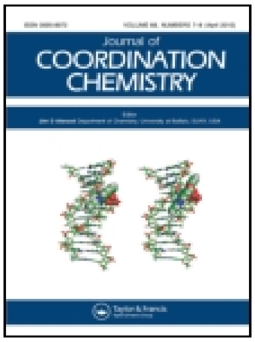

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Two 3-D Cd^{II}/Zn^{II} complexes based on mixed 1,1-cyclobutanedicarboxylate and 4,4'-bipyridine ligands

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Two 3-D Cd^{II}/Zn^{II} complexes based on mixed 1,1-cyclobutanedicarboxylate and 4,4′-bipyridine ligands

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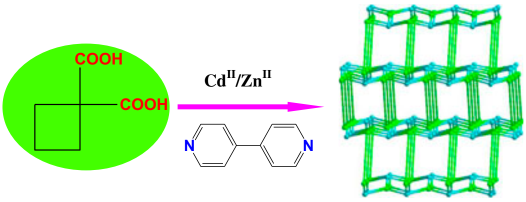

Reported here are two new Cd^{II}/Zn^{II} complexes exhibiting 3-D (3,4)-connected $(6^3)(6^5.8)$ topological network.

Two new 3-D complexes, $[M(\mathbf{L})(4bpy)_{0.5}(H_2O)]_\infty$ [M = Cd (**1**) and = Zn (**2**)], based on mixed 1,1-cyclobutanedicarboxylic acid ($H_2\mathbf{L}$) and 4,4′-bipyridine (4bpy) have been synthesized; **1** and **2** feature (3,4)-connected $(6^3)(6^5.8)$ topological networks consisting of pillared 2-D $\mathbf{[M(L)(H_2O)]_\infty}$ layered motifs. Complexes **1** and **2** are photoluminescent materials.

Keywords: Zn(II)/Cd(II) complexes; 1,1-Cyclobutanedicarboxylate ligand; Crystal/topological structures; Luminescence

1. Introduction

Coordination complexes have proven efficient for design of multifunctional materials [1] due to their potential applications in several important fields such as gas adsorption [2], separation [3], catalysis [4], drug delivery [5], molecular magnetism [6], and photoluminescence [7]. Effective synthesis of such complexes involves the appropriate choice of ligands as bridges or terminal groups (building blocks) with metal ions or metal clusters as nodes [8]. Dicarboxylic acids, such as aromatic- [9–13], heteroalicyclic- [14], and malonate-based dicarboxylic [15–17] acids have been employed in the preparation of

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*Corresponding author. Email: humin@zzuli.edu.cn various carboxylate-containing metal–organic coordination complexes, i.e. benzenedicarboxylic (1,4- [9], 1,3- [10] or 1,2- [11]), naphthalenedicarboxylic (1,4- [12] or 2,6- [13]), thiophene-2,5-dicarboxylic [14a], 2-ethyl-1H-imidazole-4,5-dicarboxylic [14a], exo-3,6-epoxy-1,2,3,6-tetrahydrophthalic [14b], malonic [15], methylmalonic [16], and phenylmalonic [17] acids.

In this research, we chose one malonate-based dicarboxylic acid, 1,1-cyclobutanedicarboxylic acid ($H_2\mathbf{L}$), to fabricate complexes. $H_2\mathbf{L}$ has been used as a ligand with magnetic metal ions such as copper [18] and other biological metal ions such as palladium, platinum, and ruthenium for its antitumor activity [19]. For Zn and Cd, $H_2\mathbf{L}$ has scarcely been employed in synthesis of complexes. As a versatile tecton [20], it contains two carboxylic groups which can be partially or completely deprotonated and exhibits various coordination modes. The presence of the cyclobutane ring could induce different conformations of the malonate bridges due to geometrical constraint. In addition, incorporation as spacers of rod-like bis-monodentate ligands such as 4,4′-bipyridine (4bpy) has provided a large number of coordination polymers [21]. The pyridine-based spacer can be a pillar to link the metal-carboxylate layers into higher dimensionality to alter the structural topology.

Two new luminescent complexes, $[M(\mathbf{L})(4bpy)_{0.5}(H_2O)]_\infty$ [M = Cd (**1**) and Zn (**2**)], based on 1,1-cyclobutanedicarboxylic acid ($H_2\mathbf{L}$) and 4,4′-bipyridine (4bpy) were obtained, which feature (3,4)-connected $(6^3)(6^5.8)$ topological networks consisting of pillared 2-D $[M(\mathbf{L})(H_2O)]_\infty$ layered motifs. Herein, we report the syntheses, crystal structures, and luminescent properties of these complexes.

2. Experimental

2.1. *Materials and general methods*

All the starting reagents and solvents for synthesis were commercially available and used as received. Elemental analyses (C, H, and N) were performed on a Vario EL III Elementar analyzer. IR spectra were recorded from 4000 to 400 cm^{-1} on a Tensor 27 OPUS (Bruker) FT-IR spectrometer with KBr pellets. Thermogravimetric analysis (TGA) experiments were carried out on a Perkin-Elmer Diamond SII thermal analyzer from room temperature to 800 °C under a nitrogen atmosphere at a heating rate of 10 °C min^{-1}. The emission/excitation spectra were recorded on an F-7000 (HITACHI) spectrophotometer at room temperature.

2.2. *Synthesis of 1 and 2*

2.2.1. $[Cd(L)(4bpy)_{0.5}(H_2O)]_\infty$ (1). A solution of 1,1-cyclobutanedicarboxylic acid ($H_2\mathbf{L}$) (7.2 mg, 0.05 mmol) and 4,4′-bipyridine (4bpy) (7.8 mg, 0.05 mmol) in CH_3OH (10 mL) was carefully layered on top of a H_2O solution (15 mL) of $Cd(ClO_4)_2{\cdot}6H_2O$ (41.9 mg, 0.1 mmol) in a test tube. Colorless block single crystals suitable for X-ray analysis appeared on the tube wall after *ca.* two weeks at room temperature. Yield: 7.9 mg, 45% based on $H_2\mathbf{L}$. Anal. Calcd for $C_{11}H_{12}CdNO_5$: C, 37.68; H, 3.45%; N, 3.99%. Found: C, 37.38; H, 3.69%;

N, 3.58%. IR (KBr pellet, cm^{-1}): 3303b, 2970w, 2361m, 1612s, 1568vs, 1424s, 1352s, 1215m, 1126w, 1073w, 1048w, 910w, 813m, 694m, 651w, 627w, 563w, 498w.

2.2.2. $[Zn(L)(4bpy)_{0.5}(H_2O)]_\infty$ (2). The same procedure as that for **1** was used for this complex except for the use of $Zn(ClO_4)_2 \cdot 6H_2O$ instead of $Cd(ClO_4)_2 \cdot 6H_2O$. Colorless block single crystals suitable for X-ray analysis appeared on the tube wall after *ca.* two weeks at room temperature. Yield: 6.5 mg, 43% based on H_2**L**. Anal. Calcd for $C_{11}H_{12}NO_5Zn$: C, 43.52; H, 3.98; N, 4.61%. Found: C, 43.29; H, 3.60; N, 4.39%. IR (KBr pellet, cm^{-1}): 3253b, 2002w, 2362w, 1607vs, 1574vs, 1490w, 1458w, 1423s, 1353s, 1254w, 1223m, 1216m, 1155w, 1122w, 1076m, 1049w, 1015w, 874w, 814m, 745m, 702m, 657w, 631m, 501w, 468w.

Caution! Although we have met no problems in handling perchlorate salts during this work, these should be treated cautiously owing to their potential explosive nature.

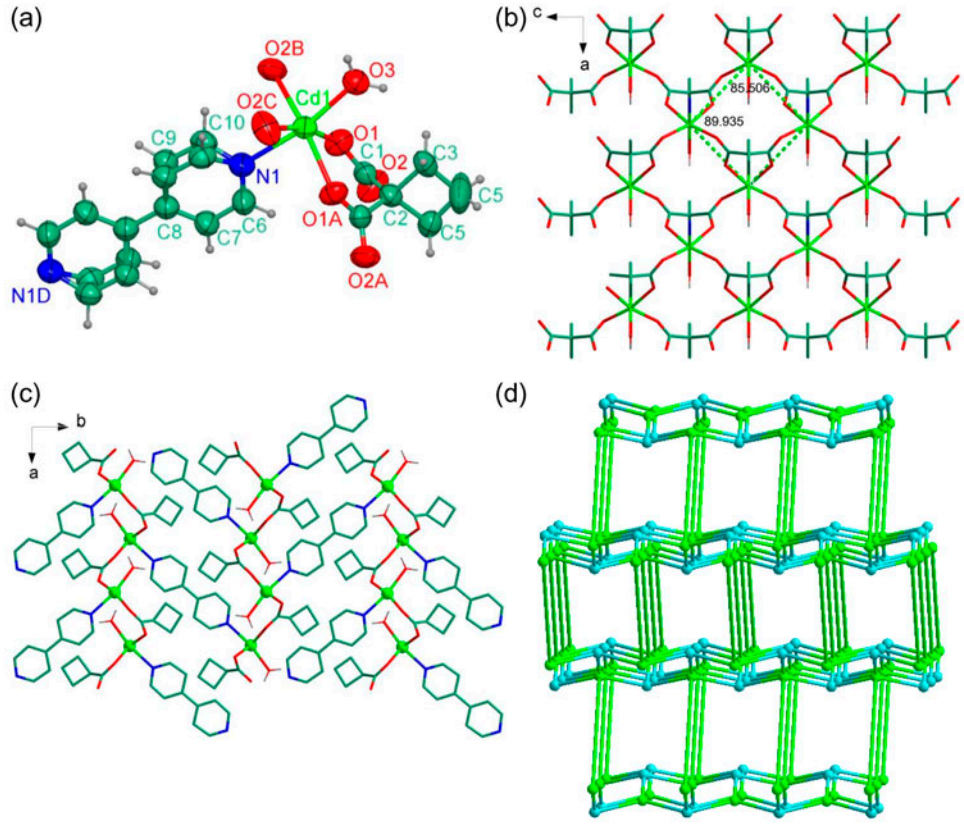

Figure 1. Views of **1** (a) the Cd^{II} surrounding environment showing the numbering scheme and the symmetry codes of each atom. The ellipsoids are at 50% probability (symmetry codes for A = x, y, $-z$; B = $x + 1/2$, $-y + 1/2$, $z - 1/2$; C = $x + 1/2$, $-y + 1/2$, $-z + 1/2$; D = $-x$, $-y$, z). (b) The 2-D layered motif parallel to the *ac* plane (4bpy ligand has been omitted for clarity). (c) The 2-D layered motif parallel to the *ab* plane. (d) The schematic representation of the binodal (3,4)-connected $(6^3)(6^5.8)$ topological network (cyan spheres represent **L** and green spheres represent the Cd nodes) (see http://dx.doi.org/10.1080/00958972.2015.1038527 for color version).

2.3. *Crystal structure determination of 1 and 2*

X-ray single-crystal diffraction data for **1** and **2** were collected on an Xcalibur Gemini Eos CCD diffractometer at 293(2) K with Mo-K_α radiation ($\lambda = 0.71073$ Å) by ω scan mode. SAINT [22] was used for integration of the diffraction profiles. Semi-empirical absorption corrections were applied using SADABS [23]. All structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL [24]. Metals in each complex were located from the *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. In **1** and **2**, the pyridine groups of 4bpy are disordered [figure 1(a)] and two crystallographic positions were found for C9 and C10, respectively. The occupancy factors for these sites were refined resulting in 0.50 (**1**), 0.5 (**2**), and an angle of 31.8(3) (**1**), 31.0(2) (**2**) between corresponding disordered carbons of the pyridine rings. The hydrogens were geometrically positioned and refined using a riding model. Those of the coordinated water were located from Fourier differences and refined with isotropic thermal factors. Further crystallographic data and structural refinement details for **1** and **2** are summarized in table 1. Selected bond lengths and angles for **1** and **2** are listed in tables S1 and S2 (see online supplemental material at http://dx.doi.org/10.1080/00958972.2015.1038527).

3. Results and discussion

3.1. *Synthesis and general characterizations*

Combination of Cd^{II}/Zn^{II} salts in water solution (5 mL) and CH_3OH solution (5 mL) of 4bpy and **L** carried out in a beaker afforded a mass of precipitate and no crystals. It is

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

Complex	**1**	**2**
Empirical formula	$C_{11}H_{12}CdNO_5$	$C_{11}H_{12}ZnNO_5$
Formula weight	350.62	303.59
Temperature (K)	293(2)	294(2)
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pnnm*	*Pnnm*
a (Å)	7.8766(6)	20.132(3)
b (Å)	20.0044(15)	7.4571(13)
c (Å)	7.5660(7)	7.4815(11)
V (Å^3)	1192.15(17)	1123.2(3)
Z	4	4
D_c (g cm^{-3})	1.953	1.795
μ (mm^{-1})	1.844	2.200
F(0 0 0)	692	620
θ range (°)	2.88–24.99	3.40–25.00
Measured reflections	3378	4478
Independent reflections	1131	1067
Data/restraints/parameters	1131/0/107	1067/6/106
R_{int}	0.0297	0.0489
$^aR_1[I > 2\sigma(I)]$	0.0766	0.0410
$^bwR_2$ (all data)	0.1978	0.837
Goodness-of-fit on F^2	1.114	1.049
$\Delta\rho_{max, min}$ (e Å^{-3})	1.703, −0.528	0.745, −0.761

$^aR_1 = \Sigma(||F_0| - |F_c||)/\Sigma|F_0|$; $^bwR_2 = [\Sigma w(|F_0|^2 - |F_c|^2)^2]/\Sigma[w(F_0^2)^2]^{1/2}$, where F_0 = observed and F_c = calculated structure factors, respectively.

apparent that lowering the reaction speed may result in the formation of crystalline products, through slow growth of well-shaped larger single crystals suitable for X-ray diffraction. Therefore, in this research, synthesis and isolation of **1** and **2** were carried out through self-assembly of Cd^{II}/Zn^{II} salts with H_2**L**, together with introduction of auxiliary 4bpy, by using the slow diffusion method in a test tube under mild conditions (ambient temperature and pressure). Complexes **1** and **2** are both air stable, maintaining their crystallinity for several months and are insoluble in common organic solvents and water, consistent with their polymeric nature.

3.2. *Descriptions of crystal structures for $[Cd(L)(4bpy)_{0.5}(H_2O)]_\infty$ (1) and $[Zn(L)(4bpy)_{0.5}(H_2O)]_\infty$ (2)*

Complexes **1** and **2** are isomorphic and crystallize in the orthorhombic space group *Pnnm*. The asymmetric unit contains one metal center, one fully deprotonated **L**, half linking 4bpy ligand, and one coordinated water. Each metal ion [figure 1(a)] exhibits a distorted octahedral geometry formed by four carboxylate oxygens of **L**, one nitrogen of 4bpy linker, and one oxygen of coordinated water; the degree of distortion depends on the metal ion involved. Four cyclobutanedicarboxylate oxygens [O1, O1A, O2B, and O2C, for **1**, M–O bond distances are 2.271(5) and 2.255(5) Å, symmetry codes for A = x, y, $-z$; B = $x + 1/2$, $-y + 1/2$, $z - 1/2$; C = $x + 1/2$, $-y + 1/2$, $-z + 1/2$; for **2**, M–O bond distances are 2.114(3) and 2.090(3) Å, symmetry codes for A = x, y, $-z$; B = $-x + 1/2$, $y + 1/2$, $-z + 1/2$; C = $-x + 1/2$, $y + 1/2$, $z - 1/2$, respectively; see tables S1 and S2] build the basal plane, whereas a nitrogen [N1] from 4bpy and a water [O3] occupy the axial positions. The M–N1 and M–O3 bond distances are 2.381(4) and 2.290(6) Å (**1**) and 2.182(5) and 2.119(4) Å (**2**), respectively (see tables S1 and S2). All the M–O and M–N bond distances are in the normal range [M–O: 2.088–2.647 Å; M–N: 2.136–2.429 Å] expected for similar complexes with metal ion in distorted octahedral geometry [16a,b, 25]. The pyridyl rings of 4bpy in **1** and **2** are coplanar because they are symmetry-related with an inversion center located at the middle of the central C–C bond between pyridyl rings.

There is only one kind of coordination mode for **L** in the structure. Each **L** forms a six-membered chelate ring MO_2C_3 at the metal ion, the values of the angle subtended at the metal are 81.8(3)° (**1**) and 86.38(16)° (**2**). Two neighboring metal ions are bridged by two carboxylate groups from one **L**, forming a 2-D corrugated (4,4) square grid $[M(\mathbf{L})(H_2O)]_\infty$ that grows in the *ac* plane with a M···M distance of 5.5728(7) (**1**) and 5.4239(10) Å (**2**) as well as a M···M···M bite angle of 85.506(0) and 89.935(9)° (**1**) and 86.855(11) and 87.210(2)° (**2**) [figure 1(b)]. The layers of corrugated (4,4) square grids in **1** and **2** are analogous to that previously reported in Cu(II)-cyclobutanemalonate [20] and they are also similar to those occurring in $[Mn_2(mal)_2(4bpy)(H_2O)_2]_n$ (mal = malonate dianion) [15a], $[Zn_2(4bpy)(Memal)_2(H_2O)_2]_n$ (Memal = methylmalonate dianion) [16a,b], $[Cu(Memal)(H_2O)]_n$ [16c], and $Cu(4bpy)(Phmal)]_n \cdot 2nH_2O$ (Phmal = phenylmalonate dianion) [17a].

The 2-D grids are pillared through bis-monodentate 4bpy along the *b* axis [figure 1(c)] to afford a 3-D supramolecular framework (figure S1). The 4bpy bridge connects two metal ions from adjacent layers with values for the metal–metal separation of 11.8216(10) Å (**1**) and 11.4852(16) Å (**2**). They are in agreement with reported values for the metal–metal distances across 4bpy in previous structural reports [16a]. Considering the carboxylate bridge as the unique connector within the *ac* plane, the 3-D structure can be topologically described as a 3,4-binodal net with a Schläfli symbol $[6^3]$ $[6^5 8]$ **ins**-net. The same net was observed in previous reports with 4bpy [16b, 26]. The size of the cyclobutane group of H_2**L** is small enough to allow 4bpy ligands to connect the layers in **1** and **2**, in contrast to what occurs in the related system with a phenylmalonate ligand [16a, 17a]. The 4bpy molecule is located alternatively above and below each layer, practically in a *trans* position with respect to the cyclobutane group of H_2**L**. The shortest centroid–centroid distances between adjacent pyridyl rings vary in the range 7.5660(7) (**1**) to 7.4815(11) Å (**2**), ruling out any π-type interaction in this family of complexes [16a, 27].

3.3. *XRPD results*

To confirm whether the crystal structures are truly representative of the bulk materials, X-ray powder diffraction (XRPD) experiments have been carried out. The XRPD experimental and computer-simulated patterns of the corresponding complexes are shown in figure S2 in the Supporting Information. The bulk synthesized materials and the as-grown crystals are homogeneous for **1** and **2**.

3.4. *Thermogravimetric analysis*

To examine the thermal stabilities of **1** and **2**, TGA experiments were performed (see figures 2 and S3). Complex **1** was stable to *ca*. 180 °C and began to decompose quickly in three consecutive steps peaking at 236, 294, and 354 °C. The first weight loss of 6.28% is consistent with removal of coordinated water (calcd: 5.19%). After this, a weight loss of 23.09% from 240 to 300 °C can be due to release of 4bpy (calcd: 22.27%). The last weight loss of 37.33% from 300 to 450 °C can be attributed to decomposition of **L** (calcd: 39.96%). The final residual weight is assigned to cadmium oxide (obsd: 34.86%, calcd: 36.62%). For **2**, the network is stable to *ca*. 170 °C and decomposes quickly with two consecutive weight loss steps upon further heating. The first weight loss of 7.02% appears between 170 and 220 °C (peaking at 213 °C), which can be attributed to loss of coordinated

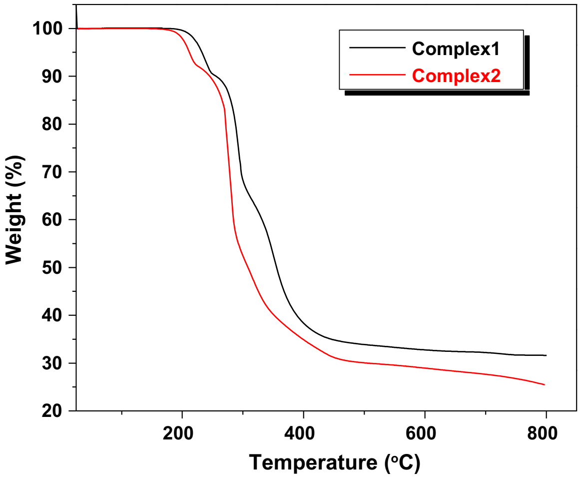

Figure 2. TGA curves of **1** and **2**.

water (calcd: 5.94%). The dehydration process is followed by sharp weight decrease (peaking at 280 °C) at 220–500 °C, which can be attributed to loss of 4bpy and **L**, showing the collapse of the 3-D coordination framework. According to the remaining weight (obsd: 29.66%), the final residue seemed to be zinc oxide (calcd: 26.81%).

3.5. *Luminescent properties*

Coordination complexes constructed from d^{10} metal centers and relevant organic linkers are promising candidates for hybrid photoactive materials with potential applications such as light-emitting diodes [7, 28]. Thus, solid-state emission spectra of **1** and **2** have been investigated at room temperature (see figure 3). They exhibit intense luminescence with the peak maximum at 398 nm for **1** and 414 nm for **2**. To further analyze the nature of these emission bands, the photoluminescent properties of H_2**L** and 4bpy have also been explored

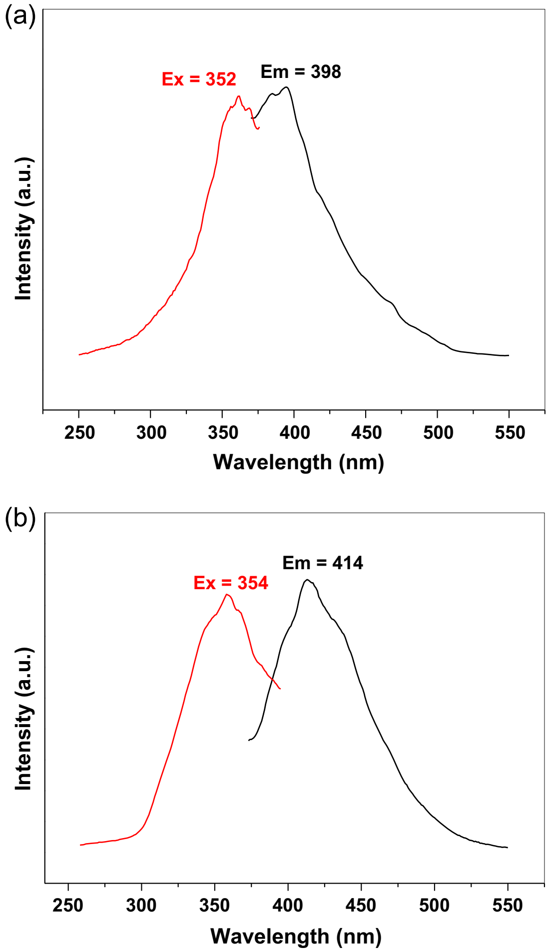

Figure 3. Solid-state excitation/emission spectra of (a) for **1** and (b) for **2** at room temperature.

in this research (figure S4). By comparing the locations and profiles of their excitation/emission peaks with **1** and **2**, the emission peaks were similar to that of 4bpy. Their origins can be tentatively assigned to the $\pi \rightarrow \pi^*$ intraligand fluorescence, ligand-to-ligand charge transfer. Emissions of these d^{10} complexes are neither metal-to-ligand charge transfer nor ligand-to-metal charge transfer [29]. Emission maxima of **1** and **2** are red-shifted compared to that of 4bpy [46 nm (**1**) and 62 nm (**2**)], which may be due to the bridging effect of the relevant ligands to the metal centers, effectively increasing the rigidity and conjugation upon metal coordination and reducing the loss of energy via a radiation-less pathway [28].

4. Conclusion

We synthesized two isomorphic 3-D complexes, $[M(\mathbf{L})(4bpy)_{0.5}(H_2O)]_\infty$ [M = Cd (**1**) and Zn (**2**)], by employing 1,1-cyclobutanedicarboxylic acid ($H_2\mathbf{L}$) and 4,4′-bipyridine (4bpy). The complexes feature (3,4)-connected $(6^3)(6^5.8)$ topological nets consisting of pillared 2-D $[M(\mathbf{L})(H_2O)]_\infty$ layers. The pyridine-based linker can be a pillar to bridge the metal-carboxylate layers into higher dimensionality to alter the structural topology. Finally, two complexes can be excited and emit strong fluorescence at room temperature, which may make them candidates for fluorescent materials.

Supplementary material

CCDC Nos. 997905 and 997906 contain the supplementary crystallographic data for **1** and **2**, respectively. These materials can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or Email: deposit@ccdc.cam.ac.uk.

Disclosure statement

No potential conflict of interest was reported by the authors.

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