

ASSEMBLY OF TWO LUMINESCENT CADMIUM(II) 4,4'-PHOSPHINI CO-DIBENZOATE COORDINATION POLYMERS

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ABSTRACT. Two new cadmium(II) coordination polymers $[\text{Cd}(\text{HL})(\text{H}_2\text{O})] \cdot 1.5\text{H}_2\text{O}$ (**1**) and $[\text{Cd}(\text{HL})(4\text{-bump})_{0.5}] \cdot 2\text{H}_2\text{O}$ (**2**) ($\text{H}_3\text{L} = 4,4'$ -phosphinicobis-dibenzoic acid, and 4-bump = N,N' -bis(4-pyridylmethyl)piperazine) have been synthesized by self-assembly of CdCl_2 with 4,4'-phosphinicobis-dibenzoate, and N,N' -bis(4-pyridylmethyl)piperazine through solvothermal/hydrothermal method. Their structures were confirmed by X-ray single crystal diffraction, infrared spectrometer (IR), and powder X-ray diffraction (PXRD) and TGA techniques. Both compounds are in $P\bar{1}$ space group and exhibited a 2D networks constructed from dinuclear $[\text{Cd}_2(\text{POO})_2]$ or paddle-wheel $[\text{Cd}_2(\text{COO})_2(\text{POO})_2]$ units, respectively. In **2**, the Cd^{2+} is five-coordinated and shows a rare tetragonal pyramidal geometry. At room temperature, the compounds exhibit moderately intense blue and green fluorescence emission with peaks at 381 nm and 509 nm, respectively.

KEY WORDS: Cadmium(II) compounds, Photoluminescence, Carboxyphosphinate ligand

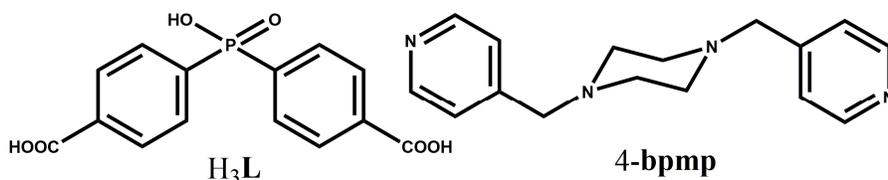
INTRODUCTION

Coordination polymers (CPs) composed of organic ligands and metal ion/atoms parts, are a kind of organic-inorganic intercrossed materials, that exhibit unique properties and broad potential applications in fluorescence, catalysis, sensing, magnetism, adsorption, and so on [1-7]. As ligands, carboxylate or phosphonate acids are widely used to build CPs, respectively [8-10]. Carboxyphosphinate acids combination of the two moieties, are a good types of ligands to construct CPs [11]. The carboxyphosphinate has abundant coordination modes, which produce structural diversity in the outcomes. Furthermore, the aromatic carboxylate of carboxyphosphinate with rigid skeletons usually connect metal ions to generate robust frameworks. In addition, the phosphinate group originating from phosphonate acid, has a strong coordination ability, which leads to strength in the stability of the resulting architecture [12, 13]. However, carboxyphosphinate ligands have not been extensively employed in assembly CPs [14, 15].

During the past years, our works have focused on using phosphinico-dibenzoate ligands to construct CPs [16, 17]. For instance, 2,2'-phosphinico-dibenzoate ligand tends to form low dimensional structures based on high-nuclear subunits, owing to the spatial hindrance between carboxylate and phosphinate [18, 19]. To reduce such steric hindrance, 4,4'-phosphinico-dibenzoate (H_3L) ligand, with carboxyl groups siting on the *para*-position of phosphinate, is used to build high-dimensional structures. As a result, its silver compound shows a 3D framework containing silver phosphinite chains [17], and its Mn(II) and Cu(II) compounds also exhibit 3D network with *crb* and *pcu* topologies, respectively [20]. N,N' -Bis(4-pyridylmethyl)piperazine (4-bump) is an N-donor linear ligand, which is often used for the formation CPs [21]. Cao *et al.* have synthesized two coordination polymers with 1D chain and 2D wave-like topologies only with 4-bump ligands and cadmium ions [22]. Furthermore, LaDuca and co-workers have also reported

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on many CPs with 2D and 3D topologies or interpenetrating mode based on the 4-bpmp ligands and carboxylate ligands [23–25]. These results indicate that the flexible long-spanning 4-bpmp ligand is an effective linker for constructing complexes with specific structures under hydrothermal conditions. To further explore and enrich the coordination characteristics of 4,4'-phosphinico-dibenzoate ligand and develop novel architectures with new functions, we utilized the linker and 4-bpmp (Scheme 1) as ligands react them with cadmium(II) ions, and harvested two 2D CPs. Both CPs exhibited 2D networks based on dinuclear $[\text{Cd}_2(\text{POO})_2]$ or paddle-wheel $[\text{Cd}_2(\text{COO})_2(\text{POO})_2]$ building blocks, respectively. It was found that Cd^{2+} showed a rare tetragonal pyramid geometry in one compound. In this paper, the syntheses, crystal structures, and luminescent properties of two compounds $[\text{Cd}(\text{HL})(\text{H}_2\text{O})] \cdot 1.5\text{H}_2\text{O}$ (**1**) and $[\text{Cd}(\text{HL})(4\text{-bpmp})_{0.5}] \cdot 2\text{H}_2\text{O}$ (**2**) are discussed in details.



Scheme 1. Diagram of H_3L and 4-bpmp.

EXPERIMENTAL

Materials and methods

All reagents and solvents employed in the present work were of analytical grade as obtained from commercial sources without further purification. 4,4'-Phosphinico-dibenzoate acid (H_3L) and *N,N'*-bis(4-pyridylmethyl)piperazine, were prepared as to previously described [26, 27]. The elemental C and H analyses were performed on a Vario EL-III elemental analyzer. IR spectra with KBr pellets were collected on a Nicolet Avatar A370 spectrophotometer. Using a Rigaku D/Max-2200 diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$), PXRD was carried over the 2θ range from 5 to 50° . TGA were performed at a $10^\circ\text{C}/\text{min}$ heating rate, on a Netzsch STA 449C thermal analyzer, in nitrogen atmosphere. The Shimadzu RF-5310 fluorescence spectrophotometer was used to record the solid luminescent spectra of the compounds.

Synthesis of $[\text{Cd}(\text{HL})(\text{H}_2\text{O})] \cdot 1.5\text{H}_2\text{O}$ (**1**)

$\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (22.8 mg, 0.1 mmol), H_3L (15.3 mg, 0.05 mmol), H_2O (4 mL), EtOH (4 mL), and two drops of $1.0 \text{ mol} \cdot \text{L}^{-1}$ NaOH solvent were mixed in a sealed 20 mL Teflon-lined stainless steel autoclave. The mixture was heated then at 120°C for three days. After cooling at the rate of $10^\circ\text{C} \cdot \text{h}^{-1}$ to room temperature, colorless block crystals of **1** were harvested in 64% yield based on H_3L ligand. Elemental analyses calcd (%) for $\text{C}_{28}\text{H}_{28}\text{Cd}_2\text{O}_{17}\text{P}_2$ (923.24): C, 36.42; H, 3.06. Found: C, 36.59; H, 3.02. IR/ cm^{-1} (KBr): 3275 (w), 1696 (s), 1577 (m), 1524 (s), 1401 (s), 1228 (m), 1173 (m), 1110 (m), 1040 (w), 1006 (w), 861 (m), 775 (m), 740 (w), 700 (w), 595 (w), 557 (w).

Synthesis of $[\text{Cd}(\text{HL})(4\text{-bpmp})_{0.5}] \cdot 2\text{H}_2\text{O}$ (**2**)

A mixture of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (37.5 mg, 0.16 mmol), H_3L (30.6 mg, 0.1 mmol), 4-bpmp (26.7 mg, 0.1 mmol), and H_2O (8 mL) with one drop of $1.0 \text{ mol} \cdot \text{L}^{-1}$ NaOH solvent was heated in a sealed autoclave at 160°C for 3 days. With a cooling rate of $10^\circ\text{C} \cdot \text{h}^{-1}$ to room temperature, colorless

block crystals of **2** were collected in 86% yield based on H₃L ligand. Elemental analyses calcd (%) for C₂₂H₂₃CdN₂O₈P (586.79): C, 45.03; H, 3.95; N, 4.77. Found: C, 45.14; H, 4.02; N, 4.68. IR/cm⁻¹ (KBr): 3423 (w), 1619 (m), 1590 (s), 1547 (m), 1394 (s), 1326 (w), 1153 (m), 1116 (m), 1033 (m), 1010 (m), 980 (w), 861 (m), 810 (m), 772 (m), 732 (m), 703 (m), 630 (w), 591 (m), 551 (w), 467 (m).

X-ray crystallography

Using the phi and omega scan technique, single-crystal X-ray diffraction data of **1** and **2** were collected on a Bruker SMART APEX CCD diffractometer with graphite monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) at room temperature. With the Bruker SAINT package [28], data reduction was conducted. Absorption corrections were done using the numerical method implemented in SADABS program [29]. Using SHELXL-2013 [30], the structures were solved by direct methods and refined on F^2 by full-matrix least-squares. All non-hydrogen atoms are anisotropic displacement parameters. H atoms were introduced in calculations with the riding model. The crystallographic data and structural refinement results are listed in Table 1.

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

Compound	1	2
Temperature (K)	150(2)	296(2)
Formula	C ₂₈ H ₂₈ Cd ₂ O ₁₇ P ₂	C ₂₂ H ₂₃ CdN ₂ O ₈ P
Formula weight	923.24	586.79
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	6.1846(3)	9.3897(11)
<i>b</i> (Å)	10.9939(5)	9.9355(12)
<i>c</i> (Å)	12.0562(6)	13.9118(17)
α (deg)	94.6600(10)	79.681(2)
β (deg)	92.724(2)	73.413(2)
γ (deg)	102.8130(10)	64.9020(10)
<i>V</i> (Å ³)	794.87(7)	1123.9(2)
<i>Z</i>	1	2
<i>D_c</i> (g cm ⁻³)	1.929	1.734
μ (mm ⁻¹)	1.519	1.096
<i>F</i> (000)	458	592
<i>R</i> _{int}	0.0327	0.0252
GOF	1.085	1.054
<i>R</i> ₁ ^[a] , <i>wR</i> ₂ ^[b] [<i>I</i> > 2 σ (<i>I</i>)] (<i>I</i>)	0.0172, 0.0458	0.0467, 0.1089
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0174, 0.0459	0.0584, 0.1173

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $wR_2 = [\sum w(|F_o|^2 - |F_c|^2)|^2 / \sum w(|F_o|^2)]^{1/2}$.

RESULTS AND DISCUSSION

Syntheses and IR spectra

In this work, we explored the coordination polymers involving H₃L and one N-donor linear auxiliary ligand under solvothermal conditions. According to our previous reports on 2,2'-phosphinico-dibenzoate ligand, low-dimensional complexes can be easily obtained [18, 19]. Whilst, multi-dimensional frameworks might be prepared, when we introduced some linear auxiliary ligands in the carboxyphosphinate system [19]. Thus, a N-donor linear auxiliary ligand *N,N'*-bis(4-pyridylmethyl)piperazine was employed in a 4,4'-phosphinico-dibenzoate reaction

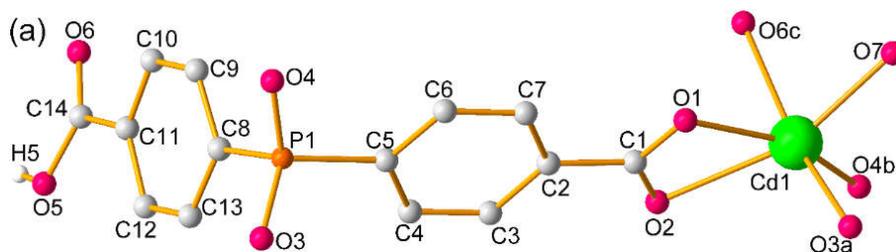
mixture with Cd(II) salts to influence the product structures, because it can be successfully employed to build metal dicarboxylate coordination polymers with plentifully unique topologies [31, 32]. Unfortunately, we found that the effect of the auxiliary ligand was negligible in this carboxyphosphinate system. The Cd(II) compound did not exhibit the expected three-dimensional structure even though ligand 4-bpmp was involved.

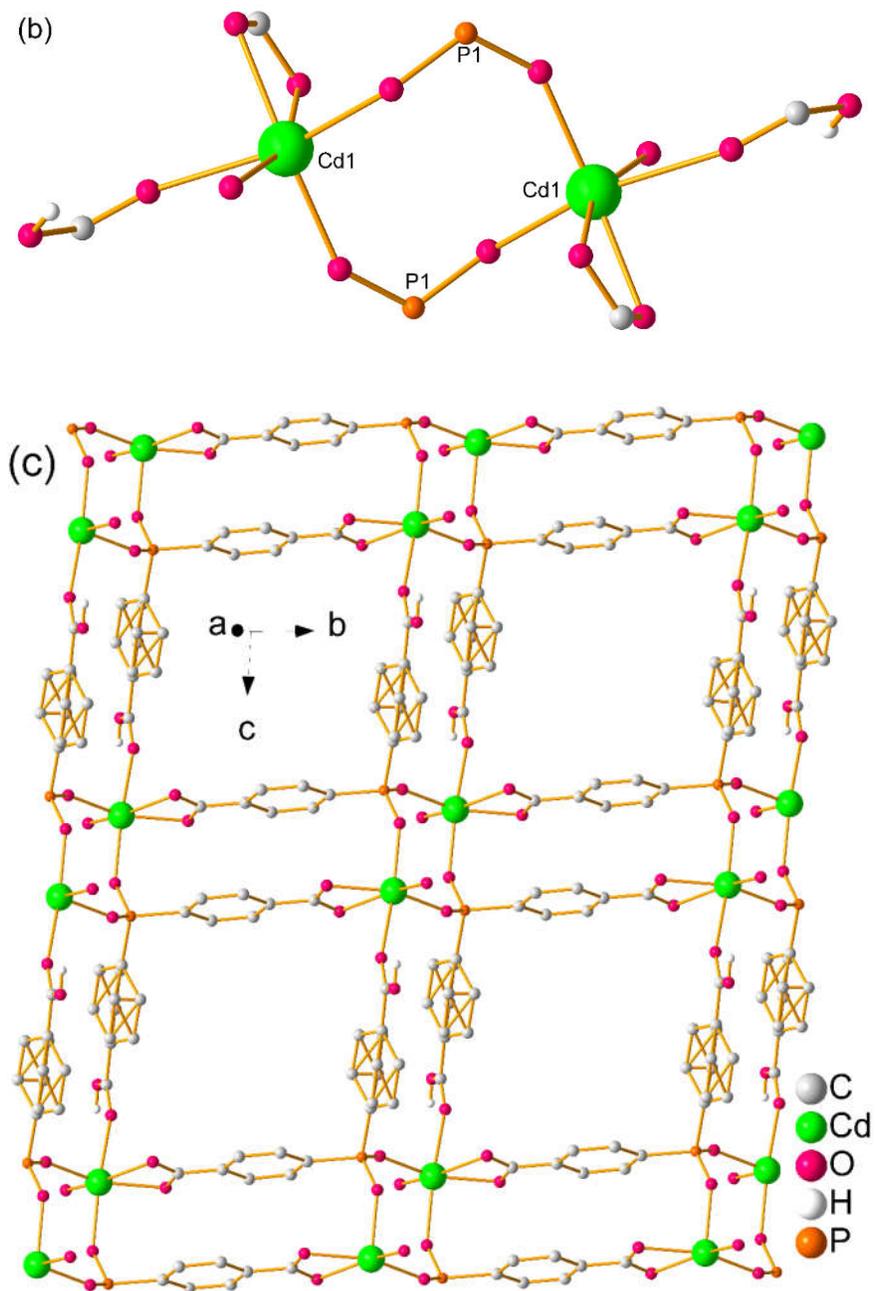
The infrared spectra of two compounds corresponding to the single crystal structural components. O-H stretching modes in water molecules exhibit weak, broad spectral features in a range of 3200-3500 cm^{-1} , along with N-H bonds of the protonated piperazinyl rings of 4-bpmp [33]. The carboxyl C-O group asymmetric (ν_{as}) and symmetric stretching vibrations (ν_{s}) are very strong, with bands near at 1524 and 1401 cm^{-1} for **1** and 1590 and 1394 cm^{-1} for **2**, respectively [34]. The P=O and P-O stretching vibration peaks appeared in the range of 1206-1122 cm^{-1} and 1069-903 cm^{-1} , respectively, which are inline to those of previously reported compounds [35]. The C-H vibrational bands from benzene ring of H_3L and pyridyl rings of the 4-bpmp are in the range of 1200-1600 cm^{-1} and 600-800 cm^{-1} , respectively [36].

Crystal structure of **1**

Compound **1** contains a 2D layer structure and crystallizes in the triclinic space group $P\bar{1}$. As in Figure 1a, the asymmetric units consist of one Cd(II) metal center, one $(\text{HL})^{2-}$ ligand, one coordinated water, and one and a half free water molecule. The Cd center displays a distorted octahedral configuration consisting of the carboxylate oxygens, phosphinate oxygens and water oxygen, respectively. The Cd-O bond distances are in the range of 2.1430(14) - 2.5047(13) Å.

In **1**, the ligand $(\text{HL})^{2-}$ adopts a $(\eta^1:\eta^1)-(\eta^1:\eta^1)-(\eta^1:\eta^0)-\mu_4$ coordination mode, connecting four Cd(II) ions. Thanks to this bridging mode, O-P=O unites two Cd(II) into a $[\text{Cd}_2(\text{POO})_2]^{2+}$ cluster (Figure 1b), which has been observed in its manganese complex $[\text{Mn}(\text{BPO})(\text{phen})]_n$ (BPO = bis(4-carboxylphenyl)phosphinic acid, phen = 1,10-phenanthroline) [37], but different from its reported cadmium(II) compound $[\text{Cd}_2(\text{HTPO})(\text{HBPO})(\text{H}_2\text{O})_2]_n$ (H_3TPO = tris(*p*-carboxylphenyl)phosphine oxide, H_3BPO = bis(4-carboxylphenyl)phosphinic acid) [38]. Linked by the carboxylates of $(\text{HL})^{2-}$ anion, these binuclear clusters are merged into a 2D network in *bc* plane (Figure 1c). Due to the single coordination pattern, the aromatic ring of a protonated carboxylic acid is in disorder along the *c*-axis, while the benzene ring of deprotonated carboxylate with chelate mode, is in order along the *b*-axis. Finally, the 2D layers grow up into a 3D supramolecular architecture as a result of hydrogen bond $\text{O5-H5}\cdots\text{O2}$ ($-x, -y+1, -z$) (Figure 1d). Meanwhile, the lattice waters sojourn in the gap of the supramolecular structure through hydrogen bonds.





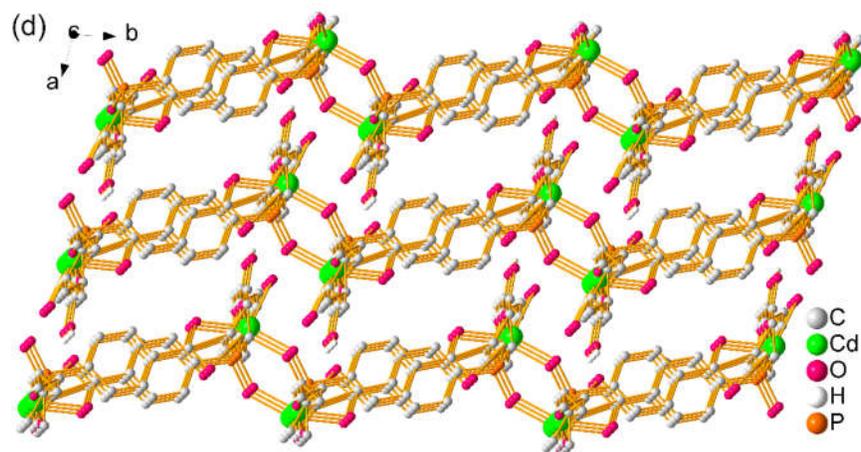
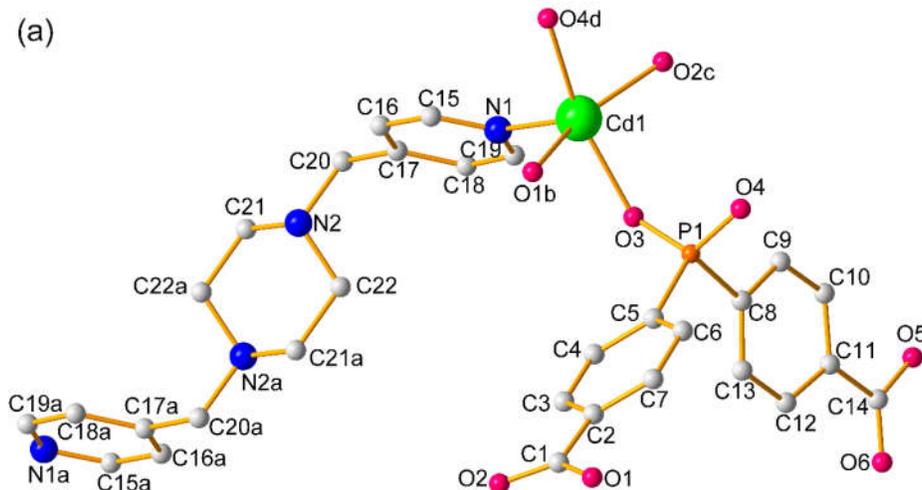
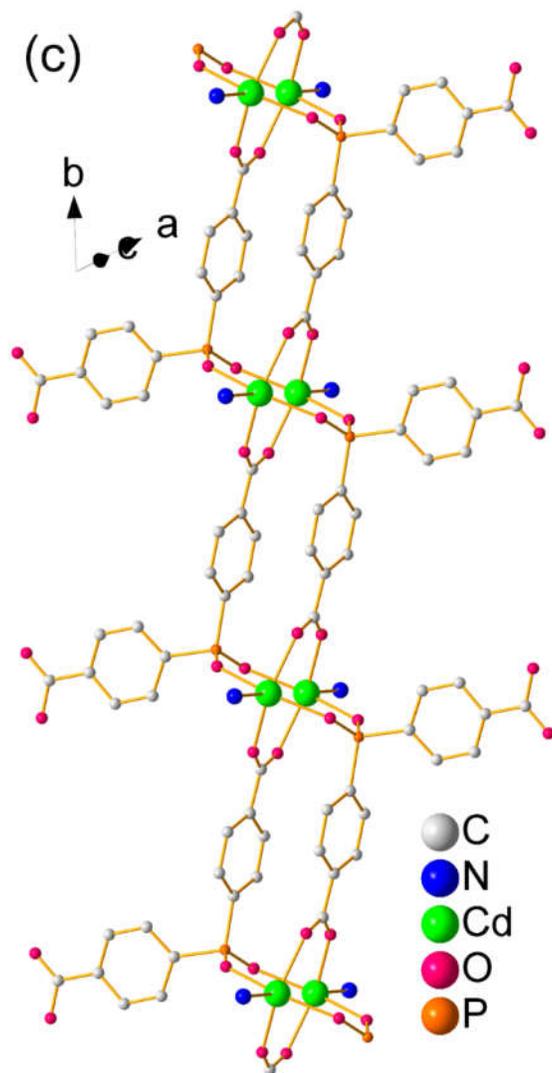
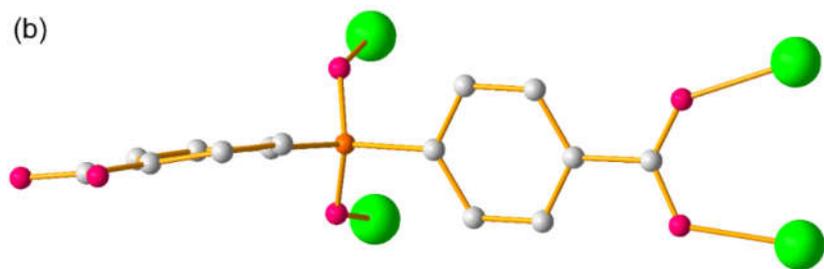


Figure 1. (a) Repeating part of **1**; (b) a $[\text{Cd}_2(\text{POO})_2]^{2+}$ cluster; (c) 2D network in bc -plane; (d) 3D supramolecular framework. For clarity, hydrogen atoms and lattice water molecules are ignored. Symmetry code: a: $-x+1, -y+1, -z+1$; b: $x, y-1, z$; c: $-x+1, -y+1, -z$.

Crystal structure of **2**

Compound **2** is a 2D structure and crystallizes in the same space group as **1**. The asymmetric moiety is made up of one Cd^{2+} center, one partially deprotonated $(\text{HL})^{2-}$ anion, half a 4-bmp ligand, and two free water molecules (Figure 2a). It should be noted that Cd1 is five-coordinated and exhibit a tetragonal pyramidal geometry, which is rare reported in the document [39, 40]. Four oxygens from two carboxylates and two phosphinates occupy the basal plane sites, and one nitrogen atom from 4-bmp is located in the apical position. The Cd-O bond lengths are in the range of 2.210(4) - 2.255(4) Å, while the Cd-N bond is 2.250(4) Å, which coincide with those of previously reported cadmium compounds [41].





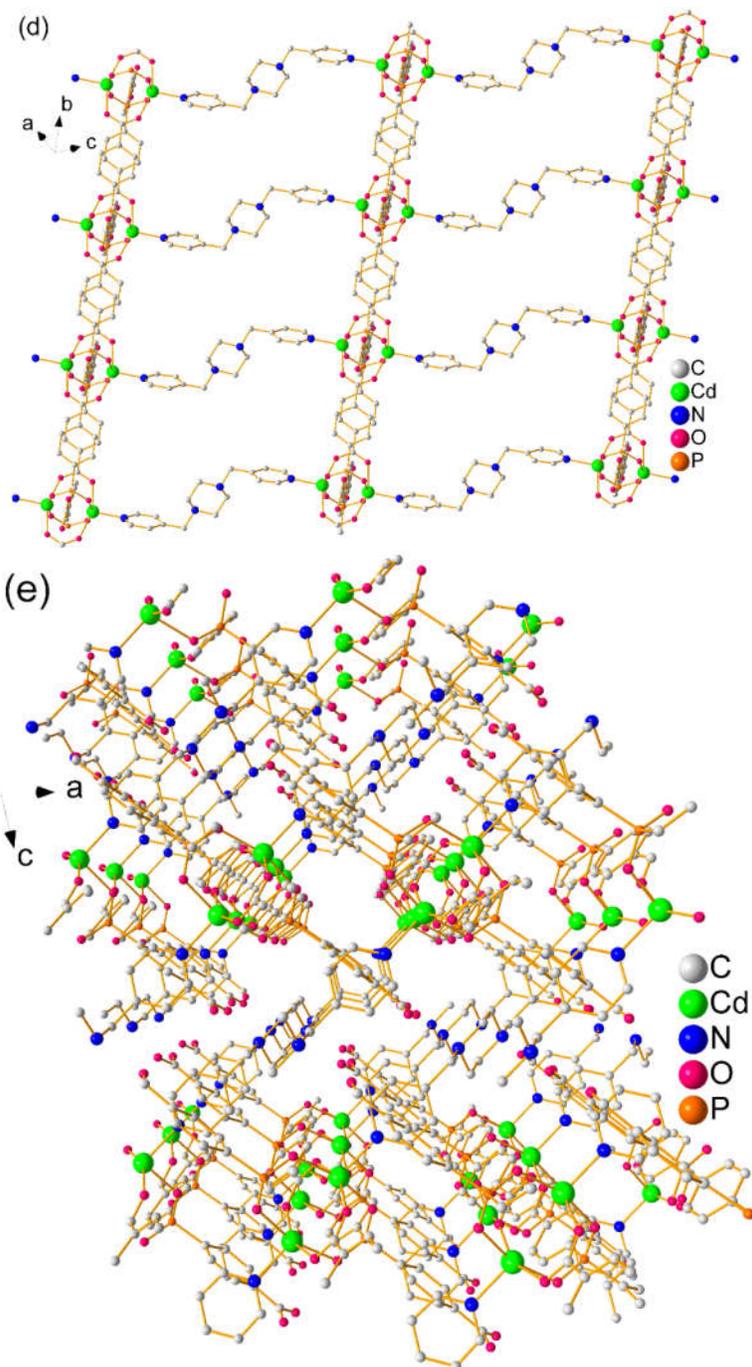


Figure 2. (a) Asymmetric unit of **2**; (b) Bridging mode of (HL)²⁻; (c) 1D chain along *b*-axis; (d) 2D layer; (e) 3D supramolecular stacking. For clarity, hydrogen atoms and lattice water molecules are deleted. Symmetry code: a: -x+2, -y, -z+1; b: -x, -y, -z+2; c: x, y+1, z; d: -x, -y+1, -z+2.

In compound **2**, the partially deprotonated (HL)²⁻ ligand demonstrates (η¹:η¹)-(η¹:η¹)-(η⁰:η⁰)-μ₄ coordination mode to connect four Cd(II) ions with carboxylate and phosphinate groups (Figure 2b). Two adjacent Cd ions are connected by two carboxylates and two phosphinates to result a paddle-wheel [Cd₂(COO)₂(POO)₂] binuclear with shortest Cd...Cd distance being 3.2364(8) Å. Meanwhile, the binuclear are linked by the deprotonated benzoate of (HL)²⁻ ligand to form a 1D chain along the *b*-axis (Figure 2c). Furthermore, bridged by 4-bpmp, the neighboring chains are extended to a 2D plane with the protonated benzoate of (HL)²⁻ ligand orienting towards outside (Figure 2d). Owing to this arrangement, the layers stack into a 3D framework through hydrogen bond O5-H5...N2 (*x*, *y*, *z*+1) occurring between protonated benzoate and 4-bpmp (Figure 2e). With hydrogen bonding interaction, free water molecules are embeded in the gap of the supramolecular framework.

Photoluminescence properties

The luminescent properties of Cd(II) compounds **1** and **2** were determined in the solid state at room temperature (Figure 3). Under the excitation of 320 nm, the photoluminescent spectra of H₃L showed a maximum emission peak at 347 nm, due to its π* → n and π* → π transitions [42]. Both compounds exhibit moderately intense blue and green fluorescence emission with the maxima at 381 nm (λ_{ex} = 333 nm) and 509 nm (λ_{ex} = 434 nm), respectively. The red shift of compound **1** can be attributed to changes in the energy levels of the metal as compared to the redshifts of free H₃L ligand, while the slightly larger red shift of emission maximum of compound **2** can be more likely ascribed to molecular orbital transition in the delocalized pyridine π system of free 4-bpmp ligand [43]. The different maximum emission wavelengths may be attributed to the disparity of coordination environment between the octahedron in **1** and the tetragonal core in **2** [44]. In comparison with free ligands, the slightly higher emission intensity of **1** and **2** can reasonably be considered as the outcome of the reduction of the energy loss mechanism of non-radiation vibration, for which the coordination of cadmium with benzene ring or pyridine ring results in conformational locking [45]. The photoluminescence study reveals that both compounds as potential luminescent materials.

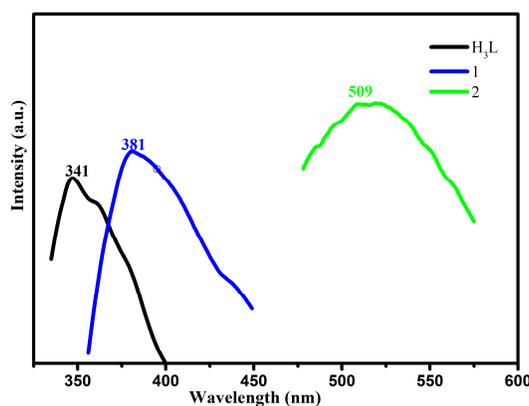


Figure 3. The solid-state luminescence of the free ligands, **1** and **2**.

PXRD and thermogravimetric analyses

To confirm the purity of the two compounds, the powder X-ray diffraction (PXRD) experiments at room temperature was carried out. As shown in Figure 4, the experimental patterns completely agreed with the simulated data, particularly at the main peak positions suggesting that the as-synthesized products are pure phase.

Under a nitrogen atmosphere, the thermal stability of polycrystalline samples **1** and **2** were determined at a heating rate of 10 K min^{-1} (Figure 5). For compound **1**, the TGA plots indicated that, the water molecule is lost until $200 \text{ }^\circ\text{C}$ (obsd 9.75%, calcd 9.74%), whilst the collapse of its skeleton came up above $400 \text{ }^\circ\text{C}$. In **2**, a slight loss of the solvent molecule with weight loss of 6.12% (calcd 6.13%) can be observed before heating to $250 \text{ }^\circ\text{C}$ attribute to water molecules lost, and its master ligand and auxiliary ligand continued to decompose at $387 \text{ }^\circ\text{C}$ and $419 \text{ }^\circ\text{C}$, respectively.

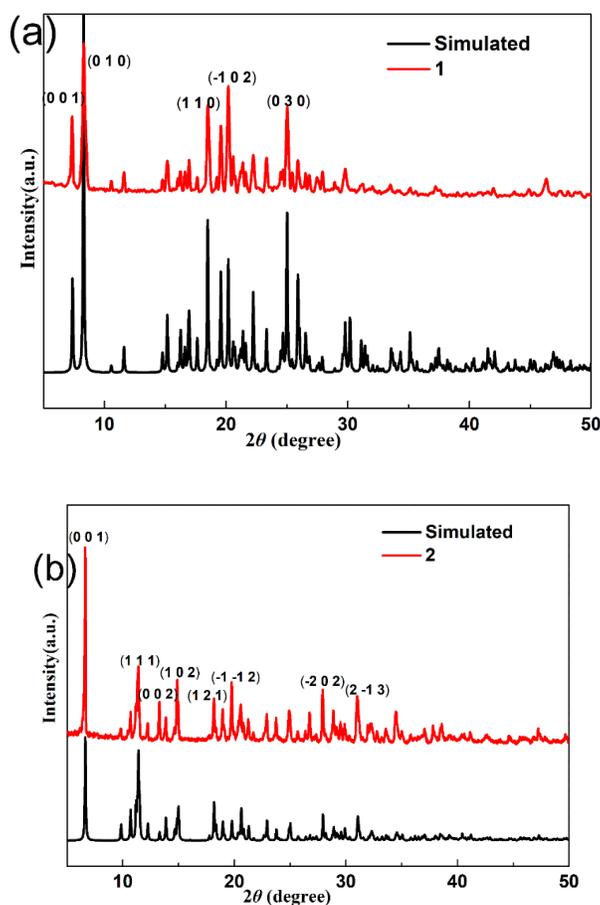


Figure 4. PXRD curves for **1** (a) and **2** (b).

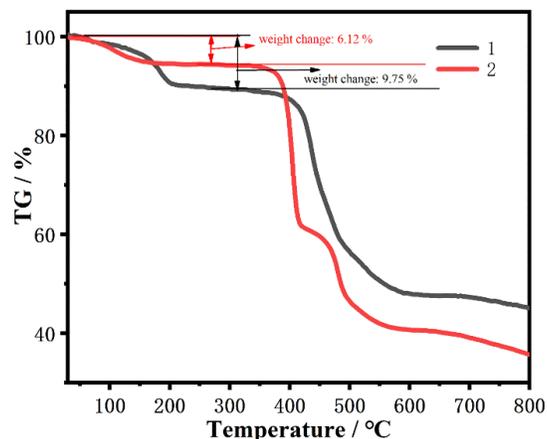


Figure 5. TGA curves for **1** and **2**.

CONCLUSION

We have successfully prepared two novel Cd(II) carboxyphosphinate coordination polymers by solvothermal/hydrothermal method and analyzed their structures by X-ray diffraction. Both **1** and **2** exhibit a 2D layer structures, even though relatively large radii of cadmium ions and co-ligands were employed in the preparation. In the two compounds, the carboxyphosphinate ligand is partially deprotonated and demonstrates a $(\eta^1:\eta^1)-(\eta^1:\eta^1)-(\eta^1:\eta^0)-\mu_4$ and $(\eta^1:\eta^1)-(\eta^1:\eta^1)-(\eta^0:\eta^0)-\mu_4$ coordination mode, respectively. For this reason, the two compounds could not expand into three-dimensional structures. However, the five-coordinated Cd^{2+} shows a rare tetragonal pyramidal geometry in compound **2**. The solid state photoluminescent properties of **1** and **2** explored at room temperature and they exhibited promising potentials as photoluminescent materials.

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Appendix A. Supplementary material

Crystallographic data for structures **1** and **2**, described in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 2084663 and 2084664, which can be obtained freely via E-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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