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New 4,5-dichlorophthalhydrazidate-bridged chained coordination polymers

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ABSTRACT

The hydrothermal self-assemblies of Pb^{2+}/Cd^{2+} salt, 4,5-dichlorophthalic acid (dcpha), $N_2H_4 \cdot H_2O$ together with 1,10-phenanthroline $\cdot H_2O$ (phen) or 2,2′-bipyridine (bpy) generated two new monoacylhydrazidate-bridged 1-D chained coordination polymers $[Pb_2(DCPTH)_4(phen)_2]$ **1** and $[Cd_3(DCPTH)_2(dcph)_2(bpy)_2]$ **2** (DCPTH=4,5-dichlorophthalhydrazidate, dcph=4,5-dichlorophthalate). The monoacylhydrazidate ligand DCPTH originated from the hydrothermal *in situ* acylation reaction between dcpha and $N_2H_4 \cdot H_2O$. In compound **1**, two types of coordination modes for DCPTH are found, which link alternately the Pb(II) centers into a 1-D chain structure of compound **1** with ancillary phen molecules. In compound **2**, DCPTH and dcph as the mixed bridges extend the Cd(II) centers into a 1-D chain structure of compound **2** with auxiliary bpy molecules. DCPTH in compound **2** shows a different coordination mode from those observed in compound **1**.

1. Introduction

Considerable attention has been paid to the study on the design and synthesis of novel coordination polymers due to the interesting structures [1–7] and the potential applications in the fields of adsorption [8–17], optics [18–27] and magnetism [28–31]. So far, even though so many coordination polymers have been reported, most of the used organic ligands are commercially available or presynthesized. Recently, the hydro(solvo)thermal ligand *in situ* preparations offer a new approach to obtain the novel organic ligands [32–34]. Under the hydro(solvo)thermal conditions, the ligand precursors and the metal salts were mixed together to self-assemble, producing finally the ligand-bridged coordination polymers. Obviously, the *in situ* reaction between the ligand precursors in the presence of metal salt created the new organic ligand. So far, several ligand *in situ* reactions such as the hydroxylation of phen or bpy [35–37], the cycloaddtion between organonitrile and azide [38–44], the *N*-alkylation between *N*-heterocyclic ligand and alcohol [45–47], and so on have been observed, and applied to construct a few novel coordination polymers. In 2004, Xu reported first the diacylhydrazidate-bridged coordination polymers obtained by applying the *in situ* acylation reaction between pyromellitic acid and hydrazine hydrate [48,49]. It is not difficult to find that the polycarboxylic acids containing at least a pair of neighboring carboxyl groups can *in situ* acylate with hydrazine hydrate (see Scheme 1). As an extension of this work, several novel monoacylhydrazidate-bridged coordination polymers with 1-D, 2-D and 3-D structures have been further prepared using phthalic acid (pha), pyridine-2,3-dicarboxylic acid (2,3-pdca), pyridine-3,4-dicarboxylic acid (3,4-pdca) [50] and benzene-1,2,4-tricarboxylic acid (btca) [51] to replace pyromellitic acid. Due to the presence of the N and O donors in the structure, the acylhydrazidate ligands are really the ideal candidate of the bridging-type ligands. In this article, a new organic polycarboxylic acid dcpha is selected to displace pyromellitic acid, and two new monoacylhydrazidate-bridged 1-D chained coordination polymers $[Pb_2(DCPTH)_4(phen)_2]$ **1** and $[Cd_3(DCPTH)_2(dcph)_2(bpy)_2]$ **2** were luckily obtained. The substituted Cl atoms on DCPTH have the important effect on the construction of the chain structures for the title compounds, compared with the chain structures of the reported phthalhydrazidate (PTH)-bridged coordination polymers. For comparison, the coordination modes of PTH and DCPTH in the complexes are given in Scheme 2. The structure of ligand [H(DCPTH)] **3** was also reported in order to better understand the character of the monoacylhydrazide molecule and the photoluminescence properties of compounds **1** and **2**.

2. Experimental

2.1. Materials and physical measurement

All chemicals are of regent grade quality, obtained from commercial sources without further purification. Elemental

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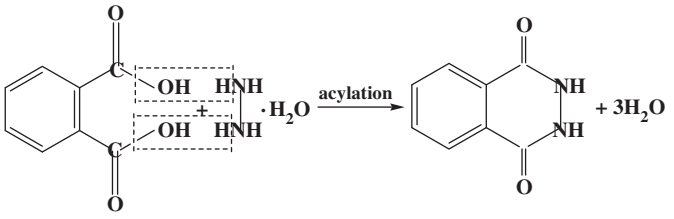
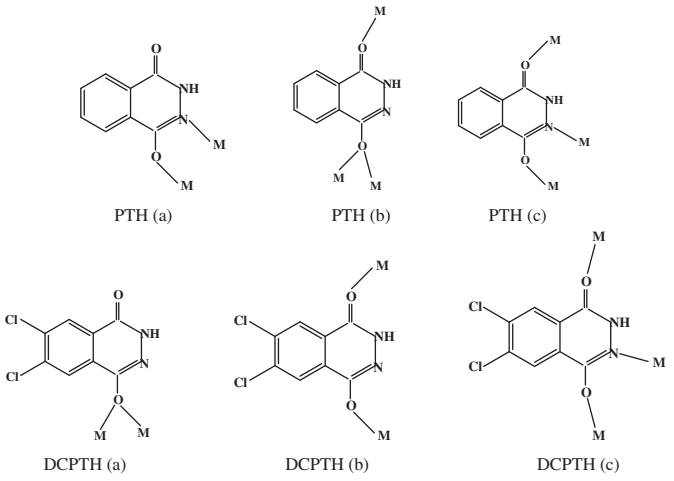


Scheme 1. Acylation reaction between organodicarboxylic acid and hydrazine hydrate.



Scheme 2. Coordination modes of PTH and DCPTH in the complexes.

Table 1
Crystallographic data for compounds **1**–**3**.

	Compound		
	1	**2**	**3**
Formula	$C_{56}H_{28}N_{12}O_8Cl_8Pb_2$	$C_{52}H_{24}N_8O_{12}Cl_8Cd_3$	$C_8H_4N_2O_2Cl_2$
M	1694.9	1573.59	231.03
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1	$P2_1/n$	$P2_1/c$
a (Å)	9.8114(3)	7.9126(3)	7.1815(14)
b (Å)	11.2357(3)	25.7233(12)	9.0468(18)
c (Å)	12.6827(3)	13.2669(6)	13.524(3)
α (deg.)	97.186(2)		
β (deg.)	92.992(2)	93.416(3)	99.67(3)
γ (deg.)	100.776(2)		
V (Å^3)	1358.57(6)	2695.5(2)	866.21(3)
Z	1	2	4
D_c (g cm^{-3})	2.072	1.939	1.772
μ (mm^{-1})	6.653	1.642	0.718
Reflections collected	10,077	19,657	8037
Unique reflections	6792	6739	1927
R_{int}	0.0313	0.0661	0.0366
Gof	1.105	1.107	1.039
R_1, $I > 2\sigma(I)$	0.0287	0.0632	0.0641
wR_2, all data	0.0826	0.1612	0.1834

analysis (C, H and N) was performed on a Perkin-Elmer 2400LS II elemental analyzer. Infrared (IR) spectrum was recorded on a Perkin-Elmer Spectrum 1 spectrophotometer in 4000–400 cm^{-1} region using a powdered sample on a KBr plate. Fluorescence spectrum in solid state was obtained on a LS 55 florescence/phosphorescence spectrophotometer at room-temperature.

2.2. Synthesis of the title compounds

[Pb_2(DCPTH)$_4$(phen)$_2$] 1: The yellow block crystals of **1** were obtained by a simple hydrothermal self-assembly of $Pb(CH_3COO)_2 \cdot 3H_2O$ (190 mg, 0.5 mmol), dcpha (118 mg, 0.5 mmol), $N_2H_4 \cdot H_2O$ (0.1 mL) and phen $\cdot$ H_2O (99 mg, 0.5 mmol) in a 15 mL aqueous solution (pH=4–5 acidified by dilute CH_3COOH) at 170 °C for 4 days. Yield: *ca.* 30% based on Pb. Anal. Calcd $C_{56}H_{28}N_{12}O_8Cl_8Pb_2$ **1**: C 39.68, H 1.67, N 9.92. Found: C 39.57, H 1.50, N 9.97%. IR (cm^{-1}): 1657s, 1634s, 1566s, 1517m, 1462s, 1423s, 1361s, 1278m, 1201s, 1063w, 810s, 724m.

[Cd_3(DCPTH)$_2$(dcph)$_2$(bpy)$_2$] 2: The light-green block crystals of **2** were obtained by a similar hydrothermal self-assembly to that of **1** except that $Cd(CH_3COO)_2 \cdot 2H_2O$ (133 mg, 0.5 mmol) replaced $Pb(CH_3COO)_2 \cdot 3H_2O$ and bpy (78 mg, 0.5 mmol) replaced phen $\cdot$ H_2O. Yield: *ca.* 40% based on Cd. Anal. Calcd $C_{52}H_{24}N_8O_{12}Cl_8Cd_3$ **2**: C 39.69, H 1.54, N 7.12. Found: C 39.73, H 1.45, N 7.01%. IR (cm^{-1}): 1635m, 1557s, 1511m, 1439m, 1400s, 1315m, 1222m, 831m, 802m, 763m.

[H(DCPTH)] 3: The yellow block crystals of **3** were obtained by a simple hydrothermal self-assembly to that of **2** except that $MnCl_2 \cdot 4H_2O$ (99 mg, 0.5 mmol) replace $Cd(CH_3COO)_2 \cdot 2H_2O$. Anal. Calcd $C_8H_4N_2O_2Cl_2$ **3**: C 41.59, H 1.75, N 12.12. Found: C 41.44, H 1.60, N 11.97%. IR (cm^{-1}): 1647s, 1580s, 1455s, 1402m, 1311s, 1261m, 1132m, 1073s, 924m, 812s, 640m.

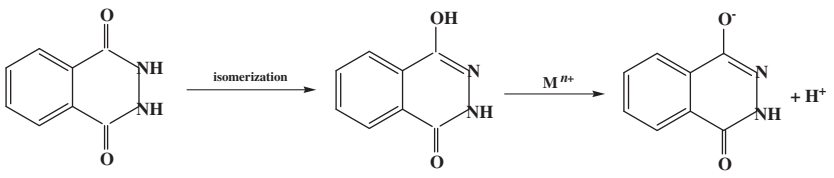
The reactions were carried out in 30 mL Teflon-lined stainless steel vessels under the autogenous pressure. The single crystals were collected by filtration, washed with distilled water and dried in air at the ambient temperature. Although some raw materials as Mn^{2+} and bpy in preparing **3** did not appear in the final framework, without them the single crystals suitable for X-ray diffraction were not obtained.

2.3. X-ray crystallography

The data were collected with Mo-*K*α radiation (λ=0.71073 Å) on a Siemens SMART CCD diffractometer for compounds **1** and **2**, and on

Table 2
C–O and C–N distances of the monoacylhydrazidate ligands in the title compounds.

	1		**2**	**3**
	(I)	**(II)**		
d(C–O$^-$) (Å)	1.296(5)	1.312(5)	1.281(9)	1.341(4)
d(C=O) (Å)	1.244(5)	1.238(5)	1.241(9)	1.242(4)
d(C=N) (Å)	1.309(6)	1.312(5)	1.293(10)	1.285(4)
d(C–N) (Å)	1.346(6)	1.349(6)	1.357(10)	1.347(4)



Scheme 3. Isomerization and the deprotonation reactions for the monoacylhydrazidate ligand.

a Rigaku R-AXIS RAPID IP diffractometer for compound **3**. With SHELXTL program, all of the title compounds were solved using direct methods, and refined by full-matrix least-squares techniques [52]. The non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement. The hydrogen atoms were treated using a riding model except those of compound **3**. The hydrogen atoms for compound **3** are obtained from the different Fourier map except that the hydrogen atom on N2 is from a riding model. The structures were then refined on F^2 using SHELXL-97 [53]. CCDC numbers of compounds **1, 2** and **3** are 787,399, 787,400 and 787,404, respectively. Basic information pertaining to the crystal parameters and structure refinement of the compounds is summarized in Table 1.

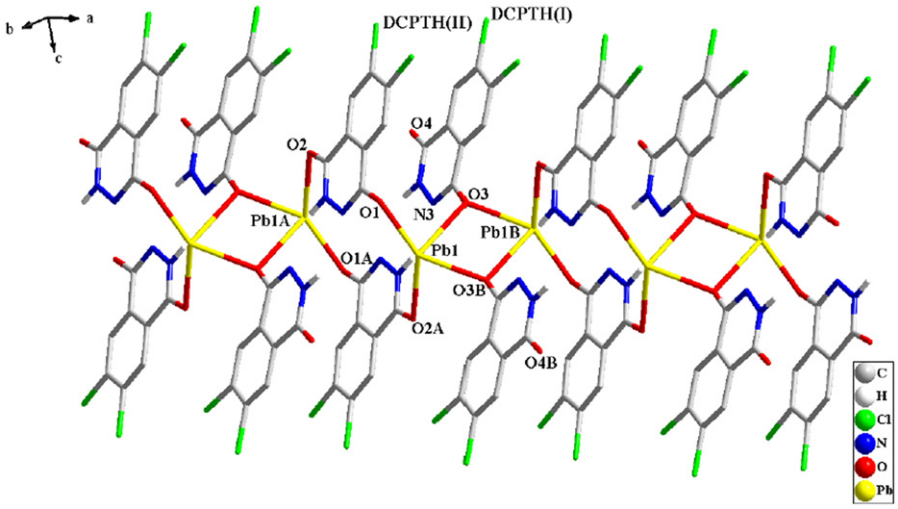


Fig. 1. 1-D chain structure of **1**, extending along the *a*-axis direction (phen is omitted for clarity).

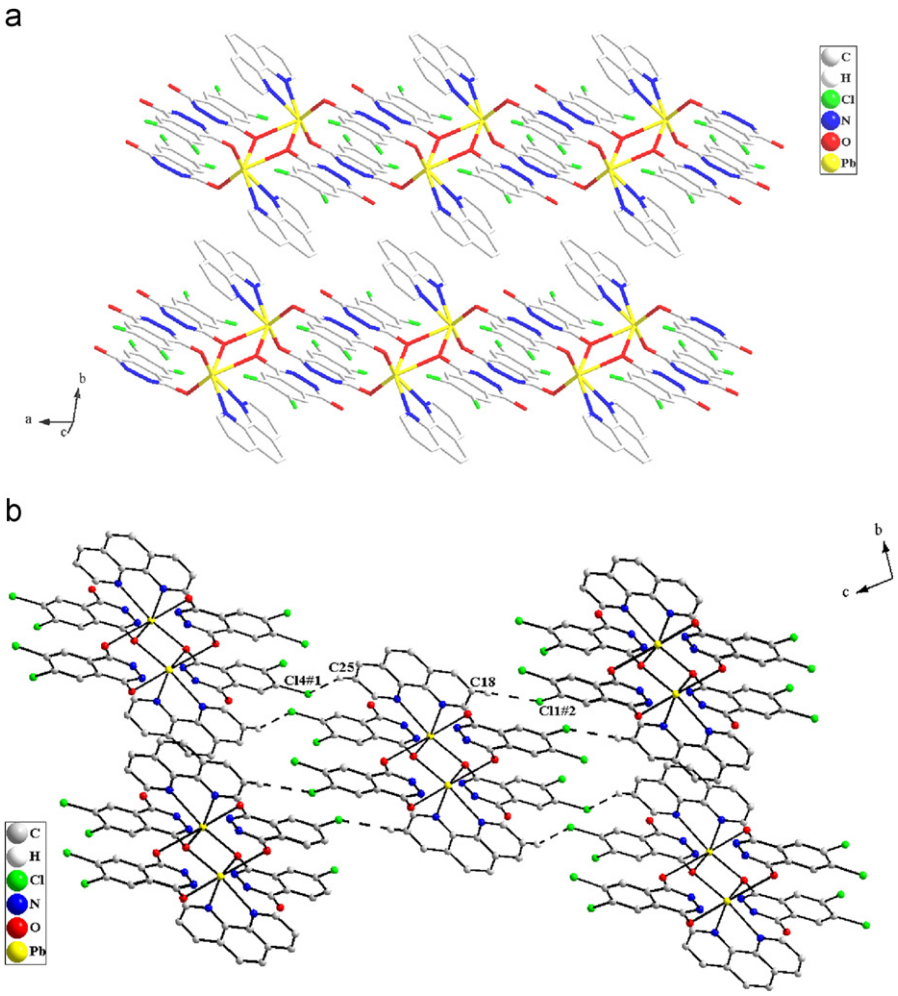


Fig. 2. π···π packings between the chains (a) and the C–H···Cl hydrogen bondings between the supramolecular layers (b) in **1**.

3. Results and discussion

3.1. Existing form and oxidation state of the monoacylhydrazidate in the complex

Based on the acylation reaction mechanism between organic polycarboxylic acid and hydrazine hydrate, organic monoacylhydrazide molecule should theoretically exhibit a diketo form (see Scheme 1). However, X-ray analysis for the obtained acylhydrazidate-containing complexes revealed that two C–O bond lengths are not equal to each other, suggesting that the acylhydrazidate ligands exist in the ketohydroxy form in the complexes. As shown in Scheme 3, the isomerization for the acylhydrazide molecule obviously occurred. This is further confirmed by the title compounds **1** and **2**. One C–O distance [1.281(9)–1.312(5) Å] for each DCPTH ligand in compounds **1** and **2** is slightly longer than the other one [1.238(5)–1.244(5) Å]. The corresponding C═N distances [1.293(10)–1.312(5) Å] are slightly shorter than the other ones [1.346(6) –1.357(10) Å] (see Table 2). When the monoacylhydrazide molecules coordinate to the metal centers, the hydroxyl group deprotonates to balance the metal charges. So the monoacylhydrazidate ligands show -1 oxidation state in the complexes. So far, no examples show that the other acylamino group could also isomerize into the hydroxylimino group.

3.2. Structural description

$[Pb_2(DCPTH)_4(phen)_2]$ 1: Compound **1** is the first example of DCPTH-bridged inorganic coordination polymer. The asymmetric unit of compound **1** is composed of one Pb(II) ion, two DCPTH ligands and one phen molecule. As shown in Fig. S1, the Pb1 center is six-fold coordinated by three hydroxylimino O atoms (O1, O3, O3B), one acylamino O atom (O2A) as well as two phen N atoms (N5, N6). The Pb–N distances of 2.490(3) and 2.690(3) Å, respectively, are normal. The Pb–$O_{hydroxylimino}$ distances of 2.403(3)–2.559(3) Å are by far shorter than that of the Pb–$O_{acylamino}$ [2.974(4) Å], which is due to the existence of so many aromatic rings around Pb1 (five in all). Despite the Pb–$O_{acylamino}$ bond distance being rather longer, it is shorter than that observed in compound $[Pb_2(2,2'\text{-bpy})_2(4,4'\text{-bpy})(NO_3)_4]$ (3.058 Å) [54]. The separation of 3.314 Å is even longer than that observed in the reported $[Pb_2(PTH)_4(phen)_2]$ [2.690(3) Å] [50], suggesting no bonding interaction exists between Pb1 and N3. The dihedral angles between phen ring and two DCPTH rings in each asymmetric unit are 18.2° and 16.3°, respectively. As shown in Fig. 1, two crystallographically independent DCPTH ligands exhibit the different coordination modes. DCPTH(I) exhibits a μ_2 coordination mode with the hydroxylimino O atom (O3) bonding to two Pb(II) centers (Pb1, Pb1B). DCPTH(II) also exhibits a μ_2 coordination mode but with two O atoms (O1, O2) bonding, respectively, to two Pb(II) centers (Pb1, Pb1A). With ancillary phen, two-types of DCPTH ligands bridge the Pb(II) centers into a 1-D infinite chain of compound **1**. Two symmetry-related DCPTH(I) ligands using the hydroxylimino O atoms (O3, O3B) first bi-bridge two Pb(II) centers (Pb1, Pb1B) into a rhomboid Pb_2O_2 subunit with a Pb···Pb contact of 4.185 Å. This Pb_2O_2 subunit is planar. Two symmetry-related DCPTH(II) using their O donors (O1, O2, O1A, O2A) extend further the Pb_2O_2 subunits into a 1-D infinite chain. Although two adjacent symmetry-related DCPTH(II) ligands are parallel to each other and the distance is close (*ca.* 3.22 Å), no π···π interaction between DCPTHs(II) are found, because their π electronic clouds have no any overlap. The weak π···π interaction is formed between adjacent DCPTH(I) and DCPTH(II) with a distance

Table 3
Hydrogen-bond parameters in compounds **1**–**3**.

	$d_{D\text{-}H}$ (Å)	$d_{H\cdots A}$ (Å)	∠DHA (deg.)	$d_{D\cdots A}$ (Å)	Symmetry mode
1					
C25-H25A···Cl4#1	0.93	2.82	150.9	3.665(5)	#1: *x*, *y*+1, *z*+1
C18-H18A···Cl1#2	0.93	2.73	153.3	3.585(5)	#2: −*x*+1, −*y*, -*z*
2					
C20-H20A···O4#1	0.93	2.43	156.0	3.306(10)	#1: -*x*+1, −*y*, −*z*+1
C23-H23A···O4#1	0.93	2.49	147.1	3.310(10)	
C25-H25A···Cl2#2	0.93	2.87	125.2	3.487(10)	#2: *x*+0.5, −*y*−0.5, *z*+0.5
3					
N2-H2A···O2#1	0.86	2.05	170.8	2.898(3)	#1: -*x*+1, −*y*−1, −*z*+2
O1-H4···O2#2	0.73	1.97	159.0	2.660(4)	#2: *x*, −*y*−0.5, *z*+0.5

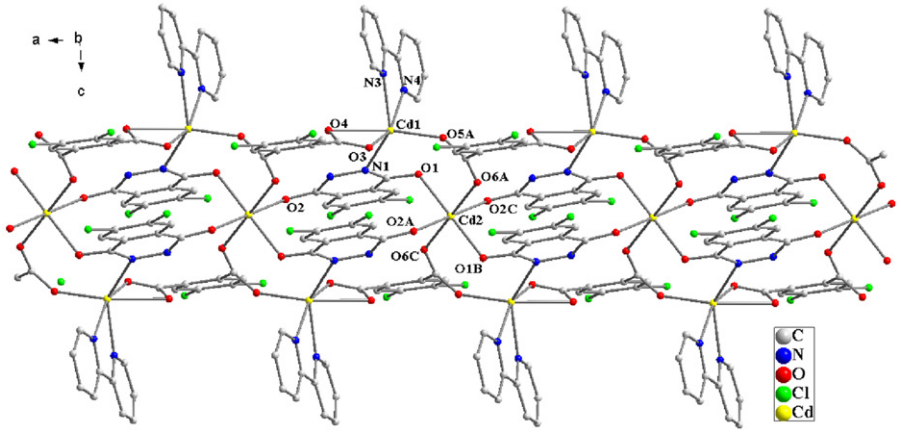


Fig. 3. 1-D chain structure of **2**, extending along the *a*-axis direction.

of *ca*. 3.35 Å, stabilizing the chain structure of compound **1**. As shown in Fig. 2a, the ancillary phen molecules protrude out from the chain, and alternate array on both side of the chain. The 1-D chains are self-assembled into a 2-D supramolecular layer via the offset face-to-face π···π interactions of the adjacent phen rings between the chains with a separation of 3.51 Å. As shown in Fig. 2b, the 2-D supramolecular layers are further propagated into a 3-D supramolecular network via the intermolecular C–H···Cl hydrogen-bonded interactions between the phen H atoms attached to C25, C18 and the substituted Cl atoms (Cl4#1, Cl1#2) of the DCPTH ligands. Compound $[Pb_2(PTH)_4(phen)_2]\cdot H_2O$ is the PTH-bridged chained Pb^{2+} coordination polymer. Although it has a similar composition to that of compound **1**, but it exhibits a different chain arrangement, and the coordination modes of the PTH ligands (PTH (a), and PTH (b) in Scheme 2) are different from those of the DCPTH ligands. These differences should be ascribed to the existence of the substituted Cl atoms on DCPTH. The hydrogen-bonded parameters for the title compounds are listed in Table 3.

$[Cd_3(DCPTH)_2(dcph)_2(bpy)_2]$ 2: Compound **2** is another containing DCPTH inorganic coordination polymer. It is interesting that dcph also appeared in the final framework of compound **2**. The asymmetric unit of compound **2** consists of two Cd(II) cations (occupancy ratio: Cd1 1.0, Cd2 0.5), one DCPTH ligand, one dcph ligand together with one bpy molecule. As shown in Fig. 3, both Cd1 and Cd2 are in the octahedral sites, but Cd1 is surrounded by three carboxyl O atoms (O3, O4, O5A), one hydroxylimino N atom (N1) and two bpy N atoms (N3, N4), whereas Cd2 is surrounded by two hydroxylimino O atoms (O1, O1B), two acylamino O atoms (O2A, O2C) and two carboxyl O atoms (O6A, O6C). The Cd1–N_{bpy} distances of 2.376(6)–2.391(6) Å are slightly longer than that of Cd1–$N_{hydroxylimino-}$ [2.306(6) Å]. The Cd1–O range of 2.185(6)–2.519(5) is obviously wider than that of Cd2–O [2.264(5)–2.304(5) Å], which maybe due to the chelating coordination of carboxyl group and bpy molecule to the Cd1 center, leading to the severe distortion of the Cd1 octahedron. Another reason is that O4 participates in the formation of intermolecular hydrogen bonds. Dcph exhibits a μ_3 coordination mode: one carboxyl group

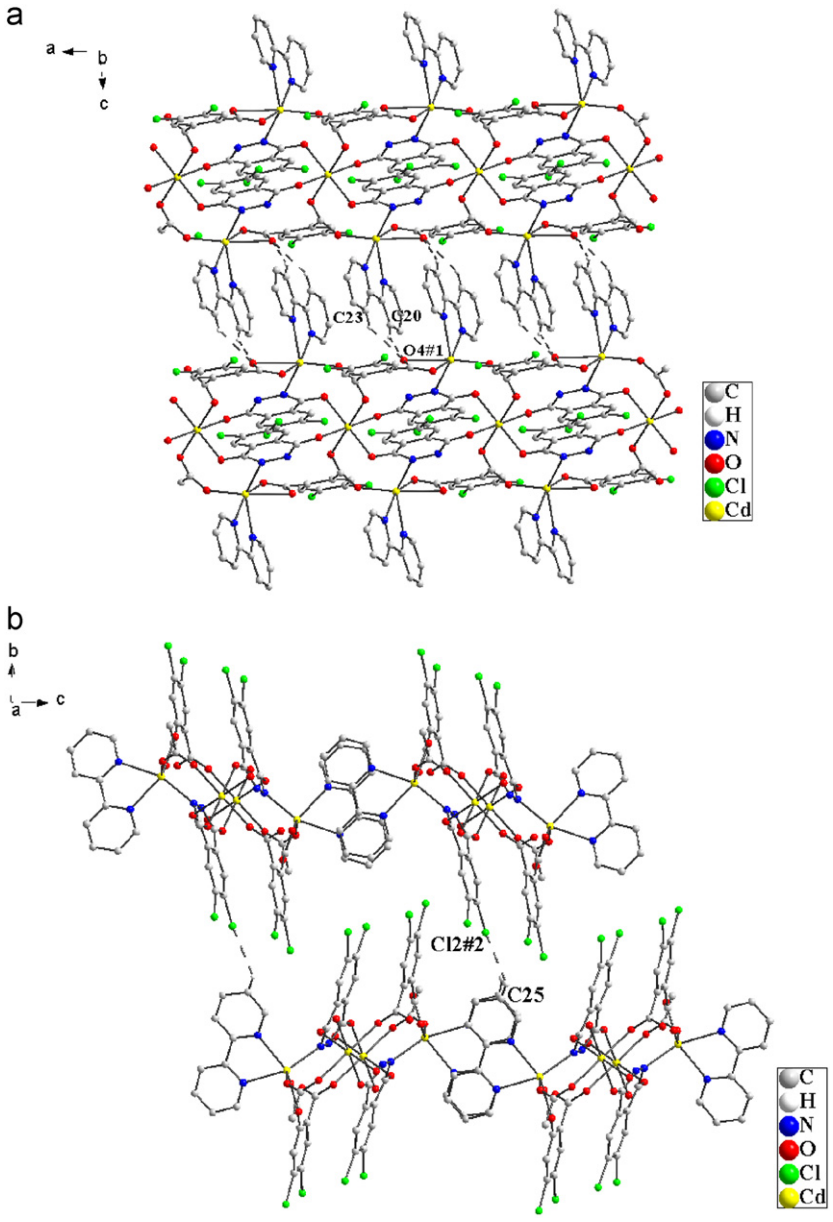


Fig. 4. Packing diagrams in (0 1 0) (a) and (1 0 0) (b) directions, showing the interactions amongst the chains in **2**.

chelates bidentately to the Cd1 center, and the other carboxyl group bridges bidentately to two Cd centers (Cd1, Cd2). The average $O_{chelateing-}$–Cd distance (2.430 Å) is longer than that of the average $O_{bridging-}$–Cd (2.245 Å). Different from the coordination modes found in compound **1**, DCPTH in compound **2** exhibit a new μ_3 one, similar to that of PTH in reported [Cu(PTH)] (see PTH (c) in Scheme 2) [50]. Besides two O atoms monodentately bonding respectively to the Cd centers, the hydroxylimino N atom further coordinates monodentately one Cd1 center. The Cd2–$O_{hydroxylimino-}$ (2.264 Å) and Cd2–$O_{acylamino-}$ bond lengths (2.266 Å) are basically compared with each other. With auxiliary bpy molecule, DCPTH and dcph as the mixed bridges extend the Cd centers into a 1-D infinite chain structure of compound **2**. DCPTH in Fig. 3 is omitted in order to better understand the chain formation (see Fig. S2a). Each dcph using three carboxyl O atoms (O3A, O4A, O5A) links first the Cd1 centers into a 1-D chain extending along the *a*-axis with a Cd–Cd separation of 7.913 Å. Via sharing the remaining carboxyl O atoms (O6A, O6C) of the dcph ligands, two 1-D chains are further linked together by the Cd2 centers into a 1-D double-chain structure with the cubic rings. The formation of this ring can be described as an alternate connection of four dcph ligands (two dcph and two $-COO^-$) and four Cd(II) centers (two Cd1 and two Cd2) with an order of Cd1-COO^-–Cd2-dcph-Cd1… with the shortest Cd⋯Cd separation of Cd1⋯Cd2=4.297 Å. Fig S2b is the projected plot of the double-chain structure in the *bc* plane (bpy is omitted for clarity). Two dcph ligands in each cubic ring are parallel to each other, and arrange on both sides of the ring plane. Two DCPTHs parallel to each other sit above or below the macroporous ring plane. Each DCPTH π⋯π interacts with the same-side dcph with a separations of 3.28 Å. As shown in Fig. 3, each DCPTH with a μ_3 mode coordinates to three Cd(II) centers of the double-chain framework, stabilizing the double-chain structure. In fact, the main role of the DCPTH in compound **2** is to bi-bridge the Cd2 centers into a 1-D chain with a Cd–Cd separation of 7.913 Å (see Fig. S2c). Different from the situation in compound **1**, the ancillary bpy is almost perpendicular to the dach and DCPTH rings with the dihedral angles of 89.5° and 94.1°, respectively. Three types of secondary bonding interactions amongst the chains are found, stabilizing the crystal structure of compound **2**. As shown in Fig. 4a, the adjacent bpy rings stack together via the offset face-to-face π⋯π interacts with a separation of 3.63 Å. At the same time, the carboxyl O4#1 atom forms the intermolecular hydrogen bonds to the bpy H atoms attached to C20 and C23 with the C⋯O contacts of C20⋯O4#1=3.306(10) and C23⋯O4#1=3.310(10) Å, respectively. As shown in Fig. 4b, the substituted Cl atom of DCPTH forms the intermolecular C–H⋯Cl hydrogen bond to the bpy H atom attached to C25 with the C⋯Cl contact of C25⋯Cl2#2=3.487(10) Å.

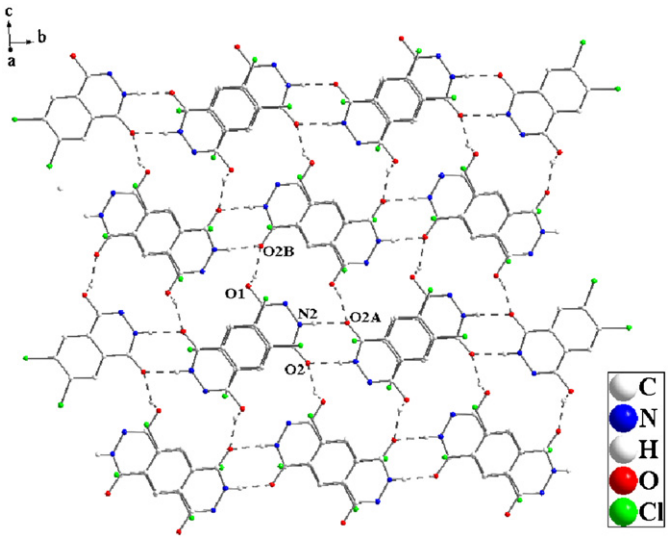


Fig. 5. 2-D supramolecular layer of **3**.

[H(DCPTH)] 3: The pure ligand [H(DCPTH)] of compound **3** was prepared and structurally characterized in order to better understand the character of the monoacylhydrazide molecule and the fluorescence properties of compounds **1** and **2**. Compound **3** is the third example of structurally characterized acylhydrazide ligands. The other two are phthalhydrazide [55] and pyromelhydrazide [50], respectively. The same as another monoacylhydrazide ligand phthalhydrazide, the organic [H(DCPTH)] ligand exists in the ketohydroxy form, which is confirmed by the different C–O and C–N distances (see Table 2). Not all of the acylhydrazide ligands exist in the ketohydroxy form. Pyromelhydrazide is just an exception, and it exists in the diketo form. As shown in Fig. 5, compound **3** contains the 2-D supramolecular layer structure. Two adjacent [H(DCPTH)] molecules form first a dimer via the intermolecular N–H⋯O interactions between the acylamino groups (see Fig. S3a for better understanding). The N⋯O contact of 2.898(3) Å is slightly weaker than those observed in the reported compounds [50,51]. Four O atoms of each dimer either as the donors or as the acceptors form further the hydrogen bonds to the O atoms from the adjacent dimers, extending the dimers into a 2-D supramolecular layer of compound **3**. The O⋯O separation of 2.660(4) Å is comparable with that observed in co-crystal [(py)(ipha)] (py=pyridine, ipha=isophthalic acid) [O⋯O=2.6696(13) Å] [56]. Due to the parallel arrangement of the adjacent dimers along the *b*-axis direction and the different directions of these two kinds of hydrogen bonds, the 2-D supramolecular layer has a certain thickness as shown in Fig. S3b.

Table 4
IR characteristic peaks for some polycarboxylic acids and the monoacylhydrazidate-coordinated complexes in the range of 1600–1750 cm^{-1}.

Organic polycarboxylic acid	ν(COO) (cm^{-1})	Monoacylhydrazidate	ν(CONH) (cm^{-1})	Ref.
pha	1693 s	$[Pb_2(PTH)_4(phen)_2]\cdot H_2O$	1632s	[50]
		[Cu(PTH)]	1646s	[50]
btca	1717 s, 1691 m	[Pb(CPTH)(phen)]	1636m	[51]
		$[Pb_4(OH)_2(H_2O)_3(CPTH)_3]\cdot 2H_2O$	1666s	[51]
2,3-pdca	1603 s	$[Pb(2,3\text{-}PDH)_2]$	1673s	[50]
		$[Mn(2,3\text{-}PDH)_2(H_2O)_2]$	1634s	[50]
3,4-pdca	1713 s, 1607 s	$[Pb(3,4\text{-}PDH)_2]$	1666s	[50]
dcpha	1683 m, 1610 m	**1**	1657s	This job
		2	1635m	This job
		3	1647s	This job

2,3-PDH=pyridine-2,3-dicarboxylhydrazidate; 3,4-PDH=pyridine-3,4-dicarboxylhydrazidate; CPTH=4-carboxylphthalhydrazidate.

3.3. Coordination character of the monoacylhydrazidate ligand

From the Scheme 2, the context and the reported references [47,48], some conclusions about the coordination character of the monoacylhydrazidate ligands can be drawn: (i) in general, the monoacylhydrazidate with the hydroxylimino O atom as the donor coordinates to the metal centers. Sometimes the hydroxylimino N atom and the acylamino O atom also participate in the coordination to the metals; (ii) the acylamino N atom has no reactivity, and no examples show that it could also coordinate to the metals; and (iii) the adjacent acylamino groups tend to form a hydrogen-bonded dimer *via* the N–H···O interactions, extending the discrete or low-dimensional molecular units into high-dimensional supramolecular networks and stabilizing them.

3.4. IR analysis

Table 4 listed the IR characteristic peaks in the range of 1600–1750 cm^{-1} for the used organic polycarboxylic acid precursors and the obtained monoacylhydrazidate-containing coordination polymers. We can find that the peaks for the polycarboxylic acid raw materials are either larger than 1680 cm^{-1} or smaller than 1610 cm^{-1}. These peaks should be assigned to the stretching vibration of the carboxyl groups. While for the monoacylhydrazidate-coordinated compounds, the stretching vibration peaks of the acylamino/hydroxylimino groups appear in the range of 1630–1675 cm^{-1}. Obviously, both ranges have no overlap. Hence, this provides a simple method to judge whether the polycarboxylic acid precursors have acylated into the acylhydrazidate ligands.

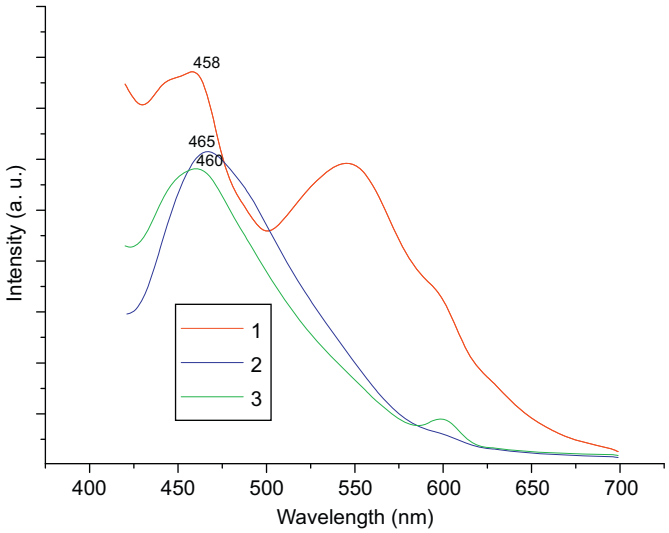


Fig. 6. Fluorescence emission spectra of the title compounds.

3.5. Fluorescence property

The room-temperature solid-state fluorescence properties of compounds **1** and **2** were investigated. Fig. 6 gives their fluorescence emission spectra. Compounds **1** and **2** show the similar fluorescence properties with the maximum emission peaks at 458 nm for **1** (λ_{ex}=400 nm) and 465 nm for **2** (λ_{ex}=400 nm), respectively. The fluorescence property of the DCPTH ligand of compound **3** was also investigated in order to better understand the fluorescence properties of compounds **1** and **2**. Obviously, the fluorescence emissions of compounds **1** and **2** should be attributed to the charge transfer of intra-DCPTH ligands, because the DCPTH ligand shows a similar fluorescence maximum emission centered at 460 nm upon excitation at 400 nm (also see Fig. 6). In order to understand the emission mechanism, the density functional theory (DFT) calculations were carried out on the excited electronic states of compound **3**. The calculation details are provided as the supplementary material. The DFT calculation results for the monomer indicate that there is a strong emission at 394 nm (f=0.0395), corresponding to the electronic transition from orbital 58 (the highest occupied molecular orbital, HOMO) to orbital 59 (the lowest unoccupied molecular orbital, LUMO). Obviously, this result is different from that of the observed one (460 nm). While the DFT calculation results for the hydrogen-bonded dimer show that around 465 nm (f=0.0045) there exists an emission, corresponding to the electronic transition from orbital 116 (HOMO) to orbital 118 (LUMO+1). This result is well comparable with that of the found one. Fig. 7 gives the characteristics of orbital 116 and orbital 118. The electron densities of the HOMO are distributed mainly on one monomer, whereas those of the LUMO+1 are located at the other monomer. Therefore, the photoluminescence emission of compound **3** should be ascribed to the charge transfer from one molecule to the other molecule through the hydrogen bonds as the bridges. The first singlet excited state structures of monomer and dimer for compound **3**, the electron density contours of the Frontier molecular orbitals of the monomer for compound **3**, and the molecular orbital compositions in the excited states of monomer and dimer for compound **3** are provided as the supplementary materials.

4. Conclusions

In summary, we reported the preparations and structural characterization of two new monoacylhydrazidate-bridged chained coordination polymers $[Pb_2(DCPTH)_4(phen)_2]$ **1** and $[Cd_3(DCPTH)_2(dcph)_2(bpy)_2]$ **2**, which were obtained by the simple hydrothermal self-assemblies of metal salts, dcpha, hydrazine hydrate as well as phen·H_2O/2,2'-bpy. The monoacylhydrazidate ligand DCPTH derived from the hydrothermal *in situ* acylation reactions between dcpha and $N_2H_4 \cdot H_2O$. Compound **1** is the first example of DCPTH-containing coordination polymer. The substituted Cl atoms on

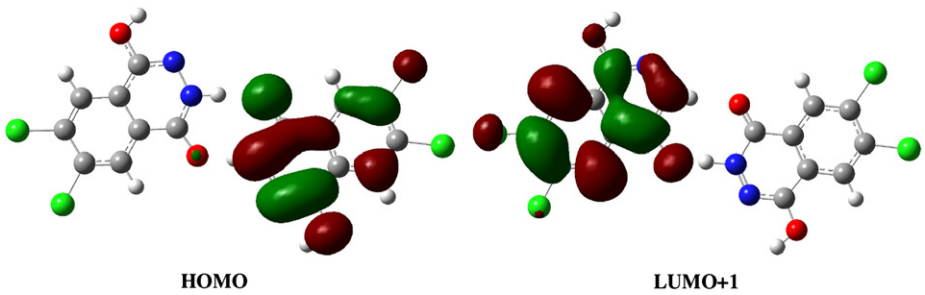


Fig. 7. Surfaces of HOMO and LUMO+1 of the dimer in compound **3** obtained at the B3LYP level.

DCPTH have an important impact on the chain formation of compound **1**, compared with that of the reported PTH-bridged coordination polymer **[**$Pb_2(PTH)_4(phen)_2$**]**$\cdot H_2O$. Due to the existence of the substituted Cl atoms, the coordination mode of the ligand changed, the chain arrangement changed and the hydrogen-bonded interactions between the chains changed. Compound **2** is the reported unique example with the mixed bridging monoacylhydrazidate and organopolycarboxylate ligands. Compounds **1**–**3** are all the potential fluorescence materials with the maximum emission around 460 nm.

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Appendix A. Supplemental Information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2011.01.034.

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