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Cadmium(II) Complexes with 2-Hydroxy-1-naphthoate Ligand: Syntheses, Crystal Structures, and Emission Properties

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Abstract. Two new Cd^{II} complexes $[Cd(L)_2(phen)]_2$ (**1**) and $\{Cd(L)_2(4bpy)_{1.5}\}_\infty$ (**2**) (L = 2-hydroxy-1-naphthoate, phen = 1,10-phenanthroline, and 4bpy = 4,4'-bipyridine) were prepared by slow solvent evaporation from mixtures of 2-hydroxy-1-naphthoic acid (HL) and $Cd(ClO_4)_2\cdot6H_2O$ in the presence of auxiliary phen and 4bpy co-ligands. Single-crystal X-ray analyses show that complex **1** features a dinuclear structure, which is assembled into a one-dimensional (1D) chain, and further into a two-dimensional (2D) network by intermolecular $\pi\cdots\pi$ stacking and C–H···π supramolecular interactions. Complex **2** has a 1D ladder-like chain, which is further interlinked to form a 2D network by the co-effects of the interchain C–H···O hydrogen bonds as well as C–H···π interactions. The structural differences between **1** and **2** are attributed to the different N-donor auxiliary ligands, phen for **1** and 4bpy for **2**. Moreover, complexes **1** and **2** exhibit strong solid-state luminescences at room temperature, which mainly originate from the intraligand $\pi \rightarrow \pi^*$ transitions of L.

Introduction

The rational design and synthesis of coordination polymers has attracted more and more attention in recent years because of their structural and topological diversities and their potential application as functional materials.[1–3] In this field, one common strategy used in building such complexes is to employ appropriate bridging ligands that are able to bind metal ions in different modes and provide a possible way to achieve more new materials with fascinating architectures and excellent physical properties.[4,5]

Among various ligands, the versatile carboxylic acid ligands, especially aromatic benzene- and naphthalene-based di- or multi-carboxylic acids, are well documented in the preparation of various Cd^{II}–carboxylato coordination complexes mainly owing to their reliable and rich coordination modes, such as 1,2-, 1,3-, and 1,4-benzenedicarboxylic acid,[6–8] 1,3,5-benzenetricarboxylic acid,[9] 1,2,4-benzenetricarboxylic acid,[10] 1,2,4,5-benzenetetracarboxylic acid,[11] 1,4- and 2,6-naphthalenedicarboxylate[12,13] as well as 1,8-naphthalenedicarboxylate.[14] Despite the remarkable achievements in this aspect,[6–14] however, to predict and control the supramolecular assembly still remains a longstanding challenge at this stage. This mainly arises from the fact that the subtle assembly progress may be influenced by many intrinsic and external parameters, such as auxiliary co-ligands,[15] solvent,[16] concentration,[17] counter-anion,[18] temperature,[19] and pH value of the solution,[20] which determine the formation of different thermodynamically favored crystalline products. For instance, the introduction of 2,2'-bipyridyl-like chelating molecules[15a] or 4,4'-bipyridyl-like bridging spacers[15b] as auxiliary co-ligands, into metal–carboxyl reaction systems will lead to the formation of interesting coordination complexes. In addition to coordination bonds, some weak interactions, such as intra- and/or intermolecular hydrogen bonding, π···π stacking, and C–H···π supramolecular interactions, also greatly affect the structures of coordination complexes.[15b,21]

In comparison with the aforementioned benzene- and naphthalene-based di- or multi-carboxylic acid ligands, however, the investigation of naphthalene-based monocarboxylic acids, such as 2-hydroxy-1-naphthoic acid used here, has been far less common to date. Taking into account the aspects mentioned above, two new Cd^{II} coordination complexes, a dinuclear motif $[Cd(L)_2(phen)]_2$ (**1**) and a 1D ladder-like array $\{Cd(L)_2(4bpy)_{1.5}\}_\infty$ (**2**) (L = 2-hydroxy-1-naphthoate, phen = 1,10-phenanthroline, and 4bpy = 4,4'-bipyridine) have been prepared through the reaction of Cd^{II} salts with 2-hydroxy-1-naphthoic acid (HL) in the presence of phen or 4bpy molecules, as a co-ligand. Herein, we report the syntheses, crystal structures, and luminescent properties of the complexes.

Experimental Section

Materials and General Methods

All the starting reagents and solvents for synthesis were commercially available and used as received without further purification. Elemental

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analyses (C, H, and N) were performed with a Vario EL III Elementar analyzer. The IR spectra were recorded in the range of 4000–400 cm^{-1} with a Tensor 27 OPUS (Bruker) FT-IR spectrometer with KBr pellets. Thermogravimetric analysis (TGA) experiments were carried out with a Perkin–Elmer Diamond SII thermal analyzer from room temperature to 900 °C under a nitrogen atmosphere at a heating rate of 10 $°C \cdot min^{-1}$. The emission/excitation spectra were recorded with an F-7000 (HITACHI) spectrophotometer at room temperature.

Caution! Although we had no problems in handling perchlorate salts during this work, these should be handled with great care because of their potential explosive nature.

Synthesis of Complexes 1 and 2

$[Cd(L)_2(phen)]_2$ (1): A mixed solution of HL (0.05 mmol) and phen (0.05 mmol) in CH_3OH (10 mL) in the presence of excess 2,6-dimethylpyridine (ca. 0.05 mL) was stirred for ca. 15 minutes. Afterwards, a solution of $Cd(ClO_4)_2 \cdot 6H_2O$ (0.1 mmol) in water (15 mL) was added to the above mixture and stirred for ca. 30 minutes. The resulting white suspension was filtered and the filtrate was kept at room temperature. Colorless single crystals suitable for X-ray analysis were obtained by slow solvent evaporation after ca. one week. Yield ≈ 40 % based on HL. $C_{34}H_{22}CdN_2O_6$: calcd. C 61.23; H 3.32; N 4.20 %; found: C 61.18; H 3.21; N 4.07 %. **IR** (KBr): $\tilde{\nu}$ = 3442 m(br), 3072 w, 1620 s, 1596 m, 1557 s, 1513 s, 1469 m, 1437 vs, 1390 s, 1347 w, 1302 m, 1264 m, 1239 m, 1208 w, 1140 m, 1101 w, 1033 w, 967 w, 900 w, 869 w, 835 m, 799 w, 754 m, 726 m, 652 w, 580 w, 534 w, 505 w cm^{-1}.

$\{Cd(L)_2(4bpy)_{1.5}\}_\infty$ (2): The same procedure as described for **1** was used for this complex except that phen was replaced by 4bpy (0.05 mmol). Colorless block single crystals suitable for X-ray analysis appeared at a beaker wall after ca. one week at room temperature. Yield ≈ 50 % based on HL. $C_{37}H_{26}CdN_3O_6$: calcd. C 61.63; H 3.63; N 5.83 %; found: C 61.76; H 3.46; N 5.78 %. **IR** (KBr): $\tilde{\nu}$ = 3424 m(br), 3054 w, 1940 w, 1621 s, 1602 vs, 1569 s, 1511 m, 1478 s, 1439 vs, 1412 vs, 1384 s, 1349 w, 1318 m, 1290 m, 1246 w, 1218 m, 1137 m, 1073 m, 1045 w, 1007 w, 972 w, 871 w, 829 m, 806 s, 737 m, 656 w, 629 m, 570 w, 537 w, 497 m, 435 w cm^{-1}.

X-ray Crystallographic Studies of 1 and 2

X-ray single-crystal diffraction data for complexes **1** and **2** were collected with a Bruker Smart 1000 CCD area-detector diffractometer at 294(2) K with Mo-K_α radiation (λ = 0.71073 Å) by ω scan mode. The program SAINT[22] was used for integration of the diffraction profiles. Semi-empirical absorption corrections were applied using SADABS program.[23] All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL.[24] The metal atoms in each complex were located from the *E*-maps and the other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. The hydrogen atoms were generated theoretically onto the specific atoms and refined with isotropic thermal parameters riding on the parent atoms. Crystallographic data and structural refinement details for **1** and **2** are summarized in Table 1. Selected bond lengths and bond angles as well as hydrogen-bonding arrangement are listed in Table 2, Table 3, and Table 4.

Table 1. Crystal data and structure refinement for complexes **1** and **2**.

	1	**2**
Empirical formula	$C_{34}H_{22}CdN_2O_6$	$C_{37}H_{26}CdN_3O_6$
Formula weight	666.95	721.04
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a /Å	8.0029(3)	11.6881(10)
b /Å	12.8883(5)	12.2842(10)
c /Å	14.7738(6)	12.4317(9)
α /°	106.889(3)	79.659(7)
β /°	104.765(4)	80.465(7)
γ /°	105.333(3)	63.902(8)
V /$Å^3$	1312.23(9)	1569.3(2)
Z	2	2
D /g cm^{-3}	1.688	1.526
μ /mm^{-1}	0.887	0.749
R_{int}	0.0212	0.0245
GOF	0.916	0.898
T /K	294(2)	294(2)
R_1[a] / wR_2[b] [$I > 2\sigma(I)$]	0.0242/0.0459	0.0285/0.0511
ρ_{max}/ρ_{min} (e $Å^{-3}$)	0.363/–0.295	0.458/–0.281

a) $R_1 = \Sigma (||F_o|-|F_c||)/\Sigma|F_o|$. b) $wR_1 = [\Sigma w(|F_o|^2-|F_c|^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, where F_o = observed and F_c = calculated structure factors, respectively.

CCDC-794269 and CCDC-794270 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: 44-1223-336-033; or E-Mail: deposit@ccdc.cam.ac.uk).

X-ray Powder Diffraction Studies of 1 and 2

The X-ray powder diffraction (XRPD) patterns of **1** and **2** were recorded at 293 K with a Bruker D8 Advance diffractometer (Cu-K_α, λ = 1.54056 Å) operated at 40 kV and 30 mA, using a Cu-target tube and a graphite monochromator. The crushed single-crystalline powder samples were prepared by crushing the crystals and the intensity data were recorded by continuous scan in a $2\theta/\theta$ mode from 3° to 80° with a step size of 0.02° and a scan speed of $8° \cdot min^{-1}$. Simulation of the XRPD patterns was carried out by the single-crystal data and diffraction-crystal module of the *Mercury* (Hg) program available free of charge via the internet at http://www.iucr.org.

Supporting Information (see footnote on the first page of this article): Coordination modes of carboxylate group of fully deprotonated **L** ligand. XRPD patterns of (a) **1** and (b) **2**. Thermogravimetric analysis (TGA) plots of (a) **1** and (b) **2**. Excitation/emission spectra of the free ligands in the solid state at room temperature.

Results and Discussion

Synthesis and General Characterizations

The presence of the carboxylate group in 2-hydroxy-1-naphthoate (L) creates the possibility of various coordination modes, such as μ_1-η^1:η^1-chelating and μ_2-η^1:η^1-*syn-anti*-bridging modes observed in this work (see Scheme S1 in the Supporting Information). The synthesis and isolation of complexes **1** and **2** were carried out by the reaction of Cd^{II} salt with HL, together

Table 2. Selected bond lengths /Å and angles /° for **1**.

Cd1–O3	2.2072(14)	Cd1–O1	2.2934(15)
Cd1–N2	2.3238(19)	Cd1–O4$^{\#1}$	2.3259(17)
Cd1–N1	2.3427(17)	Cd1–O2	2.5035(17)
O3–Cd1–O1	96.18(6)	O3–Cd1–N2	138.90(7)
O1–Cd1–N2	100.08(7)	O3–Cd1–O4$^{\#1}$	101.56(6)
O1–Cd1–O4$^{\#1}$	78.76(6)	N2–Cd1–O4$^{\#1}$	118.49(6)
O3–Cd1–N1	106.54(6)	O1–Cd1–N1	153.60(6)
N2–Cd1–N1	71.43(7)	O4$^{\#1}$–Cd1–N1	83.58(6)
O3–Cd1–O2	76.54(6)	O1–Cd1–O2	53.65(6)
N2–Cd1–O2	83.29(7)	O4$^{\#1}$–Cd1–O2	131.26(5)
N1–Cd1–O2	144.47(6)		

Symmetry code for **1**: #1 = $-x + 1$, $-y + 2$, $-z + 2$.

Table 3. Selected bond lengths /Å and angles /° for **2**.

Cd1–N2$^{\#1}$	2.3065(19)	Cd1–O3	2.3394(16)
Cd1–O1	2.3652(18)	Cd1–N3	2.3672(19)
Cd1–N1	2.369(2)	Cd1–O2	2.516(2)
Cd1–O4	2.5582(19)		
N2$^{\#1}$–Cd1–O3	87.60(7)	N2$^{\#1}$–Cd1–O1	87.06(7)
O3–Cd1–O1	85.13(7)	N2$^{\#1}$–Cd1–N3	93.31(7)
O3–Cd1–N3	139.21(7)	O1–Cd1–N3	135.66(7)
N2$^{\#1}$–Cd1–N1	175.55(7)	O3–Cd1–N1	8.93(7)
O1–Cd1–N1	89.87(7)	N3–Cd1–N1	91.15(7)
N2$^{\#1}$–Cd1–O2	95.10(7)	O3–Cd1–O2	137.67(6)
O1–Cd1–O2	52.97(6)	N3–Cd1–O2	82.92(7)
N1–Cd1–O2	85.60(7)	N2$^{\#1}$–Cd1–O4	98.01(7)
O3–Cd1–O4	52.73(6)	O1–Cd1–O4	137.00(6)
N3–Cd1–O4	86.90(7)	N1–Cd1–O4	82.06(7)
O2–Cd1–O4	163.83(6)		

Symmetry code for **2**: #1 = $x - 1$, y, z.

Table 4. Hydrogen-bonding arrangement /Å, ° for **1** and **2**.

D–H···A	D–H	H···A	D···A	D–H···A
1				
C18–H18A···*Cg*1^{a}	0.93	2.82	3.613(4)	144
2				
C27–H27A···O3^{a}	0.93	2.52	3.346(9)	147
C16–H16A···*Cg*2^{b}	0.93	2.90	3.639(7)	138

Symmetry codes for **1**: a = x, $y + 3$, $z + 2$; for **2**: a = $-x + 1$, $-y + 1$, $-z$; b = x, y, $z - 1$; [*Cg*1 and *Cg*2 are the centroids of the C2–C6/C11 phenyl ring of L ligand for both **1** and **2**].

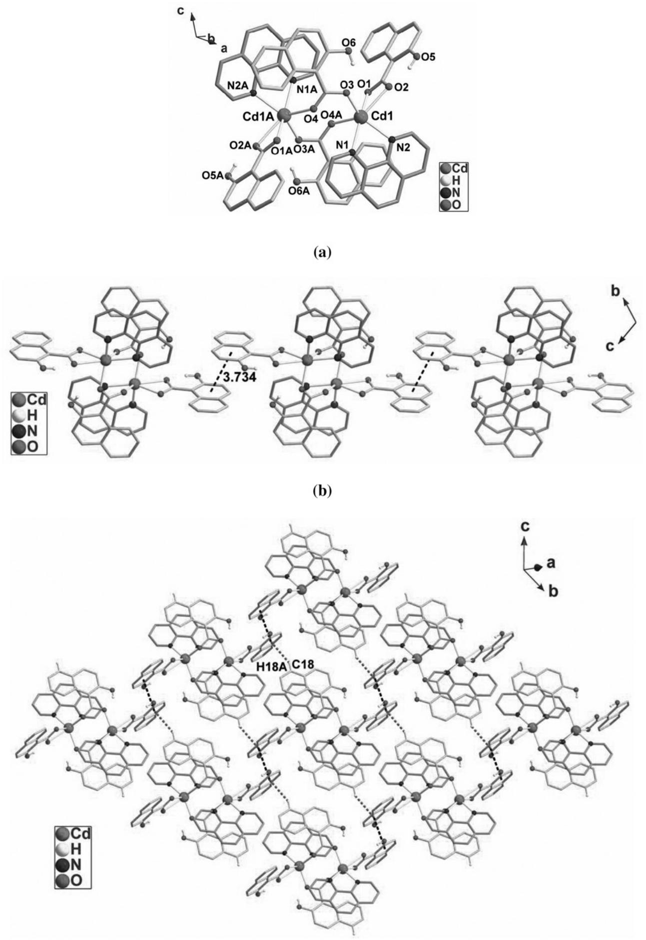
with the introduction of auxiliary chelating co-ligand phen for **1** and bridging 4bpy for **2**, and by using slow solvent evaporation in a beaker under mild conditions of ambient temperature and pressure. It should be pointed out that the use of excess 2,6-dimethylpyridine, which adjusts the pH values of the reaction systems, is a key point for the formation of **1** and **2**.

In the IR spectra of **1** and **2**, the broad bands centered at ≈ 3400 cm^{-1} (3442 cm^{-1} for **1**; 3424 cm^{-1} for **2**) indicate O–H stretching of the hydroxyl group in L. As a matter of fact, the IR absorption of carboxylate group is very complicated due to its coordination diversities with metal ions. The characteristic bands of the carboxylate groups in **1** and **2** appeared in the usual region at 1620–1557 cm^{-1} for the antisymmetric stretching vibrations and at 1439–1390 cm^{-1} for the symmetric stretching vibrations. Furthermore, the $\Delta\nu$ values [$\Delta\nu = \nu_{asym}(COO^{-}) - \nu_{sym}(COO^{-})$] are 183 and 167 cm^{-1} for **1** and 163 cm^{-1} for **2**, respectively, which are in good agreement with their solid structural features from the results of their crystal structures.[25]

Descriptions of Crystal Structures for Complexes 1 and 2

[Cd(L)$_2$(phen)]$_2$ (1)

It has been well documented that introduction of phen into a reaction system is able to reduce structural dimensionality of the final products, by blocking some of the metal-ion binding sites that would otherwise be available for bridging ligands to extend the coordination network.[26] Thus, the use of phen as a capping co-ligand leads to the formation of non-polymeric structures but discrete multinuclear complexes. Accordingly, the reaction of $Cd(ClO_4)_2·6H_2O$ with HL in the presence of phen as a co-ligand led to the formation of **1**, which has a dinuclear motif. Each asymmetric unit contains one crystallographically unique Cd^{II} ion, two L ligands, and one phen co-ligand. The Cd^{II} atom is in a distorted octahedral arrangement, being surrounded by four carboxylate oxygen atoms from three L ligands and two donor nitrogen atoms from one phen molecule (see Figure 1a). All Cd–O [2.2072(14)–2.5035(17) Å] and Cd–N [2.3238(19)–2.5035(17) Å] distances and bond angles [(53.65(6)–153.60(6)°] around each Cd^{II} atom are similar to those of other Cd^{II} carboxylato complexes reported in the literature (see Table 2).[27] For ligand L, two types of coordination modes are found for its carboxylate group, namely, μ_1-η^1:η^1-chelating for O1–C1–O2 and μ_2-η^1:η^1-*syn-anti* bridging for O3–C12–O4 (see Scheme S1 a,b in the Supporting Information). In other words, two L ligands in **1** use their four oxygen atoms from two different carboxylate groups to connect two Cd^{II} atoms to form a non-planar eight-membered ring composed of Cd1–O3–C12–O4–Cd1A–O3A–C12A–O4A with a non-bonding Cd1···Cd1A separation of 4.652(11) Å (symmetry code: A = $-x + 1$, $-y + 2$, $-z + 2$).



(a)

(b)

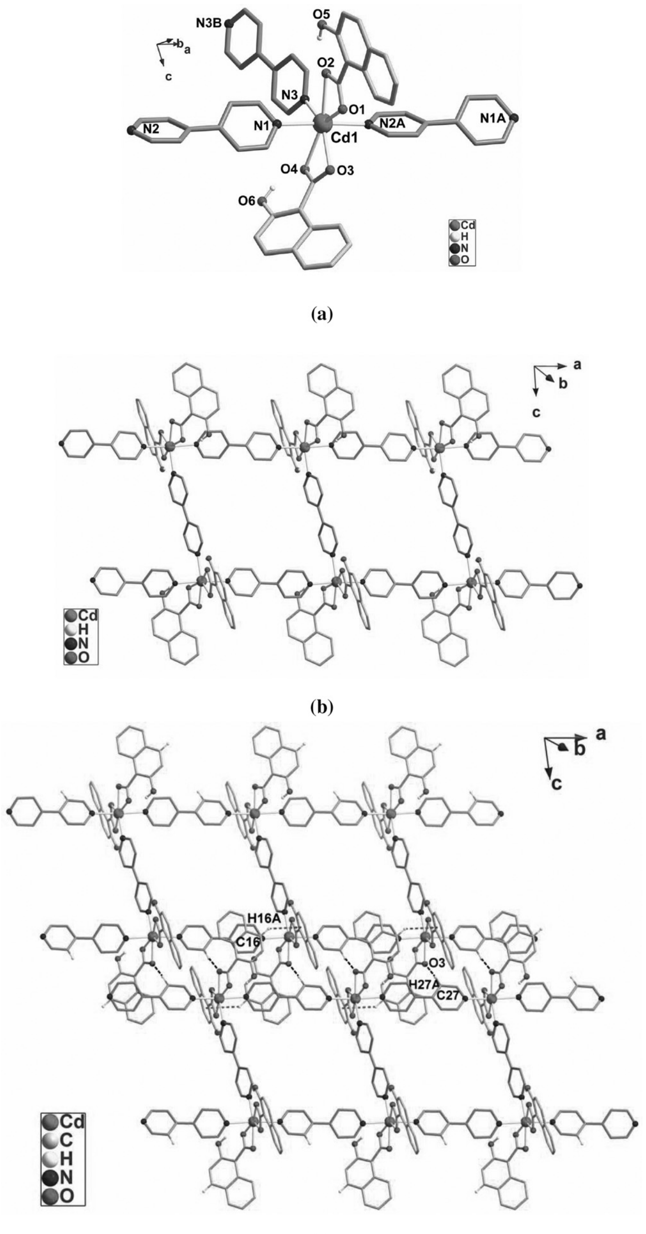
(c)

Figure 1. View of (a) the coordination environment of Cd^{II} in **1**, (b) the 1D chain, along the [111] direction, formed by intermolecular π···π stacking (black dashed lines), and (c) the 2D network, running parallel to the ($1\bar{1}0$) plane, formed by interchain C–H···π interactions (gray dashed lines). Only hydrogen atoms involved in the interactions were shown for clarity.

In addition, the adjacent dinuclear units are extended into a 1D chain (see Figure 1b) along the [111] direction by intermolecular π···π stacking between completely parallel phenyl rings of L ligands with the centroid–centroid separation of 3.734 Å. Moreover, the structure of **1** also contains inter-chain C–H···π supramolecular interactions between the phenyl rings of L ligands with an edge-to-face orientation [d = 2.816 Å, A = 144°; d and A stand for the H···π separation and C–H···π angle in the C–H···π pattern, respectively], which further link the 1D chains into a 2D layer parallel to the ($1\bar{1}0$) plane (see Figure 1c and Table 4).[28]

$\{Cd(L)_2(4bpy)_{1.5}\}_\infty$ (**2**)

When 4bpy, a rigidly linear spacer, was introduced into the reaction system as a bridging co-ligand instead of phen, a 1D ladder-like coordination polymer was obtained. The fundamental building unit contains one Cd^{II} ion, two L ligands, and one



(a)

(b)

(c)

Figure 2. View of (a) the coordination environment of Cd^{II} in **2**, (b) the 1D ladder-like chain, and (c) the 2D network, running parallel to the ($0\bar{1}1$) plane, formed by co-effects of interchain C–H···O (black dashed lines) and C–H···π (gray dashed lines) interactions. Only hydrogen atoms involved in the interactions were shown for clarity.

and a half 4bpy molecules (see Figure 2a). The Cd1 atom is located in a distorted pentagonal-dipyramidal arrangement, by coordinating to four oxygen atoms of two L ligands and three donor nitrogen atoms of three different 4bpy ligands. All Cd–O and Cd–N bond lengths are in the ranges 2.3394(16)–2.5582(19) Å and 2.3065(19)–2.369(2) Å with the bond angles around each Cd^{II} ion ranging from 52.97(6) to 175.55(7)°, which are similar to other Cd^{II} complexes reported in the literature (see Table 3).[27] In complex **2**, each 4bpy ligand takes bidentate coordination mode and links two Cd^{II} atoms by using two pyridyl nitrogen atoms to form a 1D ladder-like chain (see Figure 2b). The neighboring non-bonding Cd···Cd separations around the ladder are 11.688(1) and 11.794(4) Å. The L ligand in **2** adopts a μ_1-η^1:η^1-chelating carboxylate mode (see Scheme S1a in the Supporting Information).

In addition, adjacent 1D chains are further linked to generate a 2D sheet running parallel to the (0$\bar{1}$1) plane (see Figure 2c), by the co-effects of interchain C–H···O interactions between the pyridyl rings of 4bpy and carboxylate units of L (C27–H27A···O3; see Table 4 for its detailed parameters) and C–H···π interactions between L ligands with an edge-to-face orientation (d = 2.889 Å; A = 138°; d and A stand for the H···π separation and C–H···π angle in the C–H···π pattern, respectively).[28]

XRPD Results

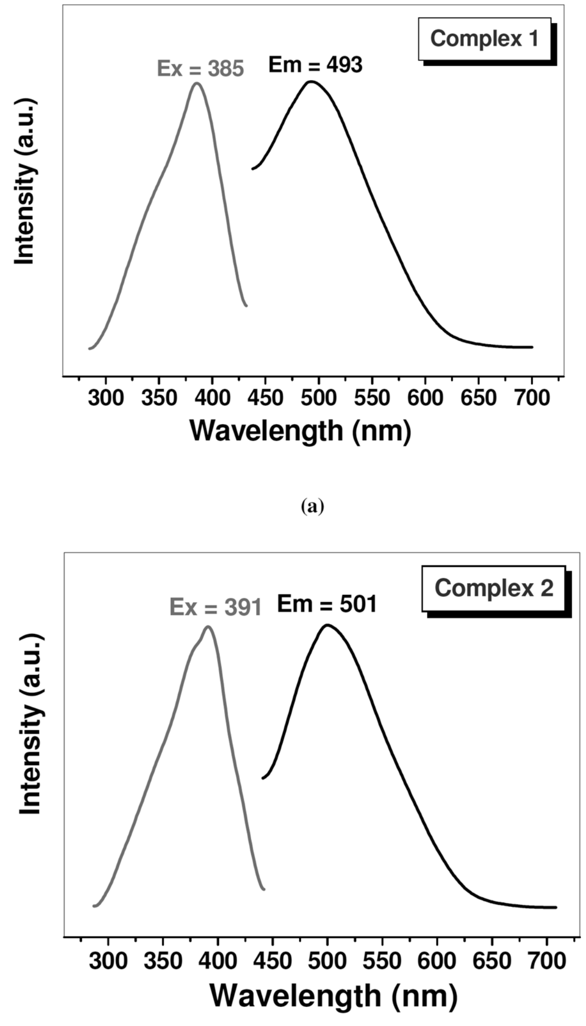
To confirm whether the crystal structures are truly representative of the bulk materials for further luminescence measurements, X-ray powder diffraction (XRPD) experiments were carried out for the phase purities of the relevant samples of **1** and **2**. The XRPD experimental and computer-simulated patterns of the corresponding complex are shown in Figure S1 (Supporting Information). Although the experimental patterns have a few unindexed diffraction lines and some are slightly broadened in comparison with those simulated from the single crystal modes, it still can be considered favorably that the bulk synthesized materials and the as-grown crystals are homogeneous for **1** and **2**.

Thermogravimetric Analysis

To examine the thermal stabilities of **1** and **2**, thermogravimetric analysis (TGA) experiments of these crystalline materials were performed by heating the corresponding complex from room temperature to 900 °C with a heating rate of 10 °C·min^{-1} under nitrogen (Figure S2 in the Supporting Information). The weight loss curves indicate that **1** is stable up to ca. 170 °C and feature three stages of weight-loss at 180, 213, and 363 °C. According to the remaining weight (obsd. 20.14 %), the final residue should be CdO (calcd. 19.25 %). Complex **2** is thermally stable upon heating to ca. 200 °C. The framework of **2** begins to decompose quickly in three consecutive steps at 237, 320, and 491 °C. The weight-loss of 86.04 % observed from 200 to 500 °C is very close to the calculated value of 84.41 %, which corresponds to 4bpy and the ligand L.

Luminescent Properties

Metal-organic coordination complexes constructed from d^{10} metal atoms and conjugated organic ligands are promising candidates for hybrid photoactive materials with potential applications such as light-emitting diodes (LEDs).[26,27] Thus, solid-state emission spectra of the as-synthesized Cd^{II} complexes **1** and **2** were investigated at room temperature (see Figure 3). Excitations of the microcrystalline samples of **1** and **2** at 385 and 391 nm produce an intense luminescence with maxima at 493 and 501 nm, respectively. To further analyze the nature of these emission bands, the emission properties of HL as well as auxiliary phen and 4bpy were also investigated under the same experimental conditions (see Figure S3 in the Supporting Information). By comparing the locations and profiles of their excitation/emission peaks with **1** and **2**, we are able to presume that these emissions are neither due to metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) because the Cd^{II} ion with d^{10} configuration is difficult to oxi-



(a)

(b)

Figure 3. Solid-state excitation/emission spectra of **1** (a) and **2** (b) at room temperature.

dize or to reduce,[29] and should mainly be ascribed to the intraligand π → π* transitions, namely ligand-to-ligand charge transfer (LLCT), of L ligands,[30] which are similar to those of complexes with a naphthalene backbone.[31] Additionally, the enhancement and the redshifts of luminescence emission maxima for **1** and **2** may be due to the chelating and bridging effects of the relevant ligands to the metal atoms, which effectively increase the rigidity and conjugation upon metal coordination and then affect the loss of energy by a radiationless pathway of the intraligand (π → π*) excited state.[32]

Conclusions

Two photoluminescent $\mathrm{Cd^{II}}$ complexes with dinuclear and 1D ladder-like structures were synthesized by using 2-hydroxy-1-naphthoic acid (HL), together with the auxiliary coligands phen for **1** and 4bpy for **2**. The different N-donor coligands (phen or 4bpy) play an important role in the shape of the final structures. Also, the isolation of **1** and **2** is a new proof of the coordination versatility of monocarboxylic acid ligands bearing a bulky aromatic skeleton, which might be generally used for the construction of other metal-organic complexes with different transition metal ions, such as $\mathrm{Cu^{II}}$, $\mathrm{Co^{II}}$, $\mathrm{Ni^{II}}$, and $\mathrm{Mn^{II}}$. This research is currently underway in our laboratory.

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