Metal ions directed assembly of two coordination polymers based on an organic phosphonate anion and a multidentate N-donor ligand

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25 ABSTRACT

Two new coordination polymers [Cd(4,4'-tmbpt)(HL)(H₂O)] (**1**) and [Cu(4,4'-tmbpt)(HL)]·H₂O (**2**) (H₃L = 2'-carboxybiphenyl-4-ylmethylphosphonic and 4,4'-tmbpt = 1-((1*H*-1,2,4-triazol-1-yl)methyl)-3,5-bis(4-pyridyl)-1,2,4-triazole) have been synthesized hydrothermally. The two compounds have the same metal to ligand ratio, but different metal ions. As a result, the two compounds display different 2D layer structures, which is mainly caused by the different coordination numbers of

the different metal ions. The effects of the metal ions on the structures, the optical band gaps and photoluminescent and photocatalytic properties of the compounds have been studied.

5 *Keywords:* Metal ions directed; Coordination polymer; Optical band gap; Photoluminescence; Photocatalysis

1. Introduction

Metal phosphonates have attracted much attention due to their diverse structures and applications in the fields of ion exchange [1], magnetism [2,3], proton-conducting [4,5], and so on. However, the preparation of crystals of metal phosphonates remains a challenge due to their poor crystallinity [6]. There are two main methods to improve the crystallinity of metal phosphonates. The first one is to introduce functional groups into the phosphonic acid ligands, which can improve the water-solubility of the final compounds and tune the crystallinity of metal phosphonates [7-10]. The second one is to introduce auxiliary ligands with excellent crystallinity into the reaction system of the phosphonic acid ligands [6].

Our previous work has demonstrated that the chelate N-donor ligands such as 1,10-phenanthroline and 2,2'-dipyridyl are good candidates for tuning the crystallinity of metal phosphonates [6], but these ligands always act as terminal ligands, which limit the extension of the structures. If we introduce other kinds of N-donor ligands such as 1,1'-(1,4-butanediyl)bis(imidazole) and 1,1'-(2,2'-oxybis(ethane-2,1-diyl))bis(1*H*-imidazole) into the reaction system of the phosphonic acid ligands, only the phosphonic acid ligands coordinate to the metal ions because of the strong coordination abilities.

On the other hand, coordination polymers are of current interest due to their various architectures and potential applications [11-16]. Coordination polymers are infinite systems constructed by metal ions and organic ligands via coordination bonds and other weak interactions. These compounds are also called metal-organic coordination networks or metal-organic frameworks (MOF) in the case of ordered structures [11].

Although innumerable coordination polymers have been reported up to now, the rational design and synthesis of coordination polymers remains a challenge because of the various influencing factors [17-21]. Among the factors, central metal ion is a key parameter.

Based on the above considerations, we have tried to introduce the multidentate N-donor ligand 1-((1*H*-1,2,4-triazol-1-yl)methyl)-3,5-bis(4-pyridyl)-1,2,4-triazole (4,4'-tmbpt, Scheme 1) with stronger coordination ability into the reaction system of 2'-carboxybiphenyl-4-ylmethylphosphonic acid (H_3L , Scheme 1), and employ two different metal ions as the central metals to investigate the influence of the metal ions on the final structures. Fortunately, two crystalline compounds [Cd(4,4'-tmbpt)(HL)(H₂O)] (**1**) and [Cu(4,4'-tmbpt)(HL)]·H₂O (**2**) were successfully obtained. In our previous work, the 4,4'-tmbpt ligand has been used to construct various coordination polymers with carboxylate or polyoxometallate anions. These compounds display different structures from 1D to 3D and exhibit diverse properties such as photoluminescence and photocatalysis [22-25]. The H_3L has been used to construct coordination polymers with the terminal ligand 1,10-phenanthroline [6]. It is the first time for us to combine H_3L and the non-terminal ligand 4,4'-tmbpt ligand into the same framework of coordination polymer.

Scheme 1. Structures of H_3L (left) and 4,4'-tmbpt (right).

2. Experimental

2.1. Materials and Instrumentation

H_3L was prepared based on the method reported previously [6]. Other chemicals and solvents were commercially available and used as received. The elemental analyses (C, H and N) data were recorded on a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra data were collected on a Mattson Alpha-Centauri spectrometer. Diffuse reflection spectra were collected on a Cary 500 spectrophotometer, which were measured from 200 to 800 nm. The photoluminescent spectrum of compound **1**

was recorded on a Perkin-Elmer FLSP920 spectrometer at room temperature. Powder X-ray diffraction (PXRD) patterns of the compounds were measured on a Rigaku Dmax 2000 X-ray diffractometer with graphite monochromatized Cu-K α radiation (λ = 0.154 nm). The experimental patterns correspond well with the corresponding simulated ones (Fig. S1 in the supporting information), indicating the purity of the bulk samples. Photocatalytic measurements were carried out in conventional processes. 30 mg of the sample was added to 200 mL methylene blue (5×10^{-5} mol·L $^{-1}$) solution. Then the mixture was stirred in the dark for 1 h to reach the adsorption equilibrium. The mixture was then stirred continuously under a 125 W Hg lamp. At 30 min intervals, 3 mL of the suspension was got out of the reactor and centrifuged to remove suspended particles. The remaining solution was then analyzed by UV-vis spectrometer. The concentration of methylene blue was estimated by the absorbance at 665 nm.

2.2. Synthesis of [Cd(4,4'-tmbpt)(HL)(H₂O)] (1)

A mixture of 4,4'-tmbpt (0.03 g, 0.1 mmol), Cd(CH₃COO)₂·2H₂O (0.035 g, 0.15 mmol), H₃L (0.029 g, 0.1 mmol), NaOH (0.012 g, 0.3 mmol) and water (8 mL) was placed in a Teflon reactor. The mixture was heated at 140 °C for 3 days. After cooling to ambient temperature, colorless crystals of **1** were obtained in a 41% yield. Anal. calcd for C₂₉H₂₅CdN₈O₆P (M_r = 724.94): C, 48.05; H, 3.48; N, 15.46. Found: C, 48.16; H, 3.55; N, 15.55%. IR data (KBr, cm $^{-1}$): 3419 (m), 2262 (w), 1614 (s), 1556 (s), 1410 (s), 1316 (w), 1280 (w), 1236 (m), 1156 (s), 1120 (s), 1046 (s), 1018 (s), 945 (s), 843 (s), 755 (s), 704 (s), 617 (s), 544 (s).

2.3. Synthesis of [Cu(4,4'-tmbpt)(HL)]·H₂O (2)

The preparation of **2** was similar to that of **1**, except that Cu(CH₃COO)₂·H₂O (0.030 g, 0.15 mmol) was used instead of Cd(CH₃COO)₂·2H₂O. Green crystals of **2** were collected in a 38% yield. Anal. calcd for C₂₉H₂₅CuN₈O₆P (M_r = 676.08): C, 51.52; H, 3.73; N, 16.57. Found: C, 51.66; H, 3.80; N, 16.55%. IR data (KBr, cm $^{-1}$): 3420 (s), 1598 (s), 1543 (s), 1408 (m), 1383 (m), 1247 (w), 1166 (s), 1044 (s), 908

(w), 827 (w), 756 (w), 718 (w), 582 (w), 541 (w).

2.4. X-ray crystallography

The X-ray intensity data of compounds **1** and **2** were collected on an Oxford
5 Diffraction Gemini R Ultra diffractometer with graphite-monochromated Mo K α
radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. All the structures were solved by Direct Method
of SHELXS-97 [26] and refined by full-matrix least-squares techniques using the
SHELXL-97 program [27]. Anisotropic displacement parameters were applied to all
the non-H atoms. O1W of compound **2** was refined as a disordered atom with the total
10 occupancy of 1. Hydrogen atoms on C atoms and the phosphonate O atoms in
compounds **1** and **2** were generated geometrically and refined using a riding model
with $d(\text{C-H}) = 0.93\text{-}0.97 \text{ \AA}$, $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ and $d(\text{O-H}) = 0.82 \text{ \AA}$, $U_{\text{iso}} = 1.5U_{\text{eq}}(\text{O})$.
Hydrogen atoms of the water molecule in compound **1** were located from different
Fourier map and refined as riding atoms with $d(\text{O-H}) = 0.849\text{-}0.850 \text{ \AA}$, $U_{\text{iso}} =$
15 $1.5U_{\text{eq}}(\text{O})$. **Hydrogen atoms of the water molecule in compound **2** were not included in
the model. Therefore, the calculated and reported formula of compound **2** are different.**
The crystallographic data and structure refinement parameters of compounds **1** and **2**
are summarized in Table 1. Selected bond distances and angles are listed in Tables
S1a-S2b.

3. Results and discussion

3.1. Crystal structure of compound **1**

Single X-ray diffraction analysis reveals that compound **1** displays a 2D layer
structure. As shown in Fig. 1, the asymmetric unit of **1** contains one Cd(II) ion, one
25 4,4'-tmbpt ligand, one HL anion and one coordinated water molecule. Cd1 is
six-coordinated in an octahedral coordination geometry, defined by one nitrogen atom
from one 4,4'-tmbpt ligand ($\text{Cd1-N1} = 2.340(4) \text{ \AA}$) and five oxygen atoms from three
different HL anions and one water molecule ($\text{Cd1-O5}^{\#1} = 2.218(3) \text{ \AA}$, $\text{Cd1-O3}^{\#2} =$
 $2.226(3) \text{ \AA}$, $\text{Cd1-O1} = 2.311(3) \text{ \AA}$, $\text{Cd1-N1} = 2.340(4) \text{ \AA}$, $\text{Cd1-O1W} = 2.370(3) \text{ \AA}$,

Cd1-O2 = 2.448(3) Å). The coordination mode of the HL anion is $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^0\text{:}\eta^1\text{:}\eta^1$ (The subscript of μ represents the number of the metal ions coordinate to each HL anion, and the superscript of η represents the number of the metal ions coordinate to each oxygen atom on the phosphonate and carboxylate groups [28-30], table 2). Each HL anion coordinates to three Cd(II) ions with the phosphonate and carboxylate groups in $\mu_2\text{-}\eta^1\text{:}\eta^1\text{:}\eta^0$ (The subscript of μ represents the number of the metal ions coordinate to each phosphonate group, and the superscript of η represents the number of the metal ions coordinate to each oxygen atom, table 2) and $\mu_1\text{-}\eta^1\text{:}\eta^1$ (The subscript of μ represents the number of the metal ions coordinate to each carboxylate group, and the superscript of η represents the number of the metal ions coordinate to each oxygen atom, table 2) coordination modes, respectively. In this way, the HL anions connect the Cd(II) ions to form a 2D layer (Fig. 2a). The 4,4'-tmbpt ligands acting as dangled arms further coordinate to the layer in monodentate modes (Fig. 2b, table 2). Moreover, there are intramolecular hydrogen bonding interactions between the oxygen atoms of the HL anions, water molecules and the nitrogen atoms of 4,4'-tmbpt ligands ($\text{O4-H4}'\cdots\text{N8}^{\#4} = 2.592(5)$ Å, $\text{O1W-H1A}\cdots\text{O5}^{\#2} = 2.806(5)$ Å, $\text{O1W-H1B}\cdots\text{O4}^{\#1} = 3.237(5)$ Å), which further stabilize the whole structure of **1**. Better insight into the structure of compound **1**, there exist π - π interactions between the triazolyl ring and phenyl ring of adjacent layers with the centroid-to-centroid distance of 4.23 Å. The 2D layer of compound **1** are further connected by the π - π interactions to form a 3D supramolecular framework (Fig. 2c). Topologically, if the HL anions and Cd(II) ions can be considered as 3-connected nodes, the 2D layer of compound **1** can be simplified as a 3-connected net with a $4\cdot 8^2$ -*fes* topology (Fig. 3).

Fig. 1. Coordination environment of the Cd(II) ion with hydrogen atoms omitted for clarity. Symmetry codes: $^{\#1}$ x, -y - 1, z + 1/2; $^{\#2}$ -x + 3/2, -y - 1/2, -z + 1.

Fig. 2. (a) View of the 2D layer formed by the Cd(II) ions and the HL anions. (b) View of the 2D layer of compound **1**. (c) 3D supramolecular framework of compound **1** connected by π - π interactions.

Fig. 3. Topological view of the 2D 3-connected 4·8²-*fes* network for compound **1**.

3.2. Crystal structure of compound **2**

Compound **2** also displays a 2D layer structure. The asymmetric unit of **2** consists of one Cu(II) ion, one 4,4'-tmbpt ligand, one HL anion and one lattice water molecule. As shown in Fig. 4, Cu1 is five-coordinated in a trigonal-bipyramid geometry, furnished by three nitrogen atoms from three different 4,4'-tmbpt ligands (Cu1-N1 = 2.039(3) Å, Cu1-N8^{#1} = 2.051(2) Å, Cu1-N7^{#2} = 2.056(2) Å) and two oxygen atoms from two individual HL anions (Cu1-O4 = 1.945(2) Å, Cu1-O2^{#3} = 2.133(2) Å). All the bond lengths and angles in compounds **1** and **2** are in the normal ranges [31-33]. Each 4,4'-tmbpt ligand coordinates to three Cu(II) ions in a tridentate mode (table 2) to generate a ladder-like chain (Fig. 5a). The coordination mode of the HL anion is $\mu_2\text{-}\eta^1\text{:}\eta^0\text{:}\eta^0\text{:}\eta^1\text{:}\eta^0$ (table 2). Each HL anion coordinates to two Cu(II) ions with the phosphonate and carboxylate groups in $\mu_1\text{-}\eta^1\text{:}\eta^0\text{:}\eta^0$ and $\mu_1\text{-}\eta^1\text{:}\eta^0$ coordination modes (table 2), respectively. In this way, the HL anions connect the chains in pairs to form a 2D layer (Fig. 5b). Moreover, there are intermolecular hydrogen bonding interactions between the oxygen atoms of the HL anions (O1-H1...O3^{#4} = 2.635(4) Å), which further connect the layers into a 3D supramolecular architecture (Fig. 5c). Topologically, if the 4,4'-tmbpt ligands can be regarded as 3-connected nodes, the Cu(II) ions can be considered as 4-connected nodes, and the HL anions can be viewed as linkers, the 2D layer of compound **2** can be simplified as a (3,4)-connected net with a (4²·6³·8)(4²·6)-V₂O₅ topology (Fig. 6). Selected bond lengths and angles and hydrogen bonding information of the two compounds are listed in tables S1a-S2b.

Fig. 4. Coordination environment of the Cu(II) ion with hydrogen atoms and lattice water molecule omitted for clarity. Symmetry codes: ^{#1} -x, -y, -z; ^{#2} -x, -y - 1, -z - 1; ^{#3} -x + 1, -y + 1, -z.

Fig. 5. (a) View of the ladder-like chain formed by the Cu(II) ions and the 4,4'-tmbpt

ligands. (b) View of the 2D layer of compound **2**. (c) 3D supramolecular framework of compound **2** linked by hydrogen bonding interactions.

Fig. 6. Topological view of the 2D (3,4)-connected $(4^2 \cdot 6^3 \cdot 8)(4^2 \cdot 6)$ - V_2O_5 network for compound **2**.

3.3 Effects of the central metals on the structures of the compounds

From the structural descriptions it can be seen that compounds **1** and **2** have the same metal to ligand ratio, but different central metals. As a result, the two compounds have different structures. The discrepancy of the structures is mainly caused by the different coordination numbers of the Cd(II) ions and Cu(II) ions. Because the radius of the Cd(II) ion is larger than the Cu(II) ion, the coordination numbers of the Cd(II) ions in **1** (6) is larger than the Cu(II) ions in **2** (5). Therefore, the structural differences between the two compounds is mainly attributed to the differences in coordination numbers of the metal ions.

3.4. Optical band gaps of compounds **1** and **2**

In order to study the conductivity of the compounds, the diffuse reflection spectra for powder samples of the compounds were measured to obtain the band gaps (E_g). The Kubelka-Munk function (K-M Function), $F = (1 - R)^2/2R$, was calculated from the diffuse reflectance data (R is the reflectance) [34-36]. Fig. 7 shows the K-M function against E plots, from which it can be clearly seen that the E_g values of the two compounds assessed from the steep absorption edge are 2.84 and 2.36 eV, respectively. The results indicate that compounds **1** and **2** may be potential semiconductive materials. Therefore, they may be used as photocatalytic materials [37,38]. The different E_g values of the two compounds may be caused by the different central metals, which can result in the different extent of orbital overlap between metal ions and organic ligands [39,40].

Fig. 7. K-M Function vs E (eV) plots of compounds **1** and **2**.

3.5. Photoluminescent properties of compounds **1** and **2**

Coordination polymers with d^{10} metal centers have many applications in the fields of display, sensor, illumination, and so on [41-44]. In this work, the luminescent property of compound **1** has been investigated in the solid state at room temperature.

The emission bands of the free H_3L and 4,4'-tmbpt are centered at 428 and 458 nm, respectively [6,45]. These emissions may be caused by the π^*-n or $\pi^*-\pi$ transition as previously reported [45]. When excited at 280 nm, the emission peak is observed at 384 nm for compound **1** (Fig. 8). With respect to the free ligand, the emission peak of **1** is highly blue-shifted by 44 and 74 nm, respectively. Since the $Cd(II)$ ion has a d^{10} electronic configuration, it is difficult to oxidize or to reduce. Therefore, the emission of **1** is neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) [46,47]. The emission may be caused by the ligand-to-ligand charge transition [48].

Fig. 8. Solid state emission spectrum of compound **1** at room temperature.

3.6. Photocatalytic properties of the compounds

Results from documents indicate that the semiconductive coordination polymers may be employed as photocatalytic materials [37,38]. Therefore, in this work, we have studied the photocatalytic properties of the compounds. Under the irradiation of UV light, only compound **1** displays photocatalytic activity toward the decomposition of methylene blue. As depicted in Fig. 9, the absorption peak of methylene blue solution decreased clearly with the use of compound **1** as photocatalyst. The C/C_0 of methylene blue solution versus reaction time was plotted (Fig. 10). The plot indicates that the photocatalytic activity of compound **1** increases from 35% (without catalyst) to 57% after 120 min of reaction. The result indicates that compound **1** has photocatalytic activity for the decomposition of methylene blue.

Fig. 9. Absorption spectra of the methylene blue solution during the decomposition

reaction without catalyst and with the use of compound **1**.

Fig. 10. C/C_0 of methylene blue solution versus irradiation time without catalyst and with the use of compound **1**.

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4. Conclusions

In conclusion, two new coordination polymers based on 2'-carboxybiphenyl-4-ylmethylphosphonic and the multidentate N-donor ligand 1-((1*H*-1,2,4-triazol-1-yl)methyl)-3,5-bis(4-pyridyl)-1,2,4-triazole have been synthesized hydrothermally. The two compounds have the same metal to ligand ratio, but different metal ions. As a result, the two compounds display different 2D layer structures, which is mainly caused by the different coordination numbers of the different metal ions. The optical band gaps values of the two compounds indicate they may be potential semiconductive materials. The photoluminescent spectrum of compound **1** indicates that it emits violet light at room temperature. The study on the photocatalytic activities of the compounds implies that compound **1** exhibits photocatalytic activity toward the degradation of methylene blue under UV light.

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Appendix A. Supplementary data

CCDC 1489699 and 1489700 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at

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Table 1. Crystal data and structure refinements for compounds **1** and **2**.

	1	2
Formula	C ₂₉ H ₂₅ CdN ₈ O ₆ P	C ₂₉ H ₂₅ CuN ₈ O ₆ P
Formula weight	724.94	676.08
Crystal system	Monoclinic	Triclinic
Space group	<i>C2/c</i>	<i>P</i> -1
<i>a</i> (Å)	25.9250(10)	11.257(6)
<i>b</i> (Å)	9.935(3)	11.372(6)
<i>c</i> (Å)	23.064(7)	13.333(7)
α (°)	90	109.461(5)
β (°)	95.469(3)	111.097(5)
γ (°)	90	97.359(4)
<i>V</i> (Å ³)	5913(3)	1440.5(13)
<i>Z</i>	8	2
D _{calc} (g·cm ⁻³)	1.629	1.559
F (0 0 0)	2928	694

Reflections (collected/unique)	12567 / 6843	9158 / 5244
R_{int}	0.0385	0.0282
Goodness-of-fit (GOF) on F^2	1.043	1.035
$R_1^{[a]}$ [$I > 2\sigma(I)$]	0.0515	0.0446
$wR_2^{[b]}$ [all data]	0.1174	0.1004

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

Table 2. Coordination modes of the HL anion and 4,4'-tmbpt in compounds **1** and **2**.

	Coordination mode of HL	Coordination mode of 4,4'-tmbpt
Compound 1
Compound 2

Figure captions

Scheme 1. Structures of H₃L (left) and 4,4'-tmbpt (right).

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Fig. 1. Coordination environment of the Cd(II) ion with hydrogen atoms omitted for clarity. Symmetry codes: ^{#1} $x, -y - 1, z + 1/2$; ^{#2} $-x + 3/2, -y - 1/2, -z + 1$.

Fig. 2. (a) View of the 2D layer formed by the Cd(II) ions and the HL anions. (b) View of the 2D layer of compound **1**. (c) 3D supramolecular framework of compound **1** connected by π - π interactions.

Fig. 3. Topological view of the 2D 3-connected $4 \cdot 8^2$ -fes network for compound **1**.

Fig. 4. Coordination environment of the Cu(II) ion with hydrogen atoms and lattice water molecule omitted for clarity. Symmetry codes: ^{#1} -x, -y, -z; ^{#2} -x, -y - 1, -z - 1; ^{#3} -x + 1, -y + 1, -z.

Fig. 5. (a) View of the ladder-like chain formed by the Cu(II) ions and the 4,4'-tmbpt ligands. (b) View of the 2D layer of compound **2**. (c) 3D supramolecular framework of compound **2** linked by hydrogen bonding interactions.

Fig. 6. Topological view of the 2D (3,4)-connected $(4^2 \cdot 6^3 \cdot 8)(4^2 \cdot 6)$ - V_2O_5 network for compound 2.

Fig. 7. K-M Function vs E (eV) plots of compounds 1 and 2.

Fig. 8. Solid state emission spectrum of compound **1** at room temperature.

Fig. 9. Absorption spectra of the methylene blue solution during the decomposition reaction without catalyst and with the use of compound **1**.

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Fig. 10. C/C_0 of methylene blue solution versus irradiation time without catalyst and with the use of compound **1**.

Two new coordination polymers based on 2'-carboxybiphenyl-4-ylmethylphosphonic and the multidentate N-donor ligand 1-((1H-1,2,4-triazol-1-yl)methyl)-3,5-bis(4-pyridyl)-1,2,4-triazole have been synthesized with different metal ions under hydrothermal conditions. [The effects of the metal ions on the structures of the compounds have been discussed.](#) Moreover, the optical band gaps, [photoluminescent and photocatalytic properties of the compounds have been studied.](#)