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Introduction

Design and assembly of metal phosphonate materials with intriguing diversity of architectures and properties have grown rapidly in recent decades due to their potential applications in catalysis, photochemistry, magnetism, ion exchange, molecular recognition and materials chemistry.¹ In order to obtain metal phosphonate compounds with a variety of architectures and interesting physical or chemical properties, an encouraging research direction is the synthesis of metal phosphonates functionalized with amine, hydroxyl and carboxylate groups. Much work of metal phosphonates has shown that the use of bi- and multifunctional phosphonic acids containing $-NH_2$, -OH, and -COOH sub-functional groups may not only result in

Zinc(II) and cadmium(II) carboxyphosphonates with a 3D pillared-layered structure: synthesis, crystal structures, high thermal stabilities and luminescent properties[†]

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Two novel divalent metal carboxyphosphonates with a 3D pillared-layered structure, [Zn(HL)] (1) and [CdCl(H₂L)] (2) (H₃L = 4-HOOCC₆H₄CH₂NHCH₂PO₃H₂), have been synthesized under hydrothermal conditions. Compounds 1 and 2 both feature three-dimensional (3D) framework structures with two-dimensional (2D) inorganic layers pillared by H₃L. In compound 1, each {ZnO₄} tetrahedron is linked *via* corner-sharing by three {CPO₃} tetrahedra to form a two-dimensional (2D) inorganic layer in the *ac*-plane. The adjacent layers are further pillared by the organic backbone { $-C_6H_4CH_2NHCH_2-$ } of the carboxyphosphonate ligand, generating a 3D pillared-layered structure. For compound 2, each Cd(II) cation is six-coordinated, and the interconnection of two {CdCl₂O₄} octahedra forms a dimer *via* edge-sharing. The dimers are interconnected by {CPO₃} tetrahedra *via* corner-sharing to form a 2D inorganic layer in the *ab*-plane. Such neighboring 2D inorganic layers are further cross-linked through the organic pillars of the carboxyphosphonate ligand, thus resulting in a 3D pillared-layered structure. An interesting feature of compounds 1 and 2 is the presence of alternate left- and right-handed helical chains in their structures. It is of note that two title compounds are both stable up to high temperature. The luminescent properties of compounds 1 and 2 have also been studied.

new structural types of metal phosphonates but also lead to interesting properties.

In recent years, a number of metal phosphonate frameworks with additional functionalities have been reported.²⁻⁴ By attaching functional groups such as amine, hydroxyl and carboxylate groups to the phosphonic acid, a series of metal phosphonates with framework structures have been isolated in our laboratory.⁵ Results from ours and other groups indicate that carboxyphosphonic acids are good candidates for the synthesis of metal phosphonates with framework structures, in which the organic part has a controllable spacer role and the -COOH and -PO₃ groups chelate metal ions to form novel structure types.⁶ Recently, increased attention has been paid to rigid aromatic carboxyphosphonate ligands, which play an important role to design metal phosphonates with novel architectures and properties.7 Three zinc carboxyphosphonates based on 4-phosphonobenzoic acid reported by Zhao and co-workers feature 3D zeolite-like structure, layer structure and 3D pillar-layered structure, respectively.^{7a} Zheng's group newly reported the synthesis of metal phosphonates with 2-carboxyphenylphosphonic acid as ligand, which show reversible dehydration-rehydration behavior and ferrimagnetism.^{7b} In a recent article, a carboxyphosphonic acid with rigid

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[†] Electronic supplementary information (ESI) available: X-ray crystallographic files in CIF format for compounds 1 and 2. IR spectra of compounds 1 and 2. XRD pattern of the intermediate products in the thermal decomposition for compounds 1 and 2 as well as XRD patterns of the experiments compared to those simulated from X-ray single-crystal data for compounds 1 and 2. CCDC reference numbers 874503 (1) and 874504 (2). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ra22571A

structure, 4-HOOCC₆H₄CH₂NHCH₂PO₃H₂ (H₃L) was used as a ligand in the synthesis of metal phosphonates with high dimensionality. To the best of our knowledge, only one investigation on the synthesis of lanthanide carboxyphosphonates based on 4-HOOCC₆H₄CH₂NHCH₂PO₃H₂ has recently been reported by Mao et al.8 However, the corresponding transition-metal carboxyphosphonates have not been reported up to now. With the aim of exploring novel metal phosphonates with interesting structures and properties, we further investigated the rigid and multifunctional carboxyphosphonic acid ligand 4-HOOCC₆H₄CH₂NHCH₂PO₃H₂ (H₃L), since it is expected to adopt various coordination modes under different reaction conditions which may result in a variety of interesting structures. More importantly, its relatively rigid structure and π -conjugated character is useful to produce coordination polymers with active photoluminescent properties. In the present paper, by employing carboxyphosphonic acid, 4-HOOCC₆H₄CH₂NHCH₂PO₃H₂ (H₃L) as ligand, we have successfully obtained two novel divalent metal carboxyphosphonates with a 3D pillared-layered structure, namely, [Zn(HL)] (1) and $[CdCl(H_2L)]$ (2). Herein, we report their syntheses, crystal structures, and thermal stabilities. The luminescence properties of compounds 1 and 2 have also been studied.

Experimental

Materials and measurements

The ligand 4-HOOCC₆H₄CH₂NHCH₂PO₃H₂ (H₃L) was synthesized according to procedures described previously.^{8,9} All other chemicals were obtained from commercial sources and used without further purification. C, H and N analyses were determined by using a PE-2400 elemental analyzer. Zn, Cd and P were determined by using an inductively coupled plasma (ICP) atomic absorption spectrometer. IR spectra were recorded on a Bruker AXS TENSOR-27 FT-IR spectrometer with KBr pellets in the range 4000-400 cm⁻¹. X-Ray powder diffraction data was collected on a Bruker AXS D8 Advance diffractometer using Cu-K α radiation ($\lambda = 1.5418$ Å) in the 2θ range of 5–60° with a step size of 0.02° and a scanning rate of 3° min⁻¹. Thermogravimetric (TG) analyses were performed on a NETZSCH STA-449-F3 at a heating rate of 10 °C min⁻¹ under an air flow from 50 to 1200 °C. The luminescence spectra were reported on a HITACHI F-7000 spectrofluorimeter (solid).

SYNTHESIS OF [ZN(HL)] (1). A mixture of $H_{3}L$ (0.12 g, 0.5 mmol) and ZnSO₄·7H₂O (0.14 g, 0.5 mmol) was dissolved in 10 mL distilled water. The pH value was adjusted to 4.0 by adding an ethylenediamine solution dropwise. The resulting solution was stirred for about 1 h at room temperature, sealed in a 20 mL Teflon-lined stainless steel autoclave, and then heated at 160 °C for 4 days under autogenous pressure. After the mixture was cooled slowly to room temperature, colorless plate crystals of compound 1 were obtained. The pH value of the resultant solution was 4.0. Yield: 64.2% (based on Zn). Anal. Calc. for C₉H₁₀NO₅PZn: C, 35.03; H, 3.27; N, 4.54; P, 10.04; Zn, 21.20. Found: C, 35.09; H, 3.23; N, 4.58; P, 10.07; Zn, 21.15%. IR (KBr, cm⁻¹): 3448(m), 3014(s), 2865(w), 2807(m), 1603(s), 1557(s), 1473(m), 1428(m), 1395(s), 1136(s), 1078(s), 1026(s), 973(m), 754(m), 598(m), 521(w), 430 (w).

SYNTHESIS OF $[CDCL(H_2L)]$ (2). A mixture of H_3L (0.24 g, 1 mmol) and $Cd(Ac)_2 \cdot 2H_2O$ (0.27 g, 1 mmol) was dissolved in 10 mL distilled water. The pH value was adjusted to 4.0 by adding 3 M HCl solution dropwise. The resulting solution was stirred for about 1 h at room temperature, sealed in a 20 mL Teflon-lined stainless-steel autoclave, and then heated at 160 °C for 4 days under autogenous pressure. After the mixture was cooled slowly to room temperature, colorless plate crystals of compound 2 were obtained. The pH value of the resultant solution was 3.5. Yield: 67.4% (based on Cd). Anal. Calc. for $C_9H_{11}NO_5ClPCd$: C, 27.57; H, 2.83; N, 3.57; P, 7.90; Cd, 28.67. Found: C, 27.52; H, 2.88; N, 3.53; P, 7.95; Cd, 28.61%. IR (KBr, cm⁻¹): 3445(m), 3033(s), 2807(w), 2535(w), 1661(s), 1609(s), 1578(m), 1460(m), 1414(m), 1324(s), 1142(s), 1084(s), 1026(m), 974(s), 851(w), 767(m), 702(w), 579(m), 527(m), 495(w).

Crystallographic studies

Data collections for compounds 1 and 2 were performed on a Bruker AXS Smart APEX II CCD X-diffractometer equipped with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 293 \pm 2 K. An empirical absorption correction was applied using the SADABS program. All structures were solved by direct methods and refined by full-matrix least-squares fitting on F^2 by SHELXS-97.¹⁰ All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms of organic ligands were generated geometrically with fixed isotropic thermal parameters, and included in the structure factor calculations. Details of crystallographic data and structural refinements of compounds 1 and 2 are summarized in Table 1. Selected bond lengths and angles of compounds 1 and 2 are listed in Table 2. Hydrogen bonds for compounds 1 and 2 are given in Table 3.

Compound	1	2
Empirical formula	C ₉ H ₁₀ NO ₅ PZn	C ₉ H ₁₁ ClNO ₅ PCd
$M_{ m r}$	308.52	392.01
Crystal system	Orthorhombic	Orthorhombic
Space group	$Pca2_1$	Pbca
a/Å	9.9240(11)	7.6418(11)
b/Å	12.4951(14)	12.7390(18)
c/Å	8.6343(9)	24.237(4)
$V/Å^3$	1070.7(2)	2359.4(6)
Ζ	4	8
$D_{\rm c}/{\rm g~cm^{-3}}$	1.914	2.207
F(000)	624	1536
Crystal size/mm	$0.05 \times 0.03 \times 0.01$	0.08 $ imes$ 0.07 $ imes$ 0.02
θ Range/°	2.62-26.49	3.15-26.49
Reflections	5792, 2075	11 804, 2442
collected/unique		
R _{int}	0.0616	0.0779
GOF on F^2	1.034	1.013
$R_1, wR_2 \stackrel{a}{=} [I > 2\sigma(I)]$	0.0542, 0.1076	0.0382, 0.0749
R_1, wR_2^a (all data)	0.0782, 0.1184	0.0663, 0.0862
$\Delta \rho_{\rm max, min}/e {\rm \AA}^{-3}$	0.611, -0.473	0.570, -0.667

Results and discussion

Syntheses

Hydrothermal synthesis has been extensively explored for the preparation of metal phosphonate materials. The product composition depends on a number of critical conditions, including pH of the medium, temperature, different metal salts and so on. With the aim to explore the optimum method for obtaining pure phase materials, two systematic experimental investigations have been designed for the system Zn²⁺/ H₃L of compound 1. The first experiment was designed to investigate the influence of the anions of zinc salts on the reaction products. Thus, four different zinc salts (ZnCl₂, Zn(Ac)₂·2H₂O, Zn(NO₃)₂·6H₂O and ZnSO₄·7H₂O) were reacted keeping a constant Zn^{2+} : $H_3L = 1 : 1$ ratio at their original pH $(T = 160 \,^{\circ}\text{C}, 96 \,\text{h})$. Our experiments demonstrated that the final reaction products synthesized from different zinc salts exhibit different phases. $ZnCl_2$ (original pH = 2.5) and $Zn(NO_3)_2 \cdot 6H_2O$ (original pH = 2) led to amorphous powders. However, mixed phases (tiny crystals and powder) for compound 1 were obtained from $Zn(Ac)_2 \cdot 2H_2O$ (original pH = 4) and $ZnSO_4 \cdot 7H_2O$ (original pH = 2). We thus realized that $ZnSO_4 \cdot 7H_2O$ and $Zn(Ac)_2 \cdot 2H_2O$ may be more adaptable zinc salts as reactants to synthesize compound 1 keeping a constant Zn^{2+} : H₃L = 1 : 1 ratio. One other variable that has a profound impact on the product formation of hydrothermal syntheses is the pH value of the reaction mixture. To gain a better understanding of the influence of the pH value within the system Zn^{2+}/H_3L , a second experiment was designed. The system Zn2+/H3L was investigated using the two more adaptable zinc salts at different pH, namely, ZnSO4·7H2O and $Zn(Ac)_2 \cdot 2H_2O$, under hydrothermal conditions keeping a

Table 2 Selected bond lengths (Å) and angles (°) for compounds 1 and 2^a						
1		2				
Zn(1)-O(3)#1 Zn(1)-O(1)	1.920(4) 1.933(4)	Cd(1)-O(3)#1 Cd(1)-O(1)#2	2.197(3) 2.276(3)			
Zn(1)-O(4)#2	1.936(4)	Cd(1) - O(2)	2.278(3) 2.288(4)			
Zn(1)-O(2)#3	1.985(5)	Cd(1)-O(5)#3	2.3874(14)			
P(1)-O(3)	1.495(5)	Cd(1)-Cl(1)	2.6118(14)			
P(1)-O(2)	1.512(4)	P(1)-O(1)	1.507(4)			
P(1)-O(1)	1.517(5)	P(1)-O(2)	1.535(4)			
P(1)-C(1)	1.831(7)	P(1)-O(3)	1.498(4)			
O(3)#1-Zn(1)-O(1)	104.7(2)	O(3)#1-Cd(1)-O(1)#2	82.58(13)			
O(3)#1-Zn(1)-O(4)#2	121.1(2)	O(3)#1- $Cd(1)$ - $O(2)$	100.39(13)			
O(1)-Zn(1)-O(4)#2	118.9(2)	O(1)#2-Cd(1)-O(2)	161.94(12)			
O(3)#1-Zn(1)-O(2)#3	100.9(2)	O(3)#1-Cd(1)-O(5)#3	102.14(10)			
O(1)-Zn(1)-O(2)#3	102.13(19)	O(1)#2-Cd(1)-O(5)#3	81.15(9)			
O(4)#2-Zn(1)-O(2)#3	105.9(2)	O(2)-Cd(1)-O(5)#3	80.81(10)			
O(3)-P(1)-O(2)	114.1(3)	O(1)#2-Cd(1)-Cl(1)	95.03(9)			
O(3)-P(1)-O(1)	110.2(3)	O(5)#3-Cd(1)-Cl(1)	163.68(5)			
O(2)-P(1)-O(1)	110.4(2)	O(3)#1-Cd(1)-Cl(1)#4	170.56(10)			
O(3)-P(1)-C(1)	106.9(3)	O(5)#3-Cd(1)-Cl(1)#4	81.13(5)			
O(2)-P(1)-C(1)	106.3(3)	Cl(1)-Cd(1)-Cl(1)#4	82.97(4)			
O(1)-P(1)-C(1)	108.7(3)	Cd(1)-Cl(1)-Cd(1)#4	97.03(4)			

^{*a*} Symmetry transformations used to generate equivalent atoms. For 1: #1 -x, -y + 2, z - 1/2; #2 x, y + 1, z; #3 x + 1/2, -y + 2, z; #4 x, y - 1, z; #5 x - 1/2, -y + 2, z; for 2: #1 -x + 1, -y + 1, -z; #2 -x + 1/2, y - 1/2, z; #3 -x + 1, y - 1/2, -z + 1/2; #4 -x, -y + 1, -z; #5 -x + 1/2, y + 1/2, z.

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D-H···A	<i>d</i> (D–H)/Å	d(H···A)/Å	θ (D-H···A)/°	d(D…A)/Å		
1						
N(1)-H(1C)····O(2)#3	0.90	1.94	178	2.840(9)		
N(1)-H(1D)O(5)#7	0.90	1.97	164	2.843(10)		
2						
-N(1)-H(1B)····Cl(1)#7	0.90	2.32	175	3.216(5)		
N(1)-H(1E)O(1)#7	0.90	1.84	166	2.726(5)		
O(4)–H(4B)····O(2)#6	0.85	1.68	170	2.524(5)		
^{<i>a</i>} Symmetry transformations used to generate equivalent atoms. For						
1: $\#3 x + 1/2$, $-y + 2$, z; $\#7 - x$, $-y + 1$, $z + 1/2$; for 2: $\#6 - x + 1$, $y + 1$						

1/2, -z + 1/2; #7 x + 1/2, -y + 3/2, -z.

constant Zn^{2+} : H₃L = 1 : 1 ratio (*T* = 160 °C, 96 h). This second experiment showed that mixed phases (tiny crystals and powder) of compound 1 were formed from $Zn(Ac)_2 \cdot 2H_2O$ as zinc salt at pH = 4, with amorphous powders forming at all other pH values under the same synthesis conditions. Unexpectedly, a pure phase of large-plate single crystals of compound 1 were obtained at pH = 4 with $ZnSO_4 \cdot 7H_2O$ as zinc salt. However, formation of amorphous powders or mixed phases (tiny crystals and powder) for compound 1 was observed at all other pH values. The results of the two experimental investigations indicate that ZnSO₄·7H₂O is the optimal zinc salt to synthesize the pure phase of single crystals for compound 1 at pH = 4 at a constant Zn^{2+} : H₃L = 1 : 1 ratio $(T = 160 \degree C, 96 h)$. Analogous experimental investigations were also designed to obtain the optimum method for synthesizing compound 2. Also, pure crystal phase production of compound 2 was achievable by appropriate adjustment: $Cd(Ac)_2 \cdot 2H_2O$ as the optimal cadmium salt at pH = 4 keeping a constant Cd^{2+} : H₃L = 1 : 1 ratio (*T* = 160 °C, 96 h).

Description of the crystal structures

X-Ray single-crystal diffraction revealed that compound 1 crystallizes in the orthorhombic space group $Pca2_1$ (Table 1). The asymmetric unit of the structure for compound 1 is comprised of one Zn(II) cation and one HL²⁻ anion. As shown in Fig. 1, the Zn(II) cation is four-coordinated by one carboxylate oxygen atom (O4C) from one HL²⁻ anion and three phosphonate oxygen atoms (O1, O2A and O3B) from three separate HL²⁻ anions. On the other hand, the carboxyphosphonate ligand acts as a tetradentate metal linker, bridging with four Zn(II) cations through three phosphonate oxygen atoms and one carboxylate oxygen atom. The phosphonate oxygen atoms (O1, O2 and O3) and one carboxylate oxygen atom (O4) are all monodentate. The Zn-O distances range from 1.920(4) to 1.985(5) Å (Table 2), which are similar to those reported for other zinc(II) carboxyphosphonates.¹¹ Both phosphonate and carboxylate groups of the ligand are deprotonated, but the amine group is protonated based on the requirement of charge balance.

Compound 1 exhibits a three-dimensional framework with pillared-layered structure. Each $\{CPO_3\}$ tetrahedron connects three $\{ZnO_4\}$ tetrahedra through three phosphonate oxygen atoms, and the $\{ZnO_4\}$ tetrahedra are interconnected by



Fig. 1 Structure unit of compound **1** showing the atom labeling. Thermal ellipsoids are shown at the 50% probability level. Symmetry code for the generated atoms: (A) x + 1/2, -y + 2, z; (B) -x, -y + 2, z - 1/2; (C) x, y + 1, z.

{CPO₃} tetrahedra via corner-sharing to form a two-dimensional (2D) inorganic layer in the ac-plane (Fig. 2a). The result of connections in this manner is formation of regular windows made up of 12 atoms, which consist of three Zn, three P and six O atoms with the sequences Zn-O-P-O-Zn-O-P-O-Zn-O-P-O in the inorganic layer. Such neighboring 2D inorganic layers are further cross-linked via the organic backbone $\{-C_6H_4CH_2NHCH_2-\}$ of the carboxyphosphonate ligands, generating a 3D pillared-layered structure with a 1D channel system along the a-axis (Fig. 2b). The channels running along the a-axis are formed by 28-membered rings composed of three Zn(II) cations, two HL²⁻ ligands and one phosphonate group of the ligand (Fig. 2c). The size of the channel is estimated to be 12.3 Å (P1-O2) × 3.2 Å (C4-C7) based on structure data. The adjacent benzyl rings of the carboxyphosphonate ligands in the pillared-layered structure of compound 1 are almost parallel to each other. The face-to-face distance (3.5 Å) between adjacent benzyl rings is in the normal range (3.3–3.8 Å) for such interactions, hence there are π - π stacking interactions in the 3D framework structure of compound 1 (Fig. 2d). In addition hydrogen bonds occur in compound 1. As shown in Fig. 3, there are intermolecular hydrogen bonds among the protonated nitrogen atom (N1), the carboxylate oxygen atom (O5) and the phosphonate oxygen atom (O2) with distances of 2.843(10) Å (N1-H1C···O5#7) and 2.840(9) Å (N1-H1D···O2#3) and corresponding angles of 164 and 178°. These hydrogen bonds give rise to an infinite threedimensional network and enhance the stability of this network.



Fig. 3 The connectivity of hydrogen bonds for compound 1 (all H atoms attached to C atoms are omitted for clarity).

A notable feature for compound **1** is the presence of left- and right-handed helical chains in the inorganic layer structure of the *ac*-plane (Fig. 4). The interconnection of one Zn(II) cation and a pair of HL^{2-} ligands by phosphonate oxygen atoms (O1, O2 and O3) leads to infinite 1D left- and right-handed helical chains along the *c*-axis. However, compound **1** exhibits an achiral 3D framework structure because of the presence of the mirror symmetry.

Compound 2 crystallizes in the orthorhombic space group *Pbca* (see Table 1). Each asymmetric unit contains one Cd(II) cation, one H_2L^- anion and one chloride anion. As shown in Fig. 5, the Cd(II) cation exhibits a six-coordinated environment, bonding to two Cl⁻ anions, one carboxylate oxygen atom (O5D) from one H_2L^- anion and three phosphonate oxygen atoms (O1B, O2 and O3C) from three separate H_2L^- anions. The carboxyphosphonate ligand functions as a tetradentate ligand, binding four Cd(II) cations through three phosphonate oxygen atoms and one carboxylate oxygen atom. The phosphonate oxygen atoms (O1, O2 and O3) and one carboxylate oxygen atom (O5) are all monodentate. The Cd–O distances range from 2.197(3) to 2.3874(14) Å. The Cd–Cl bond lengths are 2.6118(14) and 2.6804(14) Å, which are much larger than the Cd–O bonds (see Table 2). These values are in agreement



Fig. 2 (a) View of the layer structure for compound 1 in the *ac*-plane; (b) the 3D framework structure of compound **1** along the *a*-axis; (c) a 28-atom ring in compound **1** generated from equivalent positions (x, -1 + y, z), (-1/2 + x, 2 - y, z) and (-1/2 + x, 1 - y, z); (d) the π - π stacking interaction in compound **1** (a = 3.5 Å).



Fig. 4 (a) The left-handed helical chain; (b) the layer structure of compound **1** without the organic moieties of the HL^{2-} ligands viewed in the *ac*-plane; (c) the right-handed helical chain.



Fig. 5 Structure unit of compound **2** showing the atom labeling. Thermal ellipsoids are shown at the 50% probability level. Symmetry code for the generated atoms: (A) -x, -y + 1, -z; (B) -x + 1/2, y - 1/2, z; (C) -x + 1, -y + 1, -z; (D) -x + 1, y - 1/2, -z + 1/2.

with those reported for other cadmium(II) carboxyphosphonates.¹² The C9–O4 bond length (1.3109 Å) is significantly longer than that of the C9–O5 bond (1.2221 Å) in the carboxylate group of the carboxyphosphonate ligand, which is also reflected from its IR data showing a strong absorption band around 1661 cm⁻¹ associated with COOH.¹³ Based on charge balance considerations, the nitrogen atom of the amine group and the oxygen atom of the carboxylate group in the H_2L^- anion are monoprotonated, respectively. The carboxyphosphonate ligand is a univalent anion.

The structure of compound 2 also features a 3D pillaredlayered framework. The two {CdCl₂O₄} octahedra are interconnected into a dimer via edge-sharing, and the so-built dimer {Cd₂Cl₂O₈} polyhedra and {CPO₃} tetrahedra connect with each other by corner-sharing to form a 2D inorganic layer in the ab-plane (Fig. 6a). Adjacent 2D inorganic layers are further cross-linked through the carboxyphosphonate ligands from one layer to Cd(II) cations from adjacent layers into a 3D pillared-layered structure with a 1D channel system along the a-axis (Fig. 6b). The channel system running along the a-axis is assembled by 40-atom rings, and the size of the channel is estimated to be 8.9 Å (O2-O2) × 3.4 Å (C4-C7) based on structure data. The diameter of the pore (as shown by the yellow ball) inside the channel is estimated to be 3.4 Å (Fig. 6c). Hydrogen-bonding interactions are also observed in the structure of compound 2. The nitrogen atom (N1) forms a hydrogen bond with the chloride atom (Cl1): N1-H1B···Cl1#7 and the bond distance and the angle are 3.216(5) Å and 175° , respectively. Meanwhile, the nitrogen atom (N1) and the phosphonate oxygen atom (O1) also form a hydrogen bond with a distance of 2.726(5) Å for N1-H1E…O1#7. Another important hydrogen bonding interaction is between the carboxylate oxygen atom (O4) and phosphonate oxygen atom (O2): O4-H4B···O2#6, and the bond distance and the angle are 2.524(5) Å and 170° , respectively. These strong hydrogen bonds enhance the stability of the network and result in a twodimensional network in the (0, 0, 1) plane (Fig. 6d). Differently from compound 1, the close contact distance between adjacent benzyl rings, which are almost parallel to each other, is not in the normal range (3.3–3.8 Å) for such interactions and so π – π stacking interactions are not observed in the framework of compound 2. It is of note that in the Cd-phosphonate inorganic layer of the ab-plane, alternate left- and righthanded helical chains occur in this structure, which is similar to compound 1 (Fig. 7). The interconnection of one Cd(II) cation and a pair of HL²⁻ ligands by phosphonate oxygen atoms (O1, O2 and O3) leads to infinite 1D left- and righthanded helical chains along the a-axis. Compound 2 also features an achiral 3D framework structure.



Fig. 6 (a) The 2D inorganic layer structure of compound 2 in the *ab*-plane. (b) View of the 3D framework for compound 2 along the *a*-axis. (c) The 40-atom rings in compound 2; the yellow sphere represents the pore defined within the frameworks, the diameter of the yellow ball inside the channels is 3.4 Å. (d) The connectivity of hydrogen bonds for compound 2 (all H atoms attached to C atoms are omitted for clarity).



Fig. 7 (a) The left-handed helical chain, (b) the layer structure of compound **2** without the organic moieties of the H_2L^- ligands viewed in the *ab*-plane, and (c) the right-handed helical chain. (d) Space-filling model of the left- and right-handed helical chains in compound **2**.

IR spectroscopy

The IR spectra for compounds 1 and 2 were recorded in the region from 4000–400 cm^{-1} (Fig. S1 and S2, ESI†). The absorption bands at 3448 cm⁻¹ for 1 and 3445 cm⁻¹ for 2 correspond to the stretching vibration of N-H.14a The C-H stretching vibrations are observed as sharp, weak bands close to 3000 cm^{-1} for compounds 1 and 2. The strong absorption bands around 1395 cm^{-1} for 1 and 1324 cm^{-1} for 2 are assigned to the bending vibrations of C-H. For compound 1, there are two strong bands (1603 and 1557 cm⁻¹) and two medium bands (1473 and 1428 cm⁻¹), which are assigned to the antisymmetrical and symmetrical stretching vibrations of C-O bonds of the carboxylate groups. They are attributed to the carboxylate groups coordinated to the metal, thus showing that also the carboxylate groups are deprotonated and in agreement with structural results. Bands at 1609, 1578, 1460 and 1414 cm⁻¹ for compound 2 are also observed, corresponding to the asymmetric and symmetric stretching vibrations of C–O bonds of the carboxylate groups.^{14b} At the same time, the bands at around 1661 cm⁻¹ can be attributed to the C=O vibration of the carboxylic acid group, suggesting that the COOH group is protonated. The set of bands between 1200 and 900 cm⁻¹ are assigned to stretching vibrations of the tetrahedral CPO3 groups for compounds 1 and 2.14c Additional weak bands at low energy for the title compounds are found. These bands are probably due to bending vibrations of the tetrahedral CPO₃ groups.

Thermal analyses

In order to examine the thermal stabilities of compounds 1 and 2, thermogravimetric analyses were performed (Fig. 8). The TG curve shows two steps of weight losses for compound 1, which is stable up to a high temperature of 427 °C. At approximately 545 °C, compound 1 completes its first step of weight loss (36.0%), which corresponds to partial decomposition of organic groups. During the thermal decomposition of 1 intermediate compounds are formed between 545 and 870 °C. The intermediate phases contain Zn₂P₂O₇ (JCPDS 00-007-0153) and black glassy carbon, as identified by XRD powder studies and the color (Fig. S3, ESI[†]).¹⁵ The theoretical weight loss is 50.6% assuming an intermediate compound Zn₂P₂O₇ and is larger than the observed weight loss because of the presence of amorphous product.^{16,1e} A second weight loss occurs between 870 and 1068 °C, which can be attributed to the decomposition of the inorganic salt $Zn_2P_2O_7$, releasing P_2O_5 as a gas, forming ZnO,^{14c} and also decomposition of the amorphous product. The observed weight loss of 34.3% is larger than the calculated value of 23.0%, in accord with the loss of the amorphous



Fig. 8 TG curves of (a) 1 and (b) 2.



Fig. 9 PXRD patterns for (a) 1 on heating from 25 to 400 °C and (b) 2 on heating from 25 to 350 °C.

product. The total weight loss of 70.3% is close to the calculated value (73.6%) if the final product is assumed to be ZnO.¹⁷ For compound 2, the TG curve also shows a two step weight losses. The first step starts at 325 °C and was completed at 546 °C (28.3%), which corresponds to the removal of hydrogen chloride and partial decomposition of the organic ligand. During the thermal decomposition, intermediate compounds are formed between 546 and 803 °C, which are Cd₂P₂O₇ (JCPDS 00-031-0233) and black glassy carbon, as shown by XRD powder studies and the color (Fig. S4, ESI[†]). The calculated value of 49.1% for the weight loss is much larger than the observed weight loss (28.3%), similar to compound 1, again attributable to the existence of amorphous product. The second weight loss step from 803 to 1000 °C (44.6%), corresponds to the decomposition of the inorganic salt Cd₂P₂O₇ to CdO with release of P₂O₅ and loss of the amorphous product. The total weight loss of 72.9% is close to the calculated value (67.2%) if the final product is assumed to be CdO. To further understand the thermal stability of compounds 1 and 2, powder X-ray diffraction studies (PXRD) were performed from 25 to 400 °C. As shown in Fig. 9a, at 380

°C, the pattern is still similar to that at 25 °C, which indicates that the structure of compound **1** was thermally stable below 380 °C. For **2** the pattern at 25–280 °C is consistent with the simulated for **2** and changes at 300 °C. The PXRD experiment thus shows **2** is thermally stable up to 280 °C.

Luminescent properties

The solid-state luminescent properties of the free H_3L ligand as well as compounds **1** and **2** were investigated at room temperature and are shown in Fig. 10.

The free carboxyphosphonate ligand H_3L displays a fluorescent emission band at 336 nm upon excitation at 307 nm. In contrast, compounds **1** and **2** give broad fluorescent emissions under the same experimental conditions. Compound **1** displays a broad blue fluorescent emission band at $\lambda_{max} = 361$ nm upon excitation at 307 nm. Compared to the free carboxyphosphonate ligand, compound **1** shows a pronounced red-shifted emission band with slightly weakened intensities, which is probably originate from the ligand-to-metal charge transfer (LMCT).¹⁸ Compound **2** exhibits a broad emission band between 320 and 500 nm with one strong blue fluorescent



Fig. 10 (a) Solid-state emission spectra of H₃L (red line) and compound 1 (black line) at room temperature. (b) Solid-state emission spectra of H₃L (red line) and compound 2 (black line) at room temperature.

emission peak at 422 nm (λ_{ex} = 307 nm). The fluorescent spectrum of compound 2 shows a significant enhancement in intensity and a large shift to higher wavelength in emission band compared with that of the free carboxyphosphonate ligand (H₃L), which is attributed to metal-to-ligand charge transfer (MLCT).¹⁹ Unfortunately, the luminescent lifetimes of compounds 1 and 2 were too short to be measured. The luminescent intensity of compound 2 is stronger than that of compound 1, which is probably due to the differences in the metal ion and the structure of the complexes since the luminescence behavior is closely associated with the metal ions and the ligands coordinated around them.²⁰ The investigation of luminescent properties indicates that compounds 1 and 2 may be good blue-light luminescent materials.

Conclusions

In summary, two novel divalent metal phosphonates with 4-HOOCC₆H₄CH₂NHCH₂PO₃H₂ (H₃L) as ligand, namely, [Zn(HL)] (1) and $[CdCl(H_2L)]$ (2) have been synthesized under hydrothermal conditions. To the best of our knowledge, this is the first time that transition-metal carboxyphosphonates are reported with this ligand. Compounds 1 and 2 both feature three-dimensional (3D) framework structures with two-dimensional (2D) inorganic layers pillared by H₃L. In compound 1, $\{ZnO_4\}$ tetrahedra and $\{CPO_3\}$ tetrahedra connect with each other to form a 2D inorganic layer by corner-sharing. Such neighboring 2D inorganic layers are further supported by organic pillars {-C₆H₄CH₂NHCH₂-} of the carboxyphosphonate ligand to form a 3D pillared-layered structure. For compound 2, the interconnection of the $\{Cd_2Cl_2O_8\}$ polyhedra and $\{CPO_3\}$ tetrahedra is in turn linked by corner-sharing to form a 2D inorganic layer in the ab-plane. The adjacent 2D inorganic layers are further cross-linked through the organic pillars of the carboxyphosphonate ligand, generating a 3D pillared-layered structure. A remarkable characteristic of compounds 1 and 2 is the presence of alternate left- and right-handed helical chains in the structures. We have systematically investigated the influence of different metal salts and pH value on the synthesis of two title compounds. Thermal stabilities and the PXRD experiment reveal that compounds 1 and 2 are thermally stable up to 380 and 280 °C, respectively. The luminescence analysis indicates that compounds 1 and 2 may be good candidates for blue-light luminescent materials.

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References

1 (a) H. Hirao and K. Morokuma, J. Am. Chem. Soc., 2010, 132, 17901; (b) J.-A. Groves, S.-R. Miller, S.-J. Warrender, C. Mellot-Draznieks, P. Lightfoot and P.-A. Wright, *Chem. Commun.*, 2006, 3305; (*c*) P.-O. Adelani and T.-E. Albrecht-Schmitt, *Inorg. Chem.*, 2010, **49**, 5701; (*d*) W. Ouellette, M.-H. Yu, C.-J. O'Connor and J. Zubieta, *Inorg. Chem.*, 2006, **45**, 7628; (*e*) M. Plabst, L.-B. McCusker and T. Bein, *J. Am. Chem. Soc.*, 2009, **131**, 18112; (*f*) A. Clearfield, *Prog. Inorg. Chem.*, 1998, **47**, 371; (*g*) K. Maeda, *Microporous Mesoporous Mater.*, 2004, **73**, 47.

- 2 (a) M. Purgel, Z. Baranyai, A. Blas, T. Rodríguez-Blas, I. Bányai, C. Platas-Iglesias and I. Tóth, *Inorg. Chem.*, 2010, 49, 4370; (b) A.-N. Alsobrook, B.-G. Hauser, J.-T. Hupp, E.-V. Alekseev, W. Depmeierc and T.-E. Albrecht-Schmitt, *Chem. Commun.*, 2010, 46, 9167; (c) D.-P. Dong, L. Liu, Z.-G. Sun, C.-Q. Jiao, Z.-M. Liu, C. Li, Y.-Y. Zhu, K. Chen and C.-L. Wang, *Cryst. Growth Des.*, 2011, 11, 5346.
- 3 (a) E. Balogh, M. Mato-Iglesias, C. Platas-Iglesias, E. Toth,
 K. Djanashvili, J.-A. Peters, A. Beblas and T. Rodriguez-Blas, *Inorg. Chem.*, 2006, 45, 8719; (b) X.-F. Li, T.-F. Liu, Q.-P. Lin
 and R. Cao, *Cryst. Growth Des.*, 2010, 10, 608; (c) M. Feyand,
 C. Näther, A. Rothkirch and N. Stock, *Inorg. Chem.*, 2010, 49, 11158.
- 4 (a) H.-Q. Tan, W.-L. Chen, D. Liu, Y.-G. Li and E.-B. Wang, *CrystEngComm*, 2010, 12, 4017; (b) J.-T. Whitteck,
 P. Malova, S.-C. Peck, R.-M. Cicchillo, F. Hammerschmidt and W.-A. van der Donk, *J. Am. Chem. Soc.*, 2011, 133, 4236.
- 5 (a) Y.-Y. Zhu, Z.-G. Sun, H. Chen, J. Zhang, Y. Zhao, N. Zhang, L. Liu, X. Lu, W.-N. Wang, F. Tong and L.-C. Zhang, Cryst. Growth Des., 2009, 9, 3228; (b) L. Liu, Z.-G. Sun, N. Zhang, Y.-Y. Zhu, Y. Zhao, X. Lu, F. Tong, W.-N. Wang and C.-Y. Huang, Cryst. Growth Des., 2010, 10, 406; (c) K. Chen, Z.-G. Sun, Y.-Y. Zhu, Z.-M. Liu, F. Tong, D.-P. Dong, J. Li, C.-Q. Jiao, C. Li and C.-L. Wang, Cryst. Growth Des., 2011, 11, 4623; (d) D.-P. Dong, Z.-G. Sun, F. Tong, Y.-Y. Zhu, K. Chen, C.-Q. Jiao, C.-L. Wang, C. Li and W.-N. Wang, CrystEngComm, 2011, 13, 3317; (e) F. Tong, Z.-G. Sun, K. Chen, Y.-Y. Zhu, W.-N. Wang, C.-Q. Jiao, C.-L. Wang and C. Li, Dalton Trans., 2011, 40, 5059; (f) L.-Y. Cui, Z.-G. Sun, Z.-M. Liu, W.-S. You, Z.-M. Zhu, L. Meng, H. Chen and D.-P. Dong, Inorg. Chem. Commun., 2006, 9, 1232.
- 6 (a) F. Fredoueil, M. Evain, D. Massiot, M. Bujoli-Doeuff, P. Janvier, A. Clearfield and B. Bujoli, J. Chem. Soc., Dalton Trans., 2002, 1508; (b) C. Serre, N. Stock, T. Bein and G. Férey, Inorg. Chem., 2004, 43, 3159; (c) D. Cave, F.-C. Coomer, E. Molinos, H.-H. Klauss and P.-T. Wood, Angew. Chem., Int. Ed., 2005, 44, 1.
- 7 (a) Z.-X. Chen, Y.-M. Zhou, L.-H. Weng, C. Yuan and D.-Y. Zhao, *Chem.-Asian J.*, 2007, 2, 1549; (b) P.-F. Wang, D.-K. Cao, S.-S. Bao, H.-J. Jin, Y.-Z. Li, T.-W. Wang and L.-M. Zheng, *Dalton Trans.*, 2011, 40, 1307; (c) J.-M. Rueff, O. Perez, C. Simon, C. Lorilleux, H. Couthon-Gourvès and P.-A. Jaffrès, *Cryst. Growth Des.*, 2009, 9, 4262; (d) J.-L. Song, F.-Y. Yi and J.-G. Mao, *Cryst. Growth Des.*, 2009, 9, 3273.
- 8 T.-H. Zhou, F.-Y. Yi, P.-X. Li and J.-G. Mao, *Inorg. Chem.*, 2010, **49**, 905.
- 9 D.-J. Redmore, J. Org. Chem., 1978, 43, 996.
- 10 G.-M. Sheldrick, *SHELXS*–97, Program for X-ray Crystal Structure Solution and Refinement, University of Göttingen, Germany, 1997.
- 11 (a) J.-T. Li, L.-R. Guo, Y. Shen and L.-M. Zheng, CrystEngComm, 2009, 11, 1674; (b) J.-M. Taylor, R.-

K. Mah, I.-L. Moudrakovski, C.-I. Ratcliffe, R. Vaidhyanathan and G. K. H. Shimizu, *J. Am. Chem. Soc.*, 2010, **132**, 14055.

- 12 (a) C. V. K. Sharma and A. Clearfield, J. Am. Chem. Soc., 2000, 122, 1558; (b) J. Zhang, J. Li, Z.-G. Sun, R.-N. Hua, Y.-Y. Zhu, Y. Zhao, N. Zhang, L. Liu, X. Lu, W.-N. Wang and F. Tong, Inorg. Chem. Commun., 2009, 12, 276.
- 13 (a) S. Bauer, T. Bein and N. Stock, *Inorg. Chem.*, 2005, 44, 5882; (b) S. Bauer, J. Marrot, T. Devic, G. Férey and N. Stock, *Inorg. Chem.*, 2007, 46, 9998.
- 14 (a) H.-S. Martínez-Tapia, A. Cabeza, S. Bruque, P. Pertierra, S. García-Granda and M. A. G. Aranda, J. Solid State Chem., 2000, 151, 122; (b) A. Cabeza, M. A. G. Aranda and S. Bruque, J. Mater. Chem., 1998, 8, 2479; (c) A. Cabeza, X. Ouyang, C. V. K. Sharma, M. A. G. Aranda, S. Bruque and A. Clearfield, Inorg. Chem., 2002, 41, 2325.
- 15 C.-H. Lin and K.-H. Lii, Inorg. Chem., 2004, 43, 6403.
- 16 C.-A. Merrill and A.-K. Cheetham, Inorg. Chem., 2005, 44, 5273.

- 17 (a) D.-Y. Kong, D.-G. Medvedev and A. Clearfield, *Inorg. Chem.*, 2004, 43, 7308; (b) K.-R. Ma, J.-N. Xu, L.-R. Zhang, J. Shi, D.-J. Zhang, Y.-L. Zhu, Y. Fan and T.-Y. Song, *New J. Chem.*, 2009, 33, 886.
- 18 (a) J. Yang, G.-D. Li, J.-J. Cao, Q. Yue, G.-H. Li and J.-S. Chen, *Chem.-Eur. J.*, 2007, **13**, 3248; (b) X.-G. Liu, J. Huang, S.-S. Bao, Y.-Z. Li and L.-M. Zheng, *Dalton Trans.*, 2009, 9837; (c) J. Li, C.-C. Ji, L.-F. Huang, Y.-Z. Li and H.-G. Zheng, *Inorg. Chim. Acta*, 2011, **371**, 27.
- (a) C. Xu, B. Liu, S.-S. Bao, Y. Chen and L.-M. Zheng, *Solid State Chem.*, 2007, 9, 686; (b) C.-Q. Jiao, C.-Y. Huang, Z.-G. Sun, K. Chen, C.-L. Wang, C. Li, Y.-Y. Zhu, H. Tian, S.-H. Sun, W. Chu and M.-J. Zheng, *Inorg. Chem. Commun.*, 2012, 17, 64.
- 20 (a) X.-Q. Liu, Y.-Y. Liu, Y.-J. Hao, X.-J. Yang and B. Wua, Inorg. Chem. Commun., 2010, 13, 511; (b) Q.-R. Fang, G.-S. Zhu, M. Xue, J.-Y. Sun, F.-X. Sun and S.-L. Qiu, Inorg. Chem., 2006, 45, 3582.