) to complete a pentagonal bipyramidal geometry. As shown in figure 2(a), each bptc connects two Cd1's and three Cd2's by using four carboxylates. Bptc connects Cd's to form a 2-D bilayer (figure S2), with a Cd_4-cluster with Cd1 ··· Cd2 and Cd2 ··· Cd2 Å distances of 4.806 Å and 3.858 Å. Cd2 is saturated by coordinated water molecule (O9) and Cd1 is saturated by one monodentate carboxylate oxygen (O7) and four nitrogens (N1, N2, N4, N5) from two bpimb ligands, which further pillared the 2-D bilayer motifs to a 3-D framework (figure 3). Lattice water molecules and coordinated water molecules form hydrogen bonds with carboxylate of bptc, further stabilizing the 3-D framework. The hydrogen-bonding data are summarized in table S2 (Supporting information).

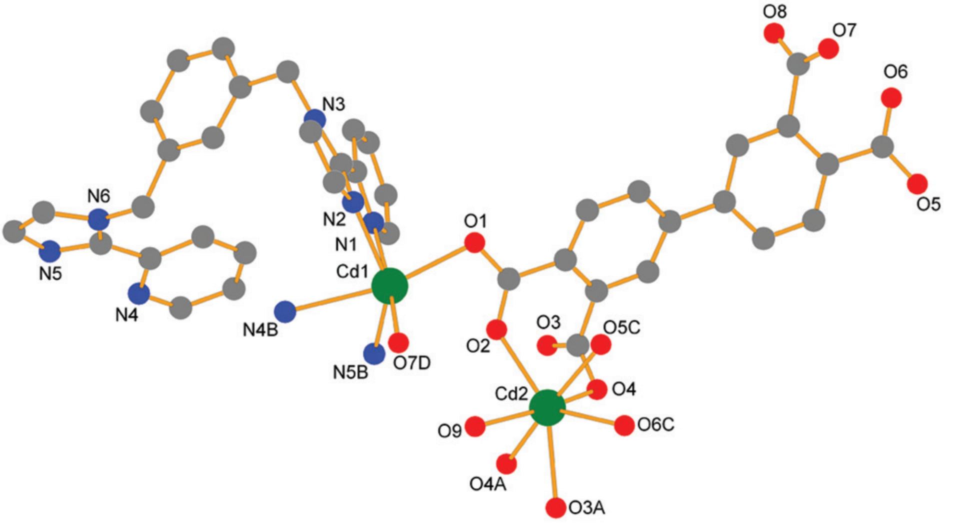

Figure 1. Coordination environment of Cd^{II} in **1**; hydrogens are omitted for clarity.

Topologically, each bptc connects three Cd_4-clusters and acts as a 3-connected node and each Cd_4-cluster connects six bptc ligands and four bpimb ligands (two bpimb are parallel and can be considered as one linear linker) and defines an 8-connected node, the overall structure of **1** is a 3-D (3,8)-connected framework (figure 4). The topology analysis by OLEX [11] suggests the (3,8)-connected net with the $(4^3)_2(4^6 \cdot 6^{18} \cdot 8^4)$ topology symbol. According to the literature [12], this net can be assigned to the *tfz-d* notation.

3.1.2. $[Cd_2(bptc)(bpib)] \cdot 4H_2O$ (2).

Compound **2** crystallizes in the triclinic space group *P*-1 and shows a (4,8)-connected framework with $(3^2 \cdot 4^2 \cdot 5^2)(3^4 \cdot 4^8 \cdot 5^{12} \cdot 6^4)$ topology. As shown in figure 5, the structure of **2** contains two kinds of Cd^{II}'s, two kinds of bptc, and one bpib. As a result, each Cd1 shows a distorted octahedral coordination geometry, surrounded by four carboxylate oxygens (Cd1–O2 2.314(6) Å, Cd1–O3 2.581(8) Å, Cd1–O3A 2.253(8) Å, Cd1–O6 2.242(7) Å) from three bptc ligands and two nitrogens (Cd1–N1 2.399(9) Å Cd1–N2 2.265(9) Å) from one bpib; each Cd2 also shows a distorted octahedral coordination geometry, ligated with four carboxylate oxygens (Cd2–O1 2.438(7) Å, Cd2–O2 2.462(6) Å, Cd2–O5 2.249(7) Å, Cd2–O7B 2.198(7) Å) from three bpib ligands and two nitrogens (Cd2–N4 2.441(9) Å, Cd2–N5 2.246(9) Å) from one bpib ligand. In **2**, there are two coordination modes of bptc. Bptc ligands in Chart 1b mode connect Cd's (Cd2, Cd1, Cd1A, Cd2A) to form a Cd_4-cluster–bptc chain with Cd2 $\cdots$ Cd1 and Cd1 $\cdots$ Cd1A distances of 4.295 and 3.983 Å. Then, bptc in Chart 1c mode connect these chains to form a 2-D layer (figure S3), which is further pillared by bpib ligands to form the final 3-D framework (figure 6). The hydrogen-bonding interactions between lattice water molecules further stabilize this framework. The hydrogen-bonding data are summarized in table S2 (Supporting information).

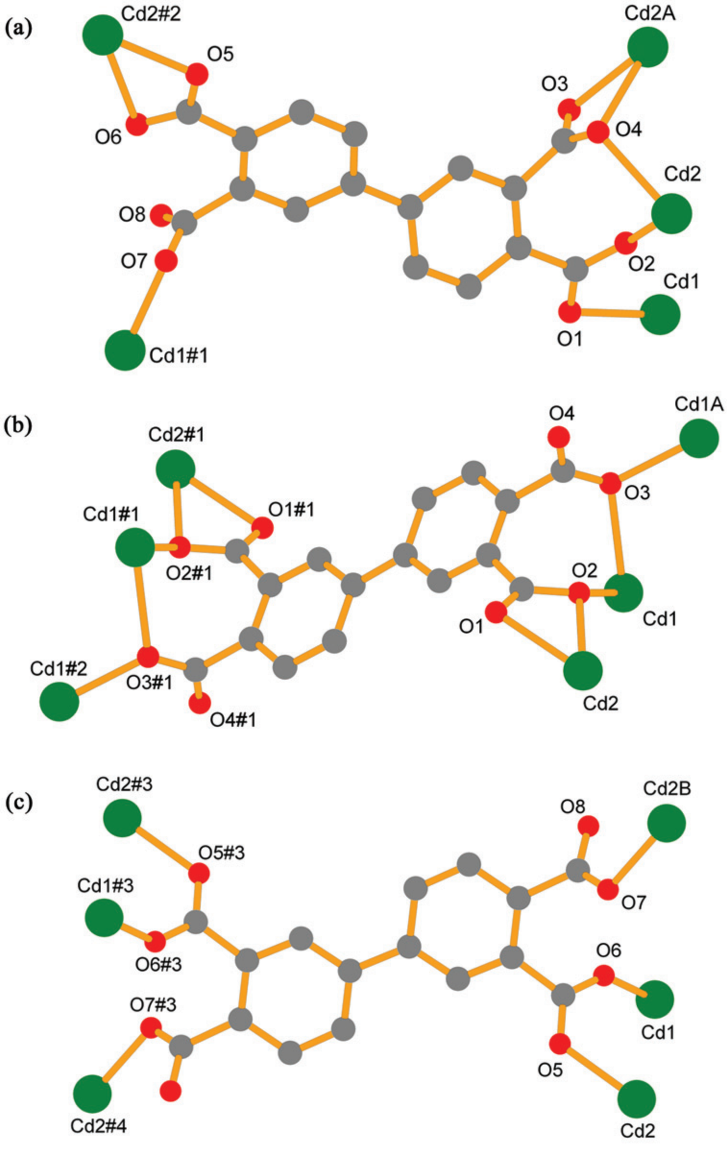

Figure 2. Coordination modes of bptc (a) in **1** (b) and (c) in **2**.

Topologically, both bptc in figure 2(b) mode and bpib connect two Cd_4-clusters as linear linkers, each bptc in figure 2(c) mode connects four Cd_4-clusters as a 4-connected node, each Cd_4-cluster connects six bptc's and four bpib's (two bpimb ligands are parallel and can be considered as one linear linker) defining it as an 8-connected node, the overall structure of **2** is a 3-D (4,8)-connected framework (figure 7). The topology analysis by OLEX [11] suggests the (4,8)-connected net with the $(3^2 \cdot 4^2 \cdot 5^2)(3^4 \cdot 4^8 \cdot 5^{12} \cdot 6^4)$ topology symbol. Previous examples of (4,8)-connected frameworks [13] are very rare, and they are reminiscent of the binary inorganic compounds fluorite

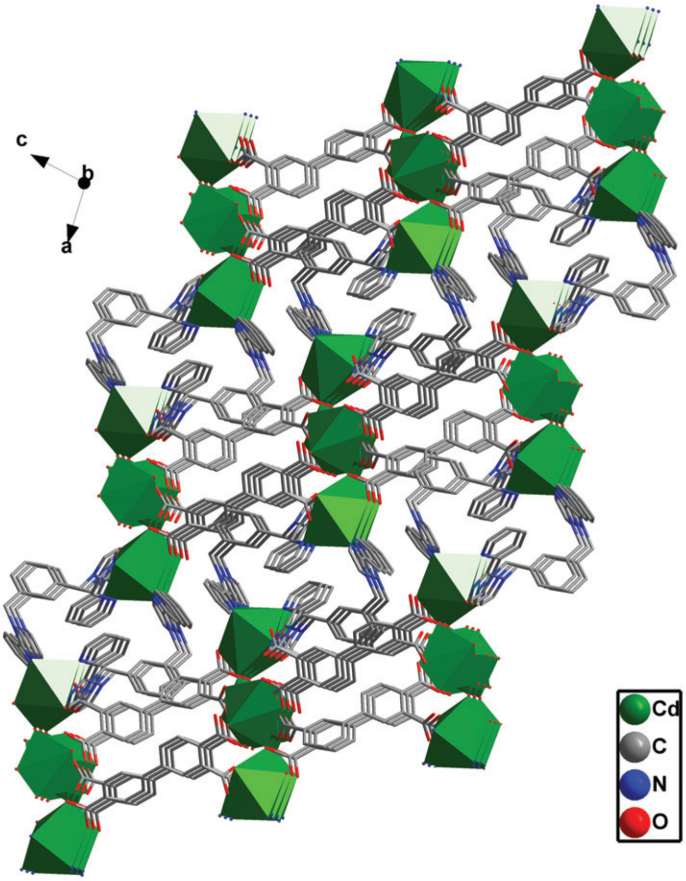

Figure 3. Infinite 3-D coordination framework of **1**.

CaF_2 (*flu*, the Schläfli symbol is $(4^6)_2(4^{12}\cdot 6^{12}\cdot 8^4)$, figure S4a) and $PoCl_2$ (*scu*, the Schläfli symbol is $(4^4\cdot 6^2)_2(4^{16}\cdot 6^{12})$, figure S4b). So the net of **2** defines a new type of (4,8)-connected topological framework previously unobserved and different from the known *flu* and *scu* networks.

The simulated and experimental PXRD patterns of **1** and **2** are shown in figure S5 (Supporting information). The peak positions are in good agreement, indicating the phase purity of the products. The differences in intensity may be due to preferred orientation of the powder samples.

3.2. *Properties*

3.2.1. Luminescent properties. The luminescent properties of **1** and **2** were examined in the solid state at room temperature. As shown in figure 8, **1** shows a maximum emission at 374 nm ($\lambda_{ex} = 285$ nm) and **2** shows a maximum emission at 417 nm ($\lambda_{ex} = 350$ nm).

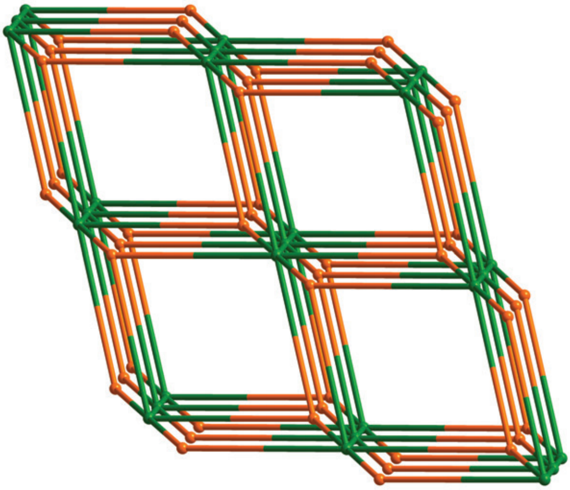

Figure 4. Schematic representation of the (3,8)-connected framework of **1** with $(4^3)_2(4^6\cdot6^{18}\cdot8^4)$ topology. (Symmetry transformations used to generate equivalent atoms: A, $2-x$, $1-y$, $-z$; B, $1-x$, $1-y$, $-z$; C, $2.5-x$, $-0.5+y$, $0.5-z$; D, $-0.5+x$, $0.5-y$, $-0.5+z$).

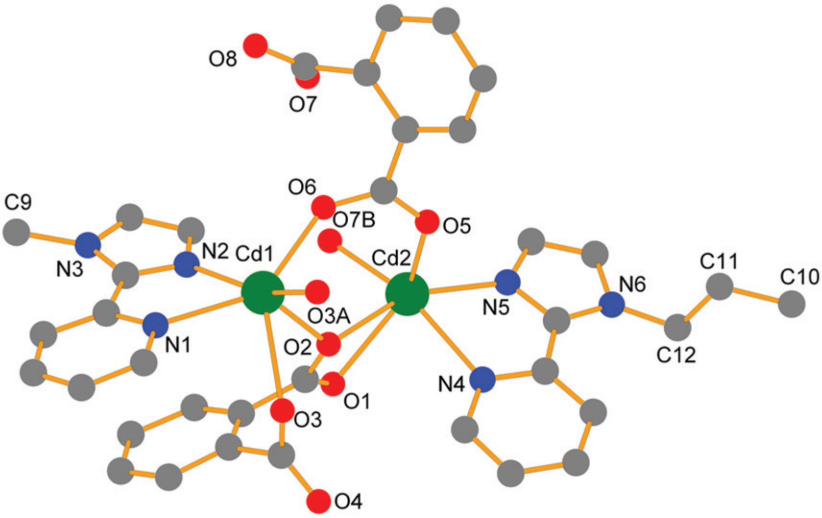

Figure 5. Coordination environment of Cd^{II} in **2**; hydrogens are omitted for clarity.

As reported [14], the photoluminescence spectra of free neutral ligands show emission maxima at 388 ($\lambda_{ex}=360$) nm for H_4bptc, 560, 360 ($\lambda_{ex}=480$) nm for bpimb, and 532 ($\lambda_{ex}=370$) nm for bpib. Emission of H_4bptc, bpimb, and bpib may be assigned to $\pi^*\rightarrow n$ and $\pi^*\rightarrow\pi$ transitions of the intraligands. By considering luminescence of free neutral ligands and emissions of previously reported Cd^{II} MOFs [15], the emissions of **1** and **2** may be attributed to ligand-to-metal charge transfer (LMCT).

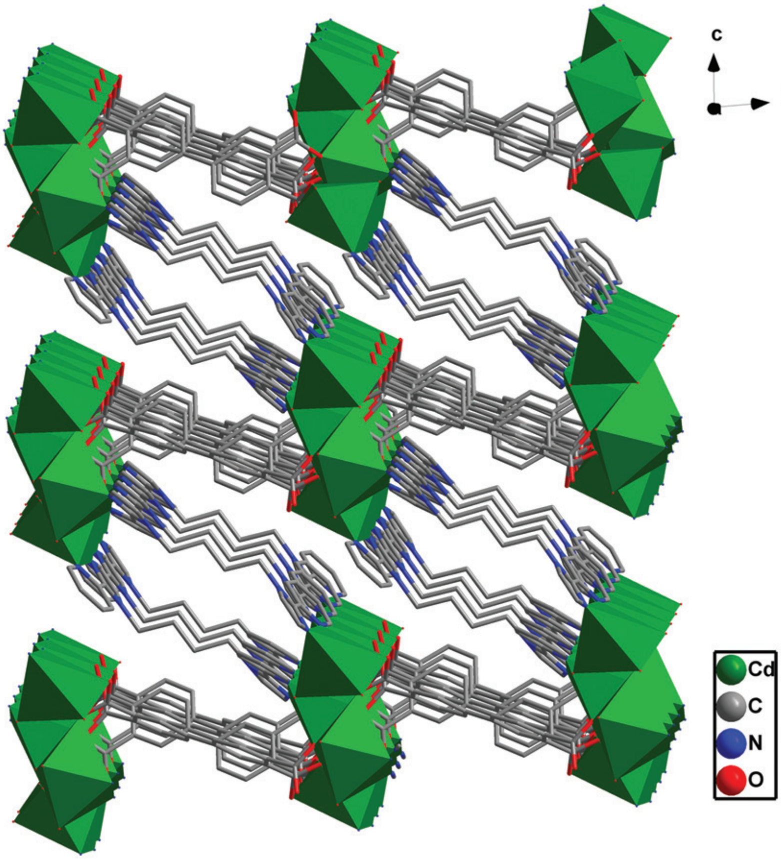

Figure 6. Infinite 3-D coordination framework of **2**.

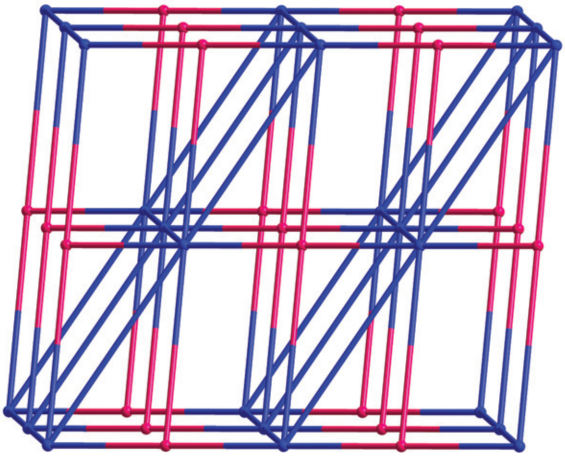

Figure 7. Schematic representation of the (4,8)-connected framework of **2** with $(3^2 \cdot 4^2 \cdot 5^2)(3^4 \cdot 4^8 \cdot 5^{12} \cdot 6^4)$ topology.

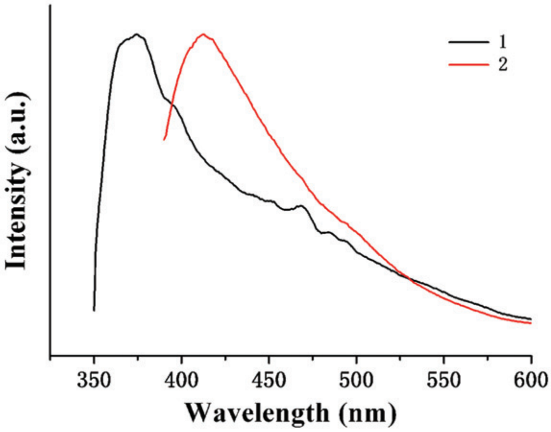

Figure 8. Emission spectra of **1** and **2**.

3.2.2. Thermal properties. TG analyses of **1** and **2** were carried out under N_2 from 40°C to 600°C with a heating rate of $5°C\,min^{-1}$ (figure S6, Supporting information). The TG curves of **1** and **2** show that the first weight losses of 5.30% and 7.46% between 70°C and 120°C correspond to the loss of coordinated and lattice water (Calcd 5.32% and 7.45%, respectively). Both frameworks collapsed gradually from 160°C to 510°C, indicating release of organic components. The remaining weight may be attributed to the formation of CdO (obsd 25.31%, Calcd 25.29% and 26.52%, Calcd 26.54%, respectively).

4. Conclusion

We have prepared and characterized two new binodal high-connected MOFs based on reactions of the corresponding cadmium salts with H_4bptc and auxiliary ligands under hydrothermal conditions. Cd_4-clusters act as 8-connected nodes and bptc ligands as 3- or 4-connected nodes (compound **1** or **2**). Compound **1** is a *tfz-d* net with $(4^3)_2(4^6\cdot6^{18}\cdot8^4)$ topology symbol and **2** presents a new type of (4,8)-connected net with unprecedented $(3^2\cdot4^2\cdot5^2)(3^4\cdot4^8\cdot5^{12}\cdot6^4)$ topology notations. In addition, the luminescence of the compounds indicates that they may be good candidates for photoactive materials. The compounds have enriched high-connected MOFs.

Supplementary material

TG curves of **1** and **2** and the additional tables are available. CCDC nos 771176 and 771177 contain the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk/data_request/cif

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