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Syntheses, structures, and properties of two metal-organic frameworks comprising bpdc (2,2'-biphenyldicarboxylate) and bipb (2,2'-bis(imidazol-1-ylmethyl)-biphenyl)

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Syntheses, structures, and properties of two metal-organic frameworks comprising bpdc (2,2'-biphenyldicarboxylate) and bipb (2,2'-bis(imidazol-1-ylmethyl)-biphenyl)

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Two new coordination polymers, $[\text{Cd}(\text{bpdc})(\text{bipb})(\text{H}_2\text{O})_2]_n$ (**1**) and $[\text{Zn}(\text{bpdc})(\text{bipb})]_n$ (**2**), have been hydrothermally synthesized from 2,2'-biphenyldicarboxylate (bpdc) and 2,2'-bis(imidazol-1-ylmethyl)-biphenyl (bipb). Polymer **1** features a 1-D tubelike porous chain along the *a* direction with coordinated water molecules occupying the pores. The double-chain of polymer **2** possesses alternating rectangular rings $[(\text{bpdc})_2\text{Zn}_2]$ and $[(\text{bipb})_2\text{Zn}_2]$ with Zn as nodes. The polymers exhibit strong fluorescent emissions in the solid state at room temperature and could be significant as photoactive materials.

Keywords: d^{10} Metal ions; Crystal structures; Fluorescent properties

1. Introduction

Design and assembly of metal coordination polymers has received considerable attention [1–5] for their crystallographic diversity and a myriad of applications [6, 7]. The design of coordination polymers depends on selection of ligands, the nature of the metal ions, counterions, and other factors [8–10]. Judicious selection of multifunctional organic ligands, which contain appropriate coordination sites linked by a spacer with special orientation, is crucial to construction of desirable frameworks [11]. Many metal-organic frameworks (MOFs) in which polycarboxylates or imidazole derivatives are used as bridging ligands to assemble coordination polymers have been reported [12]. 2,2'-biphenyldicarboxylate (bpdc) is characteristic of multifunctional coordination sites as well as structural flexibility and conformational freedom. Taking advantage of these peculiar characterizations, bpdc links metal ions or metal clusters into macrocycles or helical chains and provides abundant structural motifs [13, 14]. Transition metal ions with a d^{10} configuration can produce complexes with appealing structures and photoluminescence properties [15, 16]. To expand such interesting systems, we chose

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Zn(II) and Cd(II) to assemble with bpdc and bibp. Two new coordination polymers, $[\text{Cd}(\text{bpdc})(\text{bibp})(\text{H}_2\text{O})_2]_n$ (**1**) and $[\text{Zn}(\text{bpdc})(\text{bibp})]_n$ (**2**), were prepared and structurally characterized. The polymers exhibit varied structural features and binding modes of the ligands.

2. Experimental

2.1. Materials and methods

All chemicals were of reagent grade quality obtained from commercial sources and used as received. 2,2'-bis(imidazol-1-ylmethyl)-biphenyl was prepared according to the reported procedures [17]. Elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 240C analytical instrument. Infrared (IR) spectra were recorded on a Bruker Vector22 spectrophotometer with KBr pellets in the 4000–400 cm^{-1} region. Luminescence spectra for solid samples were recorded with a Hitachi 850 fluorescence spectrophotometer. Powder X-ray diffraction (PXRD) patterns of **1** and **2** were recorded at 293 K on a Bruker D8 Advance diffractometer (Cu-K α , $\lambda = 1.54056 \text{ \AA}$) operated at 40 kV and 30 mA using a Cu-target tube and a graphite monochromator. Thermogravimetric analyses (TGA) were carried out on a Perkin-Elmer Diamond SII thermal analyzer from room temperature to 900°C under nitrogen at a heating rate of 10°C min^{-1} .

2.2. Preparation of $[\text{Cd}(\text{bpdc})(\text{bibp})(\text{H}_2\text{O})_2]_n$ (**1**)

A mixture of $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ (0.5 mmol), bpdc (0.5 mmol), bibp (0.5 mmol), NaOH (1 mmol), and H_2O (6 mL) was placed in a Parr Teflon-lined stainless steel vessel (25 cm^3), and then the vessel was sealed and heated at 120°C for 3 days. After the mixture was slowly cooled to room temperature, colorless crystals of **1** were obtained (yield: 46% based on Cd). Calcd for $\text{C}_{34}\text{H}_{30}\text{N}_4\text{O}_6\text{Cd}$: C, 58.09; H, 4.30; N, 7.97. Found: C, 58.32; H, 4.71; N, 7.72. IR spectrum (cm^{-1}): 3445(m), 3155(m), 1600(m), 1562(s), 1477(w), 1438(m), 1405(s), 1282(w), 1250(w), 1225(w), 1107(m), 1084(m), 1030(w), 936(s), 852(m), 768(m), 752(m), 731(m), 697(w), 682(w), 656(w), 628(w), 561(w).

2.3. Preparation of $[\text{Zn}(\text{bpdc})(\text{bibp})]_n$ (**2**)

The synthesis was similar to that described for **1** except using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol) instead of $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$. The mixture was heated at 140°C for 3 days, and colorless crystals of **2** were obtained (yield: 50% based on Zn). Anal. Calcd for $\text{C}_{34}\text{H}_{26}\text{N}_4\text{O}_4\text{Zn}$: C, 65.87; H, 4.23; N, 9.04. Found: C, 65.65; H, 5.51; N, 9.23. IR spectrum (cm^{-1}): 3423(m), 3112(m), 3053(w), 1622(s), 1524(m), 1477(w), 1441(m), 1387(s), 1355(s), 1290(w), 1231(s), 1151(w), 1097(m), 1027(w), 952(w), 842(w), 763(m), 703(w), 655(w), 553(w), 452(w).

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

	1	2
Formula	C ₃₄ H ₃₀ N ₄ O ₆ Cd	C ₃₄ H ₂₆ N ₄ O ₄ Zn
Formula weight	703.02	619.96
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2(1)/ <i>n</i>
Unit cell dimensions (Å, °)		
<i>a</i>	9.165(4)	14.527(3)
<i>b</i>	12.917(6)	9.860(2)
<i>c</i>	13.188(6)	20.101(4)
α	96.506(9)	
β	91.320(8)	91.934(3)
γ	93.958(8)	
Volume (Å ³), <i>Z</i>	1546.8(13), 2	2877.4(11), 4
Temperature (K)	293(2)	293(2)
Calculated density (Mg m ⁻³)	1.509	1.431
Absorption coefficient (mm ⁻¹)	0.758	0.900
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.072	0.049
<i>R</i> ₁ (all data)	0.162	0.102
<i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.177	0.080
<i>wR</i> ₂ (all data)	0.260	0.087
Goodness-of-fit on <i>F</i> ²	1.001	1.011

2.4. X-ray crystallography

Parameters for data collection and refinement of the polymers are summarized in table 1. Intensities were collected on a Siemens SMART-CCD diffractometer with graphite-monochromated Mo-K α ($\lambda = 0.71073$ Å) radiation using the SMART and SAINT programs [18]. Forty-five frames of data were collected at 298 K with an oscillation range of 1° per frame and an exposure time of 10 s per frame. Indexing and unit cell refinement were based on all observed reflections from those 45 frames. The structures were solved by direct methods and refined on *F*² by full-matrix least-squares with SHELXTL version 5.1 [19]. All non-hydrogen atoms except disordered solvent were refined with anisotropic thermal displacement coefficients. Hydrogens were located geometrically and those of solvent were found on Fourier difference maps; all hydrogens were refined in a riding model. Bond distances and angles are provided in table 2.

3. Results and discussion

3.1. Crystal structure of [Cd(bpdc)(bibp)(H₂O)₂]_{*n*} (**1**)

A single-crystal X-ray diffraction study reveals that **1** adopts a 1-D supramolecular structure. As shown in figure 1(a), the Cd(II) has distorted octahedral coordination, defined by two different bibp nitrogen donors occupying axial positions with Cd–N bond distances varying from 2.240(1) to 2.296(1) Å, while the equatorial positions are furnished by two carboxylate oxygens from one bpdc, one carboxylate oxygen from another bpdc, and one coordinated water molecule with Cd–O bond distances varying from 2.326(1) to 2.467(1) Å. These bond lengths are comparable to reported values [12h, 12i].

The bibp establishes a bridge between Cd's, imposing Cd(1)⋯Cd(1A) separations of 6.265 Å (symmetric code A: $-x, -y, -z$) and forming a bimetallic rectangular unit with

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

Polymer 1			
Cd(1)–N(1)	2.240(1)	Cd(1)–O(5)	2.342(1)
Cd(1)–N(4)#1	2.296(1)	Cd(1)–O(4)#2	2.439(1)
Cd(1)–O(1)	2.326(1)	Cd(1)–O(3)#2	2.467(1)
N(1)–Cd(1)–O(5)	169.0(4)	N(1)–Cd(1)–O(1)	103.8(4)
N(4)#1–Cd(1)–O(1)	86.7(4)	N(1)–Cd(1)–O(5)	88.0(4)
N(4)#1–Cd(1)–O(5)	83.1(4)	O(1)–Cd(1)–O(5)	124.8(4)
N(1)–Cd(1)–O(4)#2	92.0(4)	N(4)#1–Cd(1)–O(4)#2	82.0(4)
O(1)–Cd(1)–O(4)#2	138.9(4)	O(5)–Cd(1)–O(4)#2	93.0(4)
N(1)–Cd(1)–O(3)#2	83.2(4)	N(4)#1–Cd(1)–O(3)#2	100.2(4)
O(1)–Cd(1)–O(3)#2	91.1(4)	O(5)–Cd(1)–O(3)#2	144.1(4)
O(4)#2–Cd(1)–O(3)#2	52.8(3)		
Polymer 2			
Zn(1)–O(1)#1	1.904(3)	Zn(1)–O(3)	1.958(3)
Zn(1)–N(1)	2.012(4)	Zn(1)–N(4)#2	2.028(4)
O(1)#1–Zn(1)–O(3)	95.6(2)	O(1)#1–Zn(1)–N(1)	119.3(2)
O(3)–Zn(1)–N(1)	113.1(2)	O(1)#1–Zn(1)–N(4)#2	112.1(2)
O(3)–Zn(1)–N(4)#2	118.4(2)	N(1)–Zn(1)–N(4)#2	99.7(2)

Symmetry transformations used to generate equivalent atoms: for polymer **1**: #1: $-x, -y, -z$; #2: $x-1, y, z$; for polymer **2**: #1: $-x+1, -y, -z$; #2: $-x+1, -y+1, -z$

N–Cd–N angle of 169° . Two Cd(II) centers are linked by bibp through imidazole N-donors into a 28-membered box macrocycle. This cavity, however, is arguably not a rectangular box, because not all the sides are truly face-to-face parallel. In each bibp there are dramatic twists between two phenyl rings with dihedral angles being 81.9° , approximately perpendicular. The dihedral angle between the two imidazole rings coordinated to one Cd(II) is 114.6° . Taking advantage of these twists, the approximate dimensions of the rectangles are 6.3×13.1 Å, measured by the distance between the two Cd(II) centers and the distance of between C(9) and C(9A). Fully deprotonated bpdc anions are tridentate bridging ligands, linking the bimetallic rectangular unit with chelating carboxylate and monodentate carboxylate, imposing Cd...Cd separations of 9.165 Å. Thus the dinuclear unit is interconnected through bpdc to yield a 1-D tubelike chain along the *a* direction. The symmetry related (symmetric code B: $-x, -y, -z$) phenyl rings are absolutely parallel and the closest distance is C(6)...C(23) = 3.64 Å, indicating weak $\pi \cdots \pi$ interaction. Therefore, these 1-D tubelike chains are connected through hydrogen bonds to form a 3-D supramolecular architecture.

The uncoordinated carboxylate oxygen and coordination water are included in the void and not bonded to other metals and therefore do not increase the dimensionality of the coordination frameworks. The lattice water O(1W) forms a strong hydrogen bond with the monocoordinated carboxylate oxygen O(1) and is trapped out of the pores. (The detailed data for hydrogen bonds are O(1W)...O(1) = 2.766 Å, O(1W)–H(1W) = 0.85 Å, and H(1W)...O(1) = 1.95 Å and the angle of O(1W)–H(1W)...O(1) = 160° .)

3.2. Crystal structure of [Zn(bpdc)(bibp)]_n (**2**)

Although the ligands are the same as in **1**, the structure of **2** is significantly different because of the replacement of the cadmium by zinc. In addition, two carboxylates of each bpdc are deprotonated and bpdc adopts a coordination mode, which is different

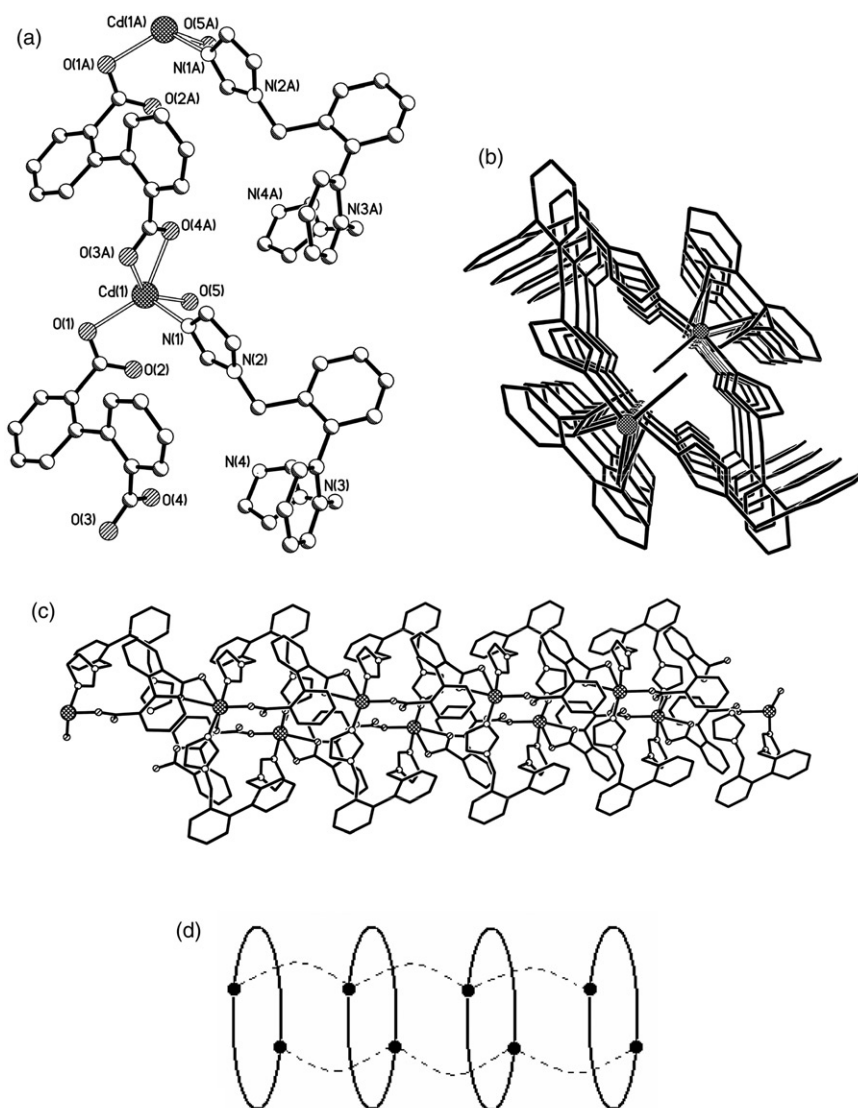


Figure 1. (a) Perspective view of the coordination environments of Cd; (b) the cavity running along the *a*-axis; (c) 1-D chain with hydrogens and free water molecules omitted for clarity in **1**; and (d) simplified 1-D chain representation of **1**. The solid line stands for bibp, dashed line for bpdc.

from that in **1**. Polymer **2** crystallizes in the space group $P2(1)/n$, and each Zn(II) exhibits tetrahedral coordination formed by two oxygens from two bpdc and two individual bibp nitrogens, as illustrated in figure 2(a). Zn–O bond distances range from 1.904(3) to 1.958(3) Å, with O–Zn–O bond angles of $95.6(2)^\circ$. The average Zn–N bond lengths are 2.020 Å, with N–Zn–N bond angles of $99.7(2)^\circ$. These bond lengths are comparable to reported values [12].

As for **1**, two bibp ligands are bridge spacers linking two Zn's and forming a bimetallic rectangle with N–Zn–N angle of 99.7° . In each bibp there are dramatic twists

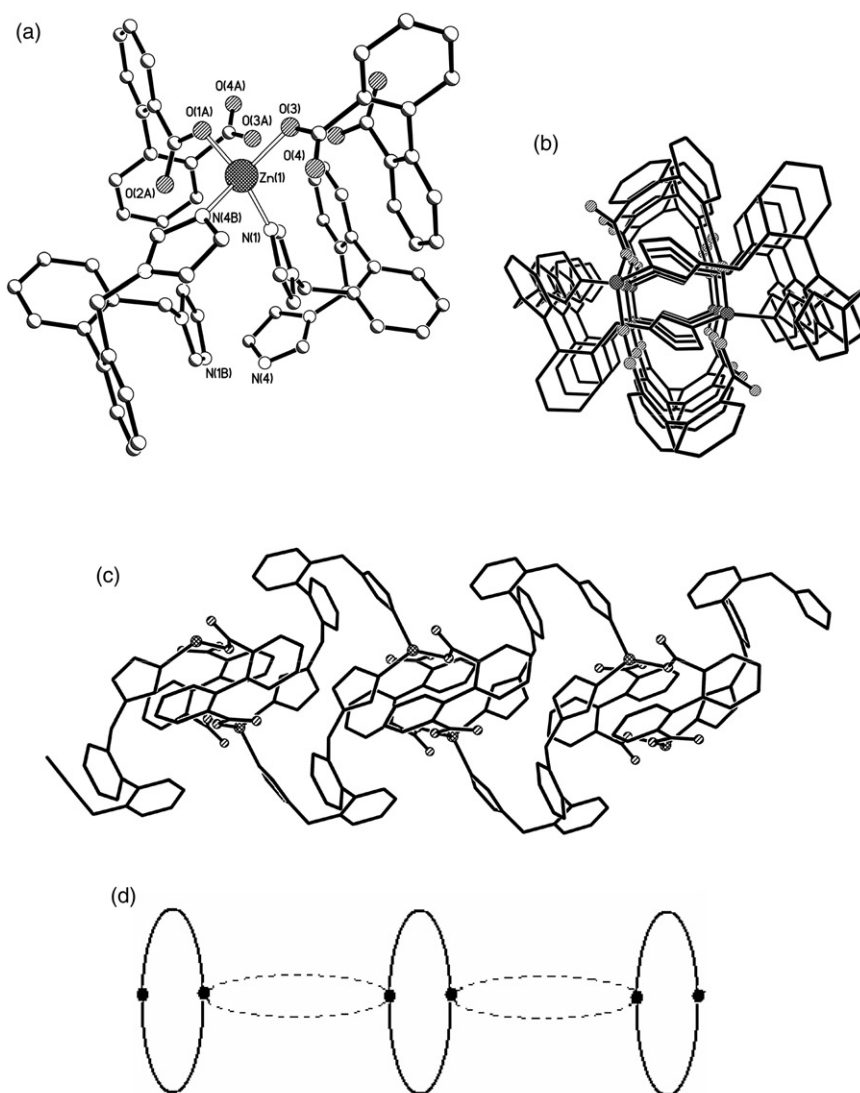


Figure 2. (a) Perspective view of the coordination environment of Zn; (b) the pore running along the *b*-axis; (c) 1-D ring-ring chain along the *a*-axis with hydrogens and free water molecules omitted for clarity in **2**; and (d) simplified 1-D chain representation of **2**. The solid line stands for bipb, dashed line for bipc.

between two phenyl rings with the dihedral angles being 100.4° , larger than that in **1**. The dihedral angle between the two imidazole rings coordinated to one Zn(II) is 85.0° . In the structure, the above two separate units are linked by two bipc ligands, which are bidentate bridging, linking Zn centers by monodentate carboxylate, forming infinite double-chains. In each bipc, the twists between two phenyl rings (dihedral angles of 101.7°) are smaller than that in **1**.

The salient structural feature of **2** is the combination of bipc and bipb containing flexible backbones, together with Zn centers (nodes) with tetrahedral coordination.

As shown in figure 2(b) and (c), the double-chains possess alternating rectangular rings [(bpdc)₂Zn₂] and [(bibp)₂Zn₂]. Taking advantage of these twists, the approximate dimensions of the rectangles are 4.5 × 8.9 Å for [(bpdc)₂Zn₂] and 8.9 × 13.2 Å for [(bibp)₂Zn₂]. Because of the hindrance from two neighboring phenyl rings, **1** and **2** only form 1-D polymers. The phenyl ring and symmetry related imidazole C(17) (symmetric code C: *x*, *y* − 1, *z*) exhibit weak C–H··· π interaction, and the distance between the shortest atoms is 3.36 Å, consolidating the 1-D structure.

3.3. PXRD and fluorescent properties of **1** and **2**

To confirm the phase purity of the bulk materials, PXRD experiments have been carried out for **1** and **2**. The PXRD experimental and computer-simulated patterns of **1** and **2** are shown in figure S1, “Supplementary material”. Although the experimental patterns have a few un-indexed diffraction lines and some are slightly broadened in comparison with those simulated from the single-crystal models, it still can be well-considered that the bulk synthesized materials and the crystals used for diffraction are homogeneous for **1** and **2**.

Metal-organic polymers with a d¹⁰ closed-shell electronic configuration exhibit fluorescence properties. Here, the fluorescent properties of **1** and **2** in the solid state at room temperature are investigated. Excitation at 360 nm leads to stronger blue fluorescent emission at 422 nm for **2** while weaker blue fluorescent emission at 427 nm for **1**, under the same conditions (figure 3). These emissions are neither metal-to-ligand charge transfer nor ligand-to-metal charge transfer since the Zn²⁺ and Cd²⁺ are difficult to oxidize or to reduce due to their d¹⁰ configuration and can probably be assigned to the intraligand (π – π^*) fluorescent emission because free bpdc and bibp ligands display fluorescent properties in the solid state with emission maxima located at 415 and 457 nm, respectively [20]. It is clear that shift of emission occurs in the polymers, probably due to differences of ligands and coordination environment around the central metal, because photoluminescence behavior is closely associated with the local environments around metal ions [21]. Polymers **1** and **2** are excellent candidates of blue fluorescent materials.

3.4. Thermal properties of **1** and **2**

The TG curve of **1** (figure S2, Supplementary material) shows a total weight loss of 82.7% at 35–900°C, which agrees with the calculated value of 81.8%. The weight loss of 4.6% at 35–120°C corresponds to loss of all coordinated water (Calcd 5.1%). The weight loss of 46.1% at 120–345°C arises from decomposition of bibp (Calcd 44.7%). The stage, occurring between 345°C and 900°C, corresponds to decomposition of bpdc. The residual percentage weight of 17.3% is consistent with the formation of CdO (Calcd 18.2%).

The TG curve of **2** from 27 to 900°C exhibits weight loss stages similar to those observed for **1** (see figure S2, Supplementary material). The overall weight loss of 85.1% is in agreement with the calculated value of 86.8%, considering the decomposition of bibp and bpdc. The residual percentage weight is consistent with the formation of ZnO.

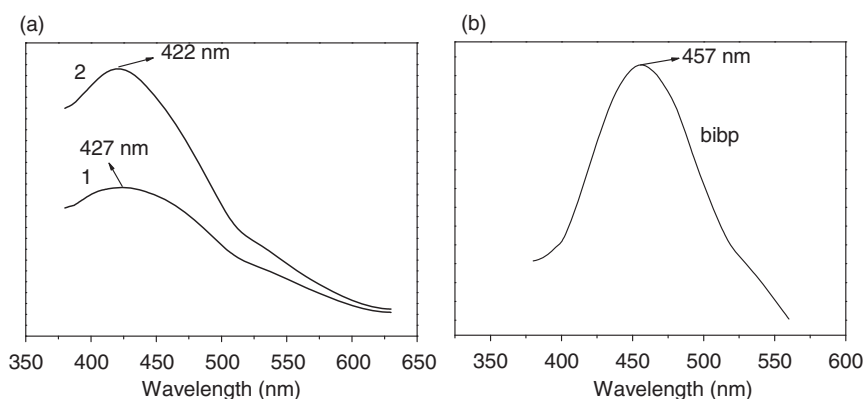


Figure 3. (a) The emission spectra of **1** and **2** and (b) free ligand bibp in the solid state at room temperature.

4. Conclusion

Two polymers with different architectures, $[\text{Cd}(\text{bpdc})(\text{bibp})(\text{H}_2\text{O})_2]_n$ (**1**) and $[\text{Zn}(\text{bpdc})(\text{bibp})]_n$ (**2**), were constructed from bpdc in the presence of bibp used as spacers under mild hydrothermal conditions. Polymer **1** features a 1-D tubelike porous chain. The double-chain of **2** possesses alternating rectangular rings $[(\text{bpdc})_2\text{Zn}_2]$ and $[(\text{bibp})_2\text{Zn}_2]$. This study demonstrates that the nature of ligands and the geometric needs of metals play an important role in the crystal packing of MOFs. In addition, PXRD, fluorescent properties, and thermal properties of polymers **1** and **2** were studied. Polymers **1** and **2** may be excellent candidates for blue fluorescent material.

Supplementary material

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Center (CCDC Nos 820802 and 820803). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code +(1223)336-033; E-mail: teched@chemcrs.cam.ac.uk).

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