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Syntheses, crystal structures, and photoluminescent properties of two new Cd(II) coordination polymers based on biphenyl-2,2',4,4'-tetracarboxylate and dipyriddy-containing ligands

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Syntheses, crystal structures, and photoluminescent properties of two new Cd(II) coordination polymers based on biphenyl-2,2',4,4'-tetracarboxylate and dipyridyl-containing ligands

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Two new Cd(II) coordination polymers, $[\text{Cd}_2(\text{btc})(\text{dpe})_{1.5}(\text{H}_2\text{O})]_n$ (**1**) and $[\text{Cd}_2(\text{btc})(\text{bpp})(\text{H}_2\text{O})]_n$ (**2**), were prepared by the hydrothermal reaction of cadmium nitrate with H_4btc (H_4btc = biphenyl-2,2',4,4'-tetracarboxylic acid) in the presence of 1,2-di(4-pyridyl)ethylene (dpe) and = 1,2-bis(4-pyridyl)propane (bpp), respectively, structurally characterized by single-crystal X-ray diffraction, and further characterized by elemental analysis, IR spectroscopy, and thermogravimetric analysis. In **1**, btc^{4-} connect six Cd^{2+} ions, forming a 3-D (3,3,6)-connected $[\text{Cd}_2(\text{btc})]$ net, and further connected by 1-D $[\text{Cd}(\text{dpe})]_n$ chains to construct the final (4,5,6)-connected $(4^2.5^2.6^5.7)(4^3.6^2.7)(4^5.5^3.6^4.7^2.8)$ net. In **2**, a 3-D $[\text{Cd}_2(\text{btc})]$ net is also constructed from btc^{4-} connecting six Cd^{2+} ions, giving a 3-D (3,4,7)-connected network. The overall structure of **2** can be regarded as a (4,4,6)-connected $(4^5.6^4)(4^2.5.6^2.8)(4^3.5^4.6^7.7)$ framework with bpp linking adjacent Cd ions. Structural comparisons show that the secondary auxiliary N-donors have important effects on the final structure and properties. Photoluminescent properties of **1** and **2** are also discussed.

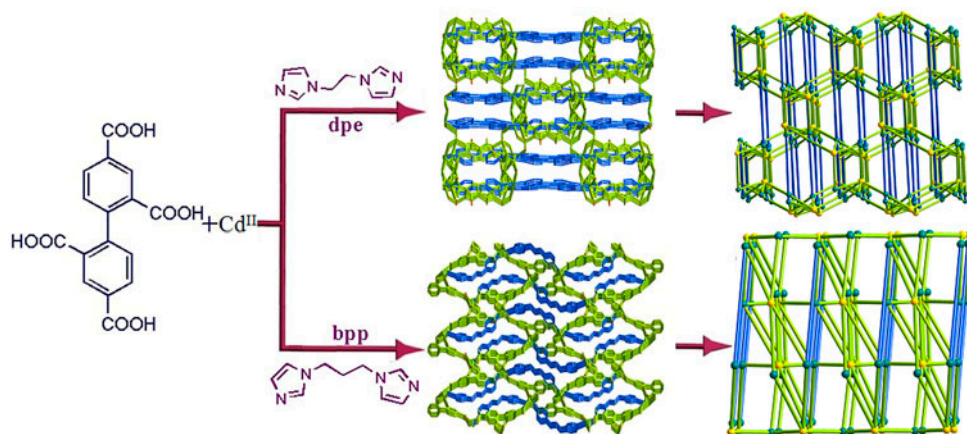
Keywords: Photoluminescent properties; Biphenyl-2,2',4,4'-tetracarboxylic acid; Cd(II); Topology

1. Introduction

The construction of coordination polymers (CPs) has attracted continuous research interest in the last decades because of their fascinating structures and potential applications as functional materials [1–6]. Numerous CPs have been designed and synthesized by chemists. However, the goal of predicting and controlling the final crystal structures remains a long-term challenge, since many factors, such as pH, solvent, template, temperature, and the nature of the ligands, significantly affect the final structure [7–12].

Generally, CPs are constructed from a relevant transition metal and an organic acid or base under suitable reaction conditions [13, 14]. A series of metal-organic structural motifs, including honeycomb, brick wall, bilayer, ladder, herringbone, diamondoid, and rectangular

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Scheme 1. Synthetic procedure for **1** and **2**.

grid, have been deliberately designed by employing bridging aromatic carboxylate ligands [15–21]. The polycarboxylate ligands exhibit diverse coordination modes and can serve as excellent candidates for building highly connected, self-penetrating, or helical coordination frameworks due to their bent backbones and versatile bridging modes [22–26].

Recent studies on coordination assemblies using aromatic biphenyl-2,2',4,4'-tetracarboxylic acid and the N-donors 2,2'-bipyridine (2,2'-bpy) and phenanthroline (phen) illustrate a reliable strategy for obtaining new topological prototypes of coordination nets [27]. A minor change can make a large difference. These considerations inspired us to explore new coordination frameworks with biphenyl-2,2',4,4'-tetracarboxylic acid and longer dipyridine derivatives dpe and bpp. In this paper, we report synthesis and characterization of two new CPs, $[\text{Cd}_2(\text{btc})(\text{dpe})_{1.5}(\text{H}_2\text{O})]_n$ (**1**) and $[\text{Cd}_2(\text{btc})(\text{bpp})(\text{H}_2\text{O})]_n$ (**2**). In **1**, btc^{4-} connect six Cd^{2+} ions to form a 3-D (3,3,6)-connected $[\text{Cd}_2(\text{btc})]$ net with $(4^2.6)(4^3)(4^5.6^4.8^6)$ topology, which is further linked by a 1-D $[\text{Cd}(\text{dpe})]_n$ chain to construct the final (4,5,6)-connected $(4^2.5^2.6^5.7)(4^3.6^2.7)(4^5.5^3.6^4.7^2.8)$ nets. In **2**, a 3-D $[\text{Cd}_2(\text{btc})]$ net was also constructed from btc^{4-} connecting six Cd^{2+} ions, giving a 3-D (3,4,7)-connected $(4^4.6^2)(4^3)(4^8.6^6.8^7)$ topology. The whole structure of **2** can be regarded as a (4,4,6)-connected $(4^5.6^4)(4^2.5.6^2.8)(4^3.5^4.6^7.7)$ network with bpp linking adjacent Cd ions. Moreover, the photoluminescent properties of **1** and **2** are discussed (scheme 1).

2. Experimental

2.1. Materials and methods

All chemicals were commercially purchased and used as received. IR spectra were recorded as KBr pellets from 4000 to 400 cm^{-1} on a Bruker EQUINOX-55 spectrometer. The C, H, and N elemental analyzes were determined with an Elementar Vario EL III elemental analyzer. Thermogravimetric analyzes (TGA) were performed from room temperature to 1000 °C under nitrogen with a heating rate of 20 °C min^{-1} using a SDT Q600 thermogravimetric analyzer. Fluorescence spectra were obtained on a Hitachi F-4500 fluorescence

spectrophotometer at room temperature. The Powder X-ray diffraction (PXRD) patterns were recorded with a SHIMADZU XRD-7000 diffractometer.

2.2. Synthesis

2.2.1. Synthesis of $[\text{Cd}_2(\text{btc})(\text{dpe})_{1.5}(\text{H}_2\text{O})]_n$ (1**).** A mixture of H_4btc (0.10 mM), $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.20 mM), dpe (0.15 mM), NaOH (0.4 mM), and 15 mL H_2O was added to a 25 mL Teflon-lined stainless steel vessel and was heated to 160 °C for 3 days, followed by slow cooling to room temperature at a descent rate of 10 °C h^{-1} , giving colorless block-shaped crystals (0.052 g, 68% yield, based on Cd). Anal. Calcd for $\text{C}_{68}\text{H}_{46}\text{Cd}_4\text{N}_6\text{O}_{18}$: C, 48.48; H, 2.75; N, 4.99%. Found: C, 48.32; H, 2.83; N, 5.03%. IR (cm^{-1}): 3167 m, 1621 vs, 1527 s, 1442 m, 1386 s, 1185 m, 1064 m, 1098 s, 787 m, 647 m, 426 w.

2.2.2. Synthesis of $[\text{Cd}_2(\text{btc})(\text{bpp})(\text{H}_2\text{O})]_n$ (2**).** Complex **2** was prepared using a similar method as described for **1** with replacement of dpe by bpp . Colorless block-shaped crystals were obtained (0.045 g, 58% yield based on Cd). Anal. Calcd for $\text{C}_{29}\text{H}_{22}\text{Cd}_2\text{N}_2\text{O}_9$: C, 45.39; H, 2.89; N, 3.65%. Found: C, 45.18; H, 2.96; N, 3.52%. IR (cm^{-1}): 3413 m, 1599 vs, 1533 s, 1407 s, 1221 w, 1007 m, 782 m, 710 m, 518 m, 431 w.

2.3. X-ray crystallography

Intensity data collection was carried out on a Bruker Smart APEX II CCD diffractometer with graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 295(2) K for **1** and 293 (2) K for **2**. The structures were solved by direct methods and successive Fourier difference synthesis (SHELXS-97) and refined by full matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97). Hydrogens bound to carbon were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2–1.5 times U_{eq} of the attached C atoms, while hydrogens attached to oxygen were refined with $\text{O-H} = 0.85 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ [28, 29]. The crystallographic data and refinement parameters for **1** and **2** are summarized in table 1. Selected bond lengths and angles are listed in table S1.

3. Results and discussion

3.1. Structure descriptions of $[\text{Cd}_2(\text{btc})(\text{dpe})_{1.5}(\text{H}_2\text{O})]_n$ (**1**)

Single-crystal X-ray analysis revealed that **1** crystallized in the monoclinic $C2/c$ space group. As shown in figure 1(a), there are two crystallographically independent Cd^{2+} ions, one btc^{4-} , one and a half dpe , and one coordinated water in the asymmetric unit. $\text{Cd}1$ is coordinated to four O atoms from three btc^{4-} ligands [$\text{Cd}(1)\text{-O}(1) = 2.402(5)$, $\text{Cd}(1)\text{-O}(5) = 2.341(5)$, $\text{Cd}(1)\text{-O}(3)\text{B} = 2.447(5)$, $\text{Cd}(1)\text{-O}(6)\text{A} = 2.330(5) \text{ \AA}$] and N atoms from two dpe ligands [$\text{Cd}(1)\text{-N}(1) = 2.257(5)$, $\text{Cd}(1)\text{-N}(2) = 2.301(5) \text{ \AA}$]. $\text{O}(1)$, $\text{O}(3)\text{B}$, $\text{O}(5)$, and $\text{O}(6)\text{A}$ occupy the equatorial positions, whereas $\text{N}(1)$ and $\text{N}(2)$ occupy the axial positions, providing a distorted octahedral coordination geometry. $\text{Cd}2$ is coordinated with four O atoms from three btc^{4-} ligands [$\text{Cd}(2)\text{-O}(1) = 2.651(5)$, $\text{Cd}(2)\text{-O}(2) = 2.238(5)$, $\text{Cd}(2)\text{-O}(4)\text{B} = 2.233(5)$, $\text{Cd}(2)\text{-O}(8)\text{C} = 2.233(5) \text{ \AA}$], an O atom from the water molecule

Table 1. Crystallographic data and refinement parameters for **1** and **2**.

	1	2
Formula	C ₆₈ H ₄₆ Cd ₄ N ₆ O ₁₈	C ₂₉ H ₂₂ Cd ₂ N ₂ O ₉
<i>M_r</i>	1684.71	767.29
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>P2(1)/n</i>
<i>a</i> (Å)	19.802(9)	7.863(8)
<i>b</i> (Å)	17.476(8)	12.300(0)
<i>c</i> (Å)	17.360(8)	28.171(2)
α (°)	90.00	90.00
β (°)	96.573(5)	92.898(0)
γ (°)	90.00	90.00
<i>V</i> (Å ³)	5968(4)	2721.3(4)
<i>Z</i>	4	4
ρ (Mg m ⁻³)	1.875	1.873
μ (mm ⁻¹)	1.490	1.623
<i>R</i> _{int}	0.0657	0.0210
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0545, 0.1335	0.0220, 0.0535
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0800, 0.1571	0.0250, 0.0551
GOF	1.065	1.057

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$$

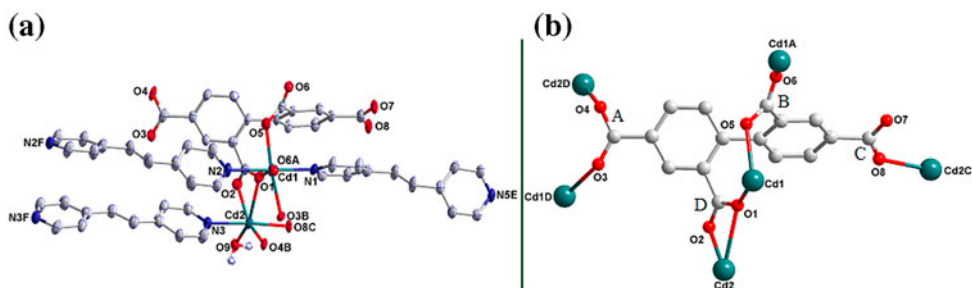


Figure 1. (a) The ORTEP drawing of **1** with 50% probability ellipsoids. Hydrogens (except hydrogens of water) are omitted for clarity. Symmetry codes: A: 0.5 - *x*, 1.5 - *y*, 1 - *z*; B: *x*, 2 - *y*, -0.5 + *z*; C: 1 - *x*, 2 - *y*, 1 - *z*. (b) The coordination mode of btc⁴⁻ in **1**.

[Cd(2)–O(9) = 2.300(5) Å], and one N atom from a dpe ligand [Cd(2)–N(3) = 2.371(6) Å]. O(1), O(2), O(9), and O(4)B occupy the equatorial positions, whereas N(3) and O(8)C occupy the axial positions, also constructing a distorted octahedral coordination geometry. The carboxylate groups in **1** exhibit three bonding modes. Starting from A in figure 1(b) and moving clockwise, there are two bridging, $\mu_2\text{-}\eta^1\text{:}\eta^1$, carboxylate groups involving O3B/OB4 and O5/O6A, one monodentate carboxylate featuring O8C, and a $\mu_2\text{-}\eta^2\text{:}\eta^1$ chelate/bridging carboxylate, atoms O1/O2. The Cd–O bond distances for the bridging carboxylates are 2.233(5) to 2.447(5) Å. The bridging/chelating carboxylate is highly asymmetrically bound with Cd–O bonds of 2.238(5), 2.402(5), and 2.651(5) Å. The differences in these bond distances can mainly be attributed to the coordination modes of the carboxyl groups, and the bond lengths and angles are within the range of values found in other similar, previously reported compounds [30–32].

The btc^{4-} ligand in **1** links six Cd^{2+} ions, constructing 3-D $[\text{Cd}_2(\text{btc})]$ networks with large channels. Considering Cd1 and Cd2 as three-connected nodes and btc^{4-} as a six-connected bridging ligand, the 3-D $[\text{Cd}_2(\text{btc})]$ network can be simplified to a (3,3,6)-connected net. The dpe ligands in **1** act as bridging ligands, linking two neighboring Cd^{2+} ions along the ac plane, giving a 1-D $[\text{Cd}(\text{dpe})]$ chain (figure S1). The 1-D chain runs across the channels of the 3-D $[\text{Cd}_2(\text{btc})]$ networks, forming an interesting 3-D structure (figure 2(a)). The topology [33] of the whole structure of **1** can be rationalized to a (4,5,6)-connected net with $(4^2.5^2.6^5.7)(4^3.6^2.7)(4^5.5^3.6^4.7^2.8)$ Schläfli symbol by denoting Cd1 as a five-connected node, Cd2 as a four-connected node, and btc^{4-} as a six-connected node (figure 2(b)). No voids were found in **1**, as determined by the PLATON software.

3.2. Structure descriptions of $[\text{Cd}_2(\text{btc})(\text{bpp})(\text{H}_2\text{O})]_n$ (**2**)

Single-crystal X-ray analysis revealed that **2** crystallized in the monoclinic $P2_1/n$ space group. As shown in figure 3(a), there are two crystallographically independent Cd^{2+} , one btc^{4-} , one bpp, and one coordinated water in the asymmetric unit. Cd1 is coordinated to four oxygens from three btc^{4-} [$\text{Cd}(1)\text{--O}(1)=2.5020(17)$, $\text{Cd}(1)\text{--O}(2)=2.2695(18)$, $\text{Cd}(1)\text{--O}(5)\text{A}=2.2169(17)$, $\text{Cd}(1)\text{--O}(8)\text{B}=2.2287(17)$ Å] and one nitrogen from one bpp [$\text{Cd}(1)\text{--N}(1)=2.275(2)$ Å]. O(1), O(2), N(1), and O(8)B occupy the basal positions, whereas O(5)A occupies the vertex position, providing a distorted square pyramidal coordination geometry. Cd2 is coordinated to four oxygens from three btc^{4-} [$\text{Cd}(2)\text{--O}(1)=2.3456(17)$, $\text{Cd}(2)\text{--O}(5)=2.3095(18)$, $\text{Cd}(2)\text{--O}(3)\text{C}=2.2339(17)$, $\text{Cd}(2)\text{--O}(7)\text{E}=2.3700(18)$ Å], an O from coordinated water [$\text{Cd}(2)\text{--O}(9)=2.3151(19)$ Å], and one N from one bpp [$\text{Cd}(2)\text{--N}(2)\text{D}=2.309(2)$ Å]. O(1), O(5), O(9), and O(7)E occupy the equatorial positions, whereas N(2)D and O(3)C occupy the axial positions, giving a distorted octahedral coordination geometry. Different from **1**, the carboxylates in **2** exhibit four bonding modes. Starting from A in figure 3(b) and moving clockwise, there is one monodentate carboxylate group with bonding via O3C, a $\mu_2\text{--}\eta^2:\eta^1$ chelate/bridging carboxylate with atoms O1/O2, a

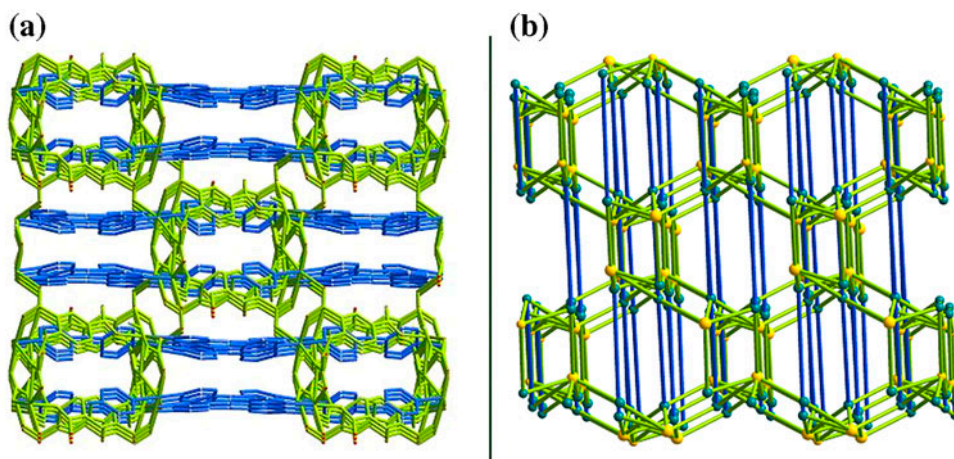


Figure 2. (a) The 3-D framework of **1** (green bonds: btc^{4-} ligands; blue bonds: dpe ligands). (b) The (4,5,6)-connected $(4^2.5^2.6^5.7)(4^3.6^2.7)(4^5.5^3.6^4.7^2.8)$ topology of **1** (teal spheres: Cd^{II} atoms; yellow spheres: btc^{4-} ligands; blue bonds: dpe ligands) (see <http://dx.doi.org/10.1080/00958972.2013.857770> for color version).

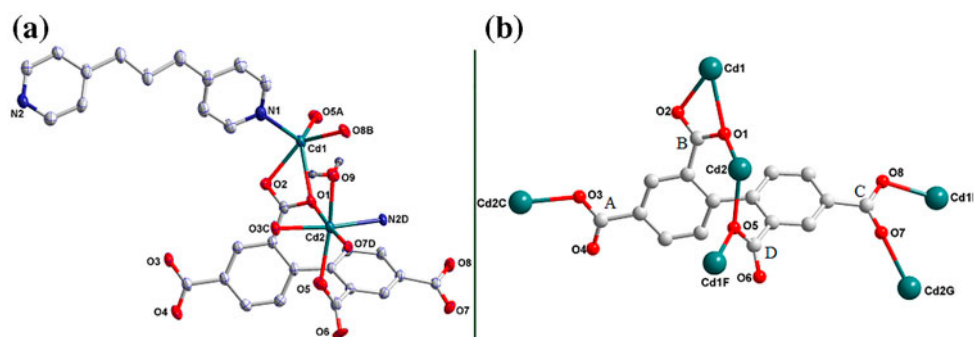


Figure 3. (a) The ORTEP drawing of **2** with 50% probability ellipsoids. Hydrogens (except hydrogens of water) are omitted for clarity. Symmetry codes: A: $-1 + x, y, z$; B: $1.5 - x, -0.5 + y, 0.5 - z$; C: $2 - x, 1 - y, -z$; D: $0.5 + x, 0.5 - y, 0.5 + z$; E: $2.5 - x, -0.5 + y, 0.5 - z$. (b) The coordination mode of btc^{4-} in **2**.

bridging, $\mu_2\text{-}\eta^1\text{:}\eta^1$, carboxylate group involving O7/O8, and a $\mu_2\text{-}\eta^2\text{:}\eta^0$ bridging, monodentate carboxylate featuring O5. As in **1**, the bridging/chelating carboxylate is highly asymmetrically bound with Cd–O bonds of 2.2695(18), 2.3456(17), and 2.5020(17) Å. The remaining Cd–O bond distances are between 2.216(9) and 2.3700(18) Å. The differences in those bond distances can mainly be attributed to the coordination modes of the carboxyl groups, and all the Cd–O/N bond distances are similar to those in **1** and therefore within expected parameters.

The btc^{4-} ligand in **2** also links six Cd^{2+} , forming a 3-D $[\text{Cd}_2(\text{btc})]$ network with large channels along the bc plane. The four-connected Cd1 atoms, the three-connected Cd2 atoms, and the seven-connected btc^{4-} ligands form (3,4,7)-connected nets. The bpp ligands connect adjacent Cd1 and Cd2 atoms, forming the final 3-D structure (figure 4(a)), an unprecedented (4,4,6)-connected $(4^5.6^4)(4^2.5.6^2.8)(4^3.5^4.6^7.7)$ Schläfli symbol, where all the Cd^{2+} ions are simplified as four-connected nodes and the btc^{4-} ligands are

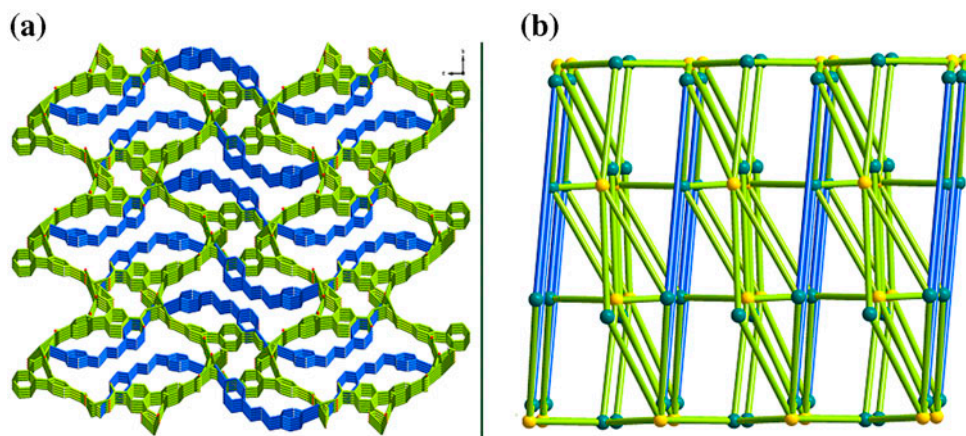


Figure 4. (a) The 3-D framework of **2** (green bonds: btc^{4-} ligands; blue bonds: bpp ligands). (b) The unprecedented (4, 4, 6)-connected $(4^5.6^4)(4^2.5.6^2.8)(4^3.5^4.6^7.7)$ topology of **2** (teal spheres: Cd^{II} atoms; yellow spheres: btc^{4-} ligands; blue bonds: bpp ligands) (see <http://dx.doi.org/10.1080/00958972.2013.857770> for color version).

considered six-connected nodes (figure 4(b)). There are no guest molecules in the void space, and the void volume of **2** is 4.1% of the crystal volume (111.5 of the 2721.3 Å³ unit cell volume), as calculated by PLATON [34].

Comparing the final structures of **1** (figure 2(a)) and **2** (figure 4(a)), the N-donors dpe and bpp have different lengths and flexibilities and play disparate roles in forming the overall structures. In **1**, the dpe ligands link Cd²⁺ ions into an infinite 1-D chain, while the bpp ligands in **2** just act as a bridge between neighboring Cd²⁺ ions. Only seven hits were obtained when searching the Cambridge Structure Database for Cd-H₄bpt compounds with the help of ConQuest version 1.3. When the cheating phen ligand was introduced, a 3-D framework was constructed [35]. Previously, we used the cheating N-donors phen and 2,2'-bpy to form a 2-D bilayer network and a 3-D metal-organic framework [36]. The Jiang group used 1,3-bis((2-(pyridin-2-yl)-1H-imidazol-1-yl)methyl)benzene and 1,4-bis(2-(pyridin-2-yl)-1H-imidazol-1-yl)butane as the co-ligands to react with the H₄bpt/Cd system to form two highly connected Cd₄ cluster-based frameworks [37]. Sun and co-workers used biphenyl-3,3',4,4'-tetracarboxylic acid and 1,1'-(2,2'-oxybis(ethane-2,1-diyl))bis(1-imidazole) ligands to obtain a 2-D corrugated network [38]. Liu and co-workers used the same 3,3',4,4' isomer and 4,4'-bis((1H-imidazol-1-yl)methyl)biphenyl as a bridging ligand to assemble a 2-D layer polymer [39]. With other metals and a variety of ancillary ligands, many CPs, ranging from 1-D chains to 3-D porous CPs, have been obtained [40–43]. A minor change can make a huge difference, as shown by the important effects secondary auxiliary N-donors have on the self-assembly and the final structure. In stark contrast to the chelating N-donors, the bridging dpe and bpp ligands are inclined to form more complicated, highly connected overall structures. The comparison above also shows that ancillary ligands feature a vital role in regulating the structural diversity [44].

3.3. X-ray Powder diffraction analysis and thermogravimetric analysis

To check the phase purity of **1** and **2**, the PXRD patterns were measured at room temperature. As shown in figures S2 and S3, peak positions of the simulated and experimental PXRD patterns are in agreement with each other, demonstrating good phase purity of the complexes.

To reveal the thermal stabilities of **1** and **2**, TGA measurements were carried out. As shown in figure S4, **1** has a weight loss of 2.91% from 160 to 190 °C, corresponding to release of coordinated waters (Calcd 2.14%). The whole structure began to collapse at about 380 °C, and final residual weight was 29.17% (CdO, Calcd 30.49%). For **2**, a weight loss of 2.51% was observed from 60 to 120 °C, which corresponds to a loss of coordinated water (Calcd 2.35%). Further weight loss was observed at about 290 °C, and the final residual weight was 35.29% (CdO, Calcd 33.47%). Both **1** and **2** show a clear change in the rate of weight loss at about 425 °C, which can be attributed to loss of ancillary dpe or bpp ligands after the primary btc⁴⁻ ligands have decomposed.

3.4. Photoluminescent properties

Many coordination complexes have been extensively studied due to their potential applications as luminescent materials [45–47]. The fluorescence spectrum of H₄btc, **1**, and **2** were examined in the solid state at room temperature. The free H₄btc ligand displays luminescence with an emission maximum at 422 nm ($\lambda_{\text{ex}} = 260$ nm). For **1** and **2**, intense fluorescent emission was observed for **1** at 398 nm and for **2** at 358 nm ($\lambda_{\text{ex}} = 260$ nm). Complex

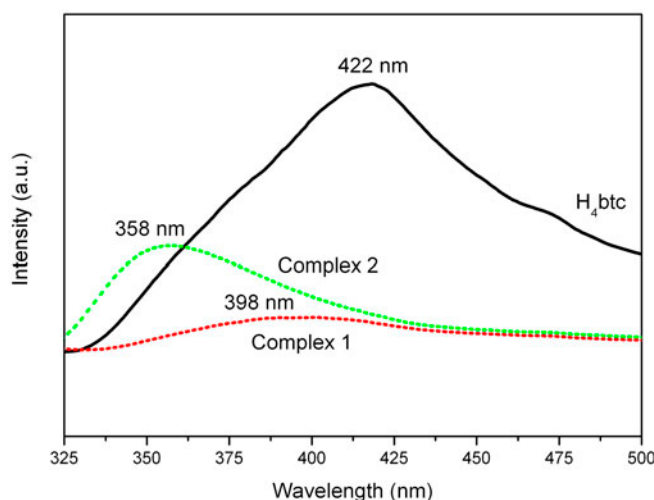


Figure 5. Emission spectra of H_4btc , **1**, and **2** in the solid state at room temperature.

1 has a blue shift of 24 nm, whereas **2** displays a blue shift of 64 nm, as shown in figure 5. The large discrepancy in the spectra can mainly be attributed to the different rigidities of the final structures of **1** and **2**, where **2** has the more rigid structure. The emission is neither metal-to-ligand charge transfer nor ligand-to-metal transfer in nature, since Cd^{2+} is difficult to oxidize or reduce due to its d^{10} configuration [48–50]. Thus, the emissions may be assigned to intraligand ($\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$) transitions.

4. Conclusion

Two new CPs were constructed under hydrothermal conditions from bridging N-donor ligands dpe and bpp and cadmium nitrate in the presence of biphenyl-2,2',4,4'-tetracarboxylic acid. In **1**, btc^{4-} connect six Cd^{2+} ions, forming a 3-D (3,3,6)-connected $[Cd_2(btc)]$ net, and these nets are further linked into the final (4,5,6)-connected $(4^2.5^2.6^5.7)(4^3.6^2.7)(4^5.5^3.6^4.7^2.8)$ net by a 1-D $[Cd(dpe)]_n$ chain. In **2**, a 3-D $[Cd_2(btc)]$ net was also constructed from btc^{4-} connecting six Cd^{2+} ions, giving a 3-D (3,4,7)-connected network. The overall structure of **2** can be regarded as an unprecedented (4,4,6)-connected $(4^5.6^4)(4^2.5.6^2.8)(4^3.5^4.6^7.7)$ framework with bpp as a bridging ligand linking adjacent Cd^{2+} ions. Structural comparisons between **1** and **2** indicate that the auxiliary N-donors have important effects on the final structure and properties.

Supplementary material

Tables of selected bond distances and angles for **1** and **2**; figure of the 1-D $[Cd(dpe)]_n$ chain in **1**; simulated and experimental PXRD patterns for **1** and **2**; DSC-TGA curves for **1** and **2**. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC 919208 for **1** and CCDC 919209 for **2**. Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road,

Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>). Supplemental data for this article can be accessed <http://dx.doi.org/10.1080/00958972.2013.857770>.

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