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Four new cadmium(II) homophthalate diimine complexes: Syntheses, structures and fluorescence

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Abstract

Four new complexes of homophthalate (hpht), $[Cd(hpht)(phen)]_n$ (1), $[Cd(hpht)(2,2'-bpy)]_n$ (2), $[Cd(hpht)(2,2'-bpy)(H_2O)]_n \cdot 2nH_2O$ (3), $[Cd(hpht)(4,4'-bpy)]_n \cdot nH_2O$ (4), have been solvothermally synthesized and characterized. Both 1 and 2 are 1-D double-chains which are further extended to 2-D layer structure by the π - π interaction of phen (for 1) and 2,2'-bpy (for 2). Complex 3 is linear chain which is stacked to 3-D supramolecular network though the π - π interaction and hydrogen bonding. Complex 4 features a 2-D network formed by the linkages of bench-like chains though 4,4'-bpy. Both 1 and 2 exhibit intense blue fluorescence emission and 3 produces a green fluorescence, while 4 features a unique and very strong red fluorescence. Complexes 1-4 may be potential candidates for photoactive materials.

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1. Introduction

Recently, the design and synthesis of inorganic–organic hybrid coordination polymeric frameworks has been a field of rapid growth due to their potential applications in many areas [1]. In this field, benzene carboxylic acids have been widely used, because their versatile coordination modes can construct a great deal of interesting frameworks with various topology and potential applications [2]. However, many unsymmetrical and flexible benzene carboxylic acids such as homophthalic acid have rarely been used, and the study on the structures constructed from these ligands remains undeveloped [3]. This is probably because that the low symmetry and the flexibility of these ligands make it difficult to forecast the final structure [4]. Our aim is to use such ligands to construct metal–organic complexes with interesting topology or properties for potential appli-

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cation, and to investigate the factors influencing the coordination mode of the ligands and control the final structure of the complexes. We hope to find out useful strategy to manipulate the design and syntheses of complexes of the unsymmetrical and flexible ligands.

Compared with phthalic acid, unsymmetrical homophthalic acid (H₂hpht) has a relative flexible ethylic carboxylate, which may be not co-planar with benzene. The flexibility makes H₂hpht has various conformations as well as coordination modes. On the other hand, the flexibility makes it more difficult to forecast and control the final structure. To our knowledge, there are only three complexes constructed from H₂hpht reported [5]. The three complexes have been synthesized by conventional solution method, and all of them are 0-D discrete dimers, in which phth²⁻ anions bridge two metal ions. Our study is to explore the solvothermal synthesis, and to construct some complexes with new 1-D, 2-D and 3-D topology. We adopt 1,10-phenanthroline(phen), 2,2'-bipyridine(2,2'-bpy), and 4,4'-bipyridine(4,4'-bpy) as auxiliary ligands, hoping that these diimine auxiliary ligands can not only adjust the final

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structures but also make the complexes have particular characters [6]. Herein, we report the syntheses and characterizations of four new complexes, $[Cd(hpht)(phen)]_n$ (1), $[Cd(hpht)(2,2'-bpy)(H_2O)]_n$. $[Cd(hpht)(2,2'-bpy)]_n$ (2), $2nH_2O(3)$, and $[Cd(hpht)(4,4'-bpy)]_n \cdot nH_2O(4)$.

2. Experimental

2.1. Materials and analyses

All chemicals are used as purchased without further purification. Thermogravimetric analyses were carried out with a NETZSCH STA 449C unit at a heating rate of 15 °C min⁻¹ under nitrogen. IR spectra were recorded on a Magna 750 FT-IR spectrophotometer as KBr pallets. Elemental analyses were carried out on an Elementar Vario EL III analyzer. Fluorescence spectroscopy was performed on an Edinburgh Analytical instrument FLS920.

2.2. Syntheses

2.2.1. $[Cd(phen)(hpht)]_n$ (1)

H₂hpht (0.055 g, 0.3 mmol), phen (0.060 g, 0.3 mmol), and $Cd(CH_3COO)_2 \cdot 2H_2O$ (0.12 g, 0.45 mmol) were put in a mixed solution of 8 mL distilled H₂O and 2 mL ethanol, and the pH was adjusted to about 5.6 by diluent HCl aqueous solution. Then, the mixture was sealed in

Table 1

Crystallographic data for complexes 1-4

25 mL Teflon-lined reactor and heated to 160 °C for 3 days, and then slowly cooled to room temperature. Colorless prism crystals of 1 were collected and washed with distilled water (yield: 67%). Complex 1 was also obtained by using $Cd(NO_3)_2 \cdot 4H_2O$ (pH 4.7, 58% yield), $CdCl_2$ (pH 5.6, 43% yield), or CdSO₄ (pH 5.4, 47% yield). Anal. Calc. for 1: H, 3.00; C, 53.58; N, 5.95. Found: H, 3.08; C, 53.47; N, 5.98%. IR(KBr) 3067m, 3011m, 2992m, 1575vs, 1548vs, 1509vs, 1389vs, 1295s, 1146m, 1097m, 844vs, 828m, 774m, 731vs, 677vs.

2.2.2. $[Cd(hpht)(2,2'-bpy)]_n$ (2)

The synthetic procedure of 2 is essentially the same as that for 1, while $Cd(NO_3)_2 \cdot 4H_2O$ and 2,2'-bpy were used, and the pH was adjusted to about 5.3 by diluent NaOH aqueous solution. Colorless prism crystals of 2 were collected and washed with distilled water (yield: 76%). Anal. Calc. for 2: H, 3.16; C, 51.08; N, 6.27. Found: H, 3.50; C, 50.89; N, 6.32%. IR(KBr) 3112m, 3077m, 3062m, 3027m, 2956m, 1590vs, 1544vs, 1485s, 1443vs, 1415vs, 1380vs, 1287s, 1061m, 1018s, 855m, 832m, 758vs, 723vs, 688s, 645m.

2.2.3. $[Cd(hpht)(2,2'-bpy)(H_2O)]_n \cdot 2nH_2O(3)$

The synthetic procedure is the same as that for 2, and the pH was adjusted to about 5.5 by diluent NaOH aqueous solution. Colorless prism crystals of 3 were collected

	1	2	3	4
Empirical formula	C ₂₁ H ₁₄ CdN ₂ O ₄	C ₁₉ H ₁₄ CdN ₂ O ₄	C ₁₉ H ₁₈ CdN ₂ O ₇	$C_{19}H_{16}N_2CdO_5$
Formula weight	470.74	446.72	498.75	464.74
<i>T</i> (K)	173(2)	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P\overline{1}$	$P2_1/n$
a (Å)	7.5827(9)	7.5458(2)	8.7507(18)	8.7140(9)
$b(\mathbf{A})$	21.9042(19)	22.3825(4)	10.051(2)	9.2743(9)
c (Å)	11.2062(17)	10.2930(3)	11.637(3)	22.003(2)
α (°)	90	90	102.865(2)	90
β (°)	108.499(5)	103.088(1)	102.865(2)	92.443(6)
γ (°)	90	90	91.519(8)	90
$V(A^3)$	1765.1(4)	1693.27(7)	943.6(4)	1776.6(3)
Z	4	4	2	4
$D_{\rm calc}$ (Mg/m ⁻³)	1.771	1.752	1.755	1.738
Absorption coefficient (mm^{-1})	1.269	1.317	1.203	1.263
F(000)	936	888	500	928
Crystal size (mm)	$0.40 \times 0.20 \times 0.04$	$0.52 \times 0.46 \times 0.12$	$0.40 \times 0.20 \times 0.10$	$0.80 \times 0.40 \times 0.30$
θ Range for data collection (°)	3.02–27.48	1.82-25.00	3.06–27.48	3.21–27.47
Index ranges	$-9 \le h \le 9$.	$-8 \le h \le 8.$	$-11 \leq h \leq 11.$	$-11 \leq h \leq 9$.
e	$-26 \leq k \leq 28$.	$-26 \leq k \leq 23.$	$-13 \le k \le 12$.	$-12 \leq k \leq 12$.
	$-10 \leqslant l \leqslant 14$	$-12 \leqslant l \leqslant 4$	$-15 \leqslant l \leqslant 13$	$-28 \leqslant l \leqslant 28$
Reflections collected	13489	4902	7729	12888
Refinement method	full-matrix	full-matrix	full-matrix	full-matrix
	least-squares on F^2	least-squares on F^2	least-squares on F^2	least-squares on F^2
Data $[I \ge 2\sigma(I)]$ /parameters	4024/253	2920/235	4245/274	4011/252
Goodness-of-fit on F^2	1.006	1.004	1.001	1.082
R_1 indices $(I \ge 2\sigma(I))$	0.0365	0.0449	0.0350	0.0339
wR_2 indices (all data)	0.0942	0.2080	0.0946	0.0840
Largest difference peak and hole (e $Å^{-3}$)	0.876 and -0.609	0.659 and -0.685	1.033 and -0.835	1.078 and -0.452

and washed with distilled water (yield: 28%). *Anal.* Calc. for **3**: H, 3.64; C, 45.75; N, 5.62. Found: H, 3.76; C, 45.73; N, 5.60%. IR(KBr) 3433mb, 3106w, 3079w, 3057w, 3030w, 1587vs, 15g60vs, 1543vs, 1478m, 1440s, 1391vs, 1162w, 1020m, 841w, 754s, 737s.

2.2.4. $[Cd(hpht)(4,4'-bpy)]_n \cdot nH_2O(4)$

The synthetic procedure is the same as that for 2, while 4,4'-bpy was used to replace 2,2'-bpy, and the pH was adjusted to about 4.7 by diluent NaOH aqueous solution. Colorless prism crystals of 4 were collected and washed with distilled water (yield: 63%). *Anal.* Calc. for 4: H, 3.47; C, 49.10; N, 6.03. Found: H, 3.64; C, 48.84; N, 5.99%. IR(KBr) 3416s, 3093m, 3077m, 3042m, 3019m, 1684m, 1605vs, 1548vs, 1489s, 1419s, 1380vs, 1314m, 1217s, 1151m, 1037s, 816s, 738s, 676s, 641s.

2.3. X-ray data collection and structure determination

The intensity data of 1, 3, 4 were collected on a Rigaku CCD diffractometer with graphite-monochromatized Mo K α ($\lambda = 0.71073$ Å) radiation at 173 K, and the empirical absorption corrections were performed using the CRYSTAL-CLEAR program [7]. The intensity data of 2 were collected on a SIEMENS SMART CCD diffractometer with graphite-monochromatized Mo K α ($\lambda = 0.71073$ Å) radiation at room temperature. The absorption correction was performed using the sadabs program [8]. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using the SHELXTL-97 program package [9]. All non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically (C-H = 0.95 Å). The H atoms of water were located from *E*-map, but those of the lattice water (O7) in 3 could not be located and were not taken into consideration, and the hydrogen atoms of the water in complex 4 were refined with AFIX 3 constraints on the O-H bonds. The crystallographic data for four complexes are listed in Table 1.

3. Results and discussion

3.1. Syntheses

As shown in Scheme 1, the coordination modes of $hpht^{2-}$ ligand are different in the four complexes. Andrew and co-workers have reported the second coordination mode, while the other two modes are new. As known, solvothermal reaction is complicated, and it is quite diffi-

cult to know what controls the coordination modes of $hpht^{2-}$ ligand and the formation of the complexes. In this work, we primarily studied the influence from auxiliary ligand, pH value, counter ion, and ratio of the starting materials.

The employment of terminal ligands 2,2'-bpy and 1,10phen prevents complexes 1-3 from being extended to 2D or 3D architectures, but yields infinite 1-D chain structures of the three complexes. When bridging ligand 4,4'-bpy was used, 2D network 4 was obtained. Unfortunately, when 1.3-di(4-bpy)propane and piperazine were used as bridging ligands, the experiments were failed. The pH value plays a crucial role for the formation of the complexes. It is only within the specific pH range that complexes 1-4 can be obtained and different pH values lead to different yields of the products. More interestingly, although the starting materials and reaction conditions are quite similar, the structures of 2 and 3 are significantly different, the slightly different of the pH values of the reaction medium might play important role, although detailed reaction mechanism still remains unclear. We also studied the influence from counter ions and the mole ratio of starting materials. The results illustrate that the two factors only induce different yields of the products and may be not the key factors for the synthetic reactions.

3.2. Crystal structures

3.2.1. Crystal structures of complexes 1 and 2

The selected bond lengths and angles of complex 1 are listed in Table 2. The asymmetric unit of 1 consists one Cd(II) ion, a phen ligand and a hpht²⁻ ligand. The Cd(II) ion is six-coordinated by two nitrogen atoms from phen and four oxygen atoms from three hpht²⁻ ligands in a distorted octahedron coordination geometry, as shown in Fig. 1. The Cd-O(N) bond distances are in the range 2.275–2.418 Å, with an average value of 2.350 Å. The hpht²⁻ ligand links three Cd(II) ions, in which the carboxylate group chelates a Cd(II) ion and the ethylic carboxylate group bridges two Cd(II) ions (Scheme 1(a)). The two Cd(II) ions connected by two bridging ethylic carboxylate groups with interatomic distance of 4.023 Å form the basic building unit, Cd₂(hpht)₂(phen)₂, of the whole structure. Each two of such units are connected together through sharing the hpht²⁻ ligands to form the final double chain structure. Two kinds of macrocyclic rings, one is 16-member ring (A) and the other is 8-member ring (B), are observed in the double chain (Fig. 2). Phen ligands are



Scheme 1. The coordination modes of $hpht^{2-}$ ligands in complexes 1–4.

selected bond lengths and angles of compl	
Cd(1)-O(4)#1	2.275(2)
Cd(1)–O(3)#2	2.282(2)
Cd(1)–O(2)	2.352(3)
Cd(1)–N(2)	2.382(3)
Cd(1)–N(1)	2.392(3)
Cd(1)–O(1)	2.418(3)
O(4)#1-Cd(1)-O(3)#2	111.5(3)
O(4)#1-Cd(1)-O(2)	90.0(3)
O(3)#2-Cd(1)-O(2)	135.8(3)
O(4)#1-Cd(1)-N(2)	78.1(3)
O(3)#2-Cd(1)-N(2)	82.2(3)
O(2)-Cd(1)-N(2)	141.4(3)
O(4)#1-Cd(1)-N(1)	123.0(3)
N(1)-Cd(1)-O(1)	94.0(4)
O(3)#2-Cd(1)-N(1)	109.1(3)
O(2)-Cd(1)-N(1)	87.6(3)
N(2)-Cd(1)-N(1)	69.6(3)
O(4)#1-Cd(1)-O(1)	128.2(3)
O(3)#2-Cd(1)-O(1)	83.8(3)
O(2)-Cd(1)-O(1)	53.6(3)
N(2)-Cd(1)-O(1)	153.5(3)

Symmetry transformations used to generate equivalent atoms: #1 -x + 1, -y, -z; #2 x - 1, y, z.

alternately attached to the two sides of the double-chain, and the vertical distance of the two adjacent phen planes at the same side is 6.897 Å. The double-chains are further stacked by π - π interaction of phen (about 3.43 Å) to form the final layer structure, and the benzene planes of hpht²⁻ anions from two layers are meshed (Fig. 3). Since the previously reported homophthalate complexes are all 0-D dimmers [5], to our knowledge, **1** is the first example of homophthalate complexes with 1-D chain structure. The selected bond lengths and angles of complex **2** are listed in Table 3. The structure of **2** is quite similar to that of **1**, only 2,2'-bpy ligands replace the phen ligands. Detailed discussion of the structure will not be made here.

3.2.2. Crystal structure of complex 3

The selected bond lengths and angles of complex 3 are listed in Table 4. The asymmetric unit of 3 consists one



Fig. 2. View of the chains in complexes 1 (a) and 2 (b). All the H atoms are omitted for clarity.



Fig. 3. View of the layer structure of complex 1 along *a*-axis. All the H atoms are omitted for clarity.



Fig. 1. Coordination environments of Cd(II) ions in complexes 1 (a) and 2 (b). All the H atoms are omitted for clarity.

 Table 2

 Selected bond lengths and angles of complex 1

Table 3 Selected bond lengths and angles of complex **2**

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Cd(1)–O(4)#1	2.220(4)
Cd(1)–N(1)	2.362(4)
Cd(1)–N(2)	2.404(5)
Cd(1)-O(3)#2	2.261(4)
Cd(1)–O(1)	2.394(5)
Cd(1)–O(2)	2.411(4)
(4)#1-Cd(1)-O(3)#2	108.0 (2)
O(3)#2-Cd(1)-N(1)	107.2(2)
O(3)#2-Cd(1)-O(1)	84.5(2)
O(4)#1-Cd(1)-N(2)	80.4(2)
N(1)-Cd(1)-N(2)	68.6(2)
O(4)#1-Cd(1)-O(2)	91.1(2)
N(1)-Cd(1)-O(2)	85.8(2)
N(2)-Cd(1)-O(2)	136.5(2)
O(4)#1-Cd(1)-N(1)	129.5(2)
O(4)#1-Cd(1)-O(1)	120.5(2)
N(1)-Cd(1)-O(1)	97.7(2)
O(3)#2-Cd(1)-N(2)	84.2(2)
O(1)-Cd(1)-N(2)	158.5(2)
O(3)#2-Cd(1)-O(2)	138.2(2)
O(1)-Cd(1)-O(2)	54.2(2)
N(1)-Cd(1)-O(1)	94.0(4)

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+1, -z; #2 x-1, y, z.

Cd(II) ion, a 2,2'-bpy ligand, a hpht²⁻ ligand, a coordinated water molecule and two guest water molecules. Cd(II) ion is seven-coordinated by two nitrogen atoms from 2,2'-bpy and five oxygen atoms, four of which from

Table 4

Selected	bond	lengths	and	angles	of	comple	ex í	3

Cd(1)–O(5)	2.287(3)
Cd(1)-O(3)#1	2.305(3)
Cd(1)–N(1)	2.346(3)
Cd(1)–O(2)	2.437(2)
Cd(1)–N(2)	2.353(3)
Cd(1)–O(1)	2.376(2)
Cd(1)–O(4)#1	2.510(2)
O(5)-Cd(1)-O(3)#1	89.6(2)
O(3)#1-Cd(1)-N(1)	107.3(2)
O(3)#1-Cd(1)-N(2)	173.8(9)
O(5)-Cd(1)-O(1)	85.6(2)
N(1)-Cd(1)-O(1)	121.9(9)
O(5)-Cd(1)-O(2)	134.9(2)
N(1)-Cd(1)-O(2)	81.6(9)
O(1)-Cd(1)-O(2)	53.2(8)
O(3)#1-Cd(1)-O(4)#1	53.78(8)
N(2)-Cd(1)-O(4)#1	120.1(9)
O(2)-Cd(1)-O(4)#1	127.0(8)
O(5)-Cd(1)-N(1)	142.3(2)
O(5)-Cd(1)-N(2)	90.5(2)
N(1)-Cd(1)-N(2)	69.2(2)
O(3)#1-Cd(1)-O(1)	101.5(9)
N(2)-Cd(1)-O(1)	84.8(2)
O(3)#1-Cd(1)-O(2)	82.7(9)
N(2)-Cd(1)-O(2)	101.6(9)
O(5)-Cd(1)-O(4)# 1	79.1(2)
N(1)-Cd(1)-O(4)# 1	84.2(9)
O(1)-Cd(1)-O(4)# 1	150.5(9)

Symmetry transformations used to generate equivalent atoms: $\#1 \ x - 1, y, z$.

two hpht²⁻ ligands and one from coordinated water in a highly distorted pentagonal bipyramid coordination geometry, with O3A and N2 in the axial positions (Fig. 4). The Cd–O(N) bond distances are in the range 2.287–2.510 Å with an average value of 2.373 Å, slightly longer than those in complex 2. Both carboxylate groups in $hpht^{2-}$ ligand adopt chelating coordination mode (Scheme 1(b)). The connections of Cd(II) ions and hpht²⁻ ligands alternately along the *a*-axis lead to the formation of 1-D linear chain, as shown in Fig. 4. All the 2,2'-bpy ligands arrange in the same side of the chain and all the $hpht^{2-}$ ligands in the other side, which is significantly different from 1 and 2. There are four types of hydrogen bondings in 3. Two types of them (O5-H20···O1 and O5-H21···O4) link linear chains to form the double-chains, and the other two types (O6–H22···O2 and O6–H23···O3) link the double-chains to form the final 2-D network structure, as shown in Fig. 5. The 2-D network is corrugated because different double-chains are parallel but not in a plane. Different layers are stacked to produce the 3-D structure by the π - π weak interaction of 2,2'-bpy ligands along the a-axis, and the vertical distance between two 2,2-bpy ligands is about 3.467 Å. The free guest H_2O molecules are hold in the channels that formed by π - π interaction and hydrogen bonding, as shown in Fig. 6.

3.2.3. Crystal structure of complex 4

The selected bond lengths and angles of complex 4 are listed in Table 5. The asymmetric unit of 4 consists a Cd(II) ion, a hpht^{2–} ligand, a 4,4'-bpy ligand, and a guest water molecule. Cd(II) ion is seven-coordinated by two nitrogen atoms from two 4,4'-bpy ligands and five oxygen atoms from three hpht²⁻ anions in a slightly distorted pentagonal bipyramid coordination geometry (Fig. 7). Each hpht²⁻ ligand links three Cd(II) ions, in which the methyl carboxylate group adopts bridging mode and the ethyl carboxylate adopts bridging-chelating mode (Scheme 1(c)). Two Cd(II) ions connected by two ethyl carboxylate groups with interatomic distance of 4.318 Å, Cd₂(hpht)₂, form the basic building unit of the whole structure. Each two of such units are connected together through the bridging carboxylate groups to form the 1-D chains, with benzene planes arrange on two sides of the chains reversely, which make the chain like long bench, as shown in Fig. 8. The 4,4'bpy ligands link 1-D chains to form the final 2-D layer structure and to complete the coordination sphere of



Fig. 4. View of the chain structure in complex 3. All the H atoms are omitted for clarity.



Fig. 5. View of the corrugated 2-D network in complex 3. All the 2,2'-bpy and free guest water molecules are omitted for clarity, as well as the H atoms bonded to C atoms.

Table 5



Fig. 6. View of the 3-D structure of complex 3 along *a*-axis. All the H atoms bonded to C atoms are omitted for clarity.

Cd(II) ions, and the free water molecules are hold between layers, as shown in Fig. 9.

3.3. Thermal gravimetric analysis

Thermal gravimetric analysis (TGA) diagram revealed that **1** was stable up to 317 °C, and then decomposed rapidly by the oxidation of the organic component. Complex **2** was stable up to 243 °C, and then the structure collapsed rapidly. For **3**, the first weight loss of 11.07% from 81 to 294 °C is attributed to the release of all water molecules (Calc. 10.78%). We note that the crystallization guest water is released at the same time as the coordinated water, supporting the structural evidence of hydrogen bonding in **3**. Complex **4** loses 3.78% of total weight in a range of 120–170 °C, corresponding to the loss of the free guest water (Calc. 3.87%), the framework is stable till 234 °C and then decomposed.

3.4. Fluorescence

The emission spectra of complexes 1-4 in the solid state at room temperature are shown in Fig. 11. It can be seen

Selected bond lengths and angles of comple	x 4
Cd(1)–N(2)# 1	2.289(2)
Cd(1)–N(1)	2.328(2)
Cd(1)–O(3)	2.428(3)
Cd(1)–O(3)#3	2.606(3)
Cd(1)–O(1)	2.328(2)
Cd(1)-O(2)#2	2.347(2)
Cd(1)–O(4)#3	2.462(3)
N(2)#1-Cd(1)-O(1)	93.7(8)
O(1)-Cd(1)-N(1)	87.6(8)
O(1)-Cd(1)-O(2)#2	85.8(8)
N(2)#1-Cd(1)-O(3)	99.4(2)
N(1)-Cd(1)-O(3)	86.6(2)
N(2)#1-Cd(1)-O(4)#3	89.8(9)
N(1)-Cd(1)-O(4)#3	87.7(9)
O(3)-Cd(1)-O(4)#3	109.1 (2)
O(1)-Cd(1)-O(3)#3	142.6(8)
O(2)#2-Cd(1)-O(3)#3	131.3(8)
O(4)#3-Cd(1)-O(3)#3	49.8(9)
N(2)#1-Cd(1)-N(1)	173.9(9)
N(2)#1-Cd(1)-O(2)#2	91.3(9)
N(1)-Cd(1)-O(2)#2	82.9(8)
O(1)-Cd(1)-O(3)	82.2(9)
O(2)#2-Cd(1)-O(3)	164.3(2)
O(1)-Cd(1)-O(4)#3	167.5(9)
O(2)#2-Cd(1)-O(4)#3	82.1(9)
N(2)#1-Cd(1)-O(3)#3	83.0(2)
N(1)-Cd(1)-O(3)#3	99.5 (2)
O(3)-Cd(1)-O(3)#3	61.9(2)

Symmetry transformations used to generate equivalent atoms: #1 x - 1/2, -y + 1/2, z - 1/2; #2 -x + 1, -y + 1, -z; #3 -x + 1, -y, -z.

that 1 exhibits an intense blue photoluminescence emission at $\lambda_{max} = 406$ nm and a very weak band at $\lambda_{max} = 524$ nm ($\lambda_{ex} = 350$ nm). The emission of 1 probably can be assigned to the intraligand fluorescent emission since very similar emissions are also observed for free H₂hpht (Fig. 10, $\lambda_{ex} = 274$ nm) and phen ligands [10].

Complex 2 exhibits an intense blue emission band $(\lambda_{\text{max}} = 422, 498 \text{ nm}, \text{ with a shoulder at 530 nm})$ from



Fig. 7. Coordination environment of Cd(II) ions in complex 4. All the H atoms are omitted for clarity.



Fig. 8. View of the chain formed by Cd(II) ions and $hpht^{2-}$ ligands in complex 4. All the H atoms are omitted for clarity.

375 to 650 nm on excitation at 310 nm (Fig. 11). The peak at 422 nm can be assigned to the intraligand emission of H₂pht, since the free H₂pht ligand exhibits intense emission at $\lambda_{max} = 455$ nm upon excitation at 370 nm (Fig. 10), and the coordination of the ligand may lead to the blue-shift. The peak at 498 nm may be attributed to the intraligand emission from the 2,2'-bpy ligand [11]. It is known that the free 2,2'-bpy molecule displays a weak luminescence at ca. 535 nm. The enhancement and significant blue-shift



Fig. 10. Emission spectrum of homophthalic acid in the solid state.



Fig. 11. Emission spectrum of complexes 1-4 in the solid state.

of the photoluminescence of the coordinated 2,2'-bpy ligand compared to that of the free 2,2'-bpy molecule may, therefore, be attributed to the chelating of the 2,2'-bpy ligand to the metal ion, which effectively increases the rigidity of the ligand and reduces the loss of energy by radiationless decay of the intraligand emission excited state [12]. The shoulder emission at 530 nm may be assigned as ligand-to-metal-charge-transfer (LMCT) [13].



Fig. 9. View of the layer structure of complex 4 along *b*-axis. All the H atoms are omitted for clarity.

Complex 3 exhibits a broad green emission band $(\lambda_{max} = 459, 481 \text{ nm}, \text{ with a shoulder at 603 nm})$ from 385 to 700 nm on excitation at 372 nm (Fig. 11). We noted that the photoluminescence of 3 is similar to that of 2, and the peaks can be assigned similarly. Compared with their analogs, both the peak at 459 nm and the shoulder red-shift and have lower intensity, which may be attributed to the different coordination mode of the ligand and different coordination environment of metal ions.

Complex 4 exhibits a very intense red photoluminescence emission at $\lambda_{max} = 577$, upon excitation at 455 nm, which has rarely been reported for cadmium complexes. While a very similar emission band of the free 4, 4'-bpy molecule with $\lambda_{max} = 432$ nm ($\lambda_{ex} = 344$ nm) is observed, the emission may be assigned to the ligand-to-metal charge transfer (LMCT) [14].

In a word, the photoluminescence properties of complexes 1–4 exhibit a broad range of visible light. Since complexes 1–4 are insoluble in common solvents and thermally stable, they may be potential candidates for photoactive materials.

4. Conclusion

In conclusion, four new complexes, 1-4, have been successfully synthesized from the solvothermal reactions of cadmium salts, H₂phth and different auxiliary diimine ligands. The four complexes are stable and have particular fluorescence properties, and they may have promising application in photophysical chemistry.

5. Supplementary material

For the four complexes, full list of atomic coordinates, isotropic thermal parameters, bond lengths and angles are available from the authors on request. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 278028–278031 for complexes 1–4, respectively. Copies of the data can be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internet.) +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk.

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