

Syntheses, Structural Characterization and Fluorescence of Zn(II) and Cd(II) Polymers from 5-(Pyridin-2-ylmethylamino)isophthalic acid

Xiao-Chun Cheng, Xiao-Hong Zhu and Hai-Wei Kuai

Faculty of Life Science and Chemical Engineering, Huaiyin Institute of Technology, Huaian 223003, China

Reprint requests to Dr. Hai-Wei Kuai. Fax: +86-517-83559044. E-mail: hyitshy@126.com

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The hydrothermal reaction of Zn(II) nitrate with 5-(pyridin-2-ylmethylamino)isophthalic acid (H_2L) yields the complex $[Zn(L)(H_2O)] \cdot 2H_2O$ (**1**). When 2,2'-bipyridine (bpy) as auxiliary ligand and Cd(II) nitrate were used in the alkaline reaction system, $[Cd(L)(H_2O)(bpy)] \cdot 3H_2O$ (**2**) was obtained. Complexes **1** and **2** have been characterized by single-crystal and powder X-ray diffraction, IR, elemental and thermogravimetric analyses. Complex **1** shows a 2D *fes* network structure with uninodal 3-connected (4.8^2) topology, which is further linked by hydrogen bonding to give rise to a 3D supramolecular framework; complex **2** displays a chain structure. Interestingly, tetranuclear water clusters were generated in **1**, which are interlinked to fabricate a water chain structure. The fluorescence properties of **1** and **2** were investigated.

Key words: Zinc(II), Cadmium(II), Structural Characterization, Fluorescence

Introduction

During the past few decades, the rational design and synthesis of coordination polymers with well-defined sizes and shapes have attracted more and more attention, which is justified due to their fascinating architectures and potential applications in many fields such as heterogeneous catalysis, ion-recognition, nonlinear optics, and molecular adsorption [1–3]. The great number of polymers with a variety of structural motifs and interesting properties has been discussed in some comprehensive reviews [4–6]. It is known that one of the effective strategies for the construction of such inorganic-organic hybrid materials is to select suitable organic ligands as building blocks to bridge metal centers into infinite frameworks, which enable the control of structural motifs and functional properties. Among popularly employed ligands, rigid or flexible *N*- and/or *O*-donors are always regarded as excellent building blocks for the frameworks [7–9].

Recently, we have been focusing our attention on the utilization of the semi-rigid *N*- and *O*-donor ligand 5-(pyridin-2-ylmethylamino)isophthalic acid (H_2L) as a building block for the construction of polymers under different synthetic conditions. Compared with other *N*-

and *O*-donors, the H_2L ligand possesses several distinctive traits. In the first place, H_2L contains a *N,N*-bidentate [pyridin-2-ylmethylamino] group, to shape an *N,N*-chelated metallacycle, which may effectively reduce the uncertainty of coordination. Secondly, given suitable coordinating capacities, appropriate connectivity, and abundant coordination modes of carboxylate groups, the H_2L ligands could reliably act as bridging rods in the construction of complexes [10–12]. Thirdly, due to the presence of an *N*-H group as potential donor or acceptor, hydrogen bonding interactions may be available to extend the coordination networks and lead to 3D supramolecular frameworks.

In our previous studies, we employed different transition metal salts to react with 5-(pyridin-2-ylmethylamino)isophthalic acid and a series of complexes with the L^{2-} ligand were obtained [13, 14]. As an extension of our work, we have tested more experimental conditions, such as the alteration of the reaction temperature and the presence of auxiliary ligands, for further investigating correlations between synthetic conditions and structures of complexes. Two complexes, $[Zn(L)(H_2O)] \cdot 2H_2O$ (**1**) and $[Cd(L)(H_2O)(bpy)] \cdot 3H_2O$ (**2**), have been obtained. We report herein the syntheses, structural characterization

and properties of the complexes. The fluorescence of **1** and **2** was examined.

Results and Discussion

Preparation

The hydrothermal reaction of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with H_2L in the co-solvent of H_2O -DMF at 100°C yields the complex $[\text{Zn}(\text{L})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ (**1**). In previous studies, a closely related zinc complex with the same ligand L^{2-} of composition $[\text{Zn}(\text{L})(\text{H}_2\text{O})]$ was reported by us, which was synthesized *via* the hydrothermal method at 180°C in the presence of NaOH as alkaline reagent for the deprotonation.

When H_2L reacts with $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ under hydrothermal conditions in the presence of 2,2'-bipyridine (bpy) as auxiliary ligand at 120°C , complex $[\text{Cd}(\text{L})(\text{H}_2\text{O})(\text{bpy})] \cdot 3\text{H}_2\text{O}$ (**2**) is obtained. Complexes **1** and **2** are stable in air.

Structural description of $[\text{Zn}(\text{L})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ (**1**)

X-Ray crystal structural analysis has shown that complex **1** exhibits a 2D network structure in the monoclinic system with space group $P2_1/c$ and $Z = 4$. The H_2L ligand was deprotonated to the L^{2-} anion. In the asymmetrical unit there are one Zn^{2+} ion, one L^{2-} ligand, and one coordinated and two solvate water molecules. As shown in Fig. 1a, each Zn^{2+} ion is six-coordinated by two nitrogen atoms from one L^{2-} ligand, one oxygen atom from the coordinated water molecule, and three carboxylate oxygen atoms from two different L^{2-} ligands to furnish a distorted octahedral coordination geometry $[\text{ZnN}_2\text{O}_4]$. The two carboxylate groups of the L^{2-} ligand exhibit different coordination modes: one adopts a $\mu_1\text{-}\eta^1\text{:}\eta^1$ -chelating mode [the value of the angle subtended at the Zn^{2+} ion being $57.86(17)^\circ$], while the other is in the terminal monodentate mode. The Zn–O and

$[\text{Zn}(\text{L})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ (1)			
Zn(1)–O(1)	2.059(6)	Zn(1)–O(2)	2.392(5)
Zn(1)–O(5)	2.104(5)	Zn(1)–N(11)#1	2.362(5)
Zn(1)–N(12)#1	2.073(6)	Zn(1)–O(3)#2	1.970(5)
O(1)–Zn(1)–O(2)	57.86(19)	O(1)–Zn(1)–O(5)	93.5(2)
O(1)–Zn(1)–N(11)#1	91.8(2)	O(1)–Zn(1)–N(12)#1	148.6(2)
O(1)–Zn(1)–O(3)#2	102.8(2)	O(2)–Zn(1)–O(5)	86.72(18)
O(2)–Zn(1)–N(11)#1	89.04(17)	O(2)–Zn(1)–N(12)#1	93.0(2)
O(2)–Zn(1)–O(3)#2	160.1(2)	O(5)–Zn(1)–N(11)#1	170.1(2)
O(5)–Zn(1)–N(12)#1	96.3(2)	O(3)#2–Zn(1)–O(5)	100.2(2)
N(11)#1–Zn(1)–N(12)#1	75.0(2)	O(3)#2–Zn(1)–N(11)#1	86.73(19)
O(3)#2–Zn(1)–N(12)#1	104.7(2)		
$[\text{Cd}(\text{L})(\text{H}_2\text{O})(\text{bpy})] \cdot 3\text{H}_2\text{O}$ (2)			
Cd(1)–O(3)	2.620(3)	Cd(1)–O(4)	2.288(3)
Cd(1)–O(5)	2.282(3)	Cd(1)–N(1)	2.346(3)
Cd(1)–N(2)	2.351(3)	Cd(1)–O(1)#1	2.334(3)
Cd(1)–O(2)#1	2.484(3)		
O(3)–Cd(1)–O(4)	52.56(9)	O(3)–Cd(1)–O(5)	78.62(10)
O(3)–Cd(1)–N(1)	92.51(10)	O(3)–Cd(1)–N(2)	96.27(10)
O(1)#1–Cd(1)–O(3)	133.50(10)	O(2)#1–Cd(1)–O(3)	166.37(11)
O(4)–Cd(1)–O(5)	98.57(10)	O(4)–Cd(1)–N(1)	138.73(10)
O(4)–Cd(1)–N(2)	90.52(10)	O(1)#1–Cd(1)–O(4)	85.03(10)
O(2)#1–Cd(1)–O(4)	137.93(12)	O(5)–Cd(1)–N(1)	94.15(10)
O(5)–Cd(1)–N(2)	163.34(10)	O(1)#1–Cd(1)–O(5)	91.75(11)
O(1)#1–Cd(1)–N(1)	133.79(11)	O(2)#1–Cd(1)–N(1)	80.75(12)
O(1)#1–Cd(1)–N(2)	102.98(11)	O(2)#1–Cd(1)–N(2)	92.57(12)
O(1)#1–Cd(1)–O(2)#1	53.44(12)	N(1)–Cd(1)–N(2)	70.07(10)
O(2)#1–Cd(1)–O(5)	89.99(12)		

Table 1. Selected bond lengths (Å) and angles (deg) for complexes **1** and **2**^a.

^a Symmetry transformations used to generate equivalent atoms: for **1**: #1 $1-x, 1-y, 1-z$; #2 $x, 1/2-y, 1/2+z$; for **2**: #1 $x, 1+y, z$.

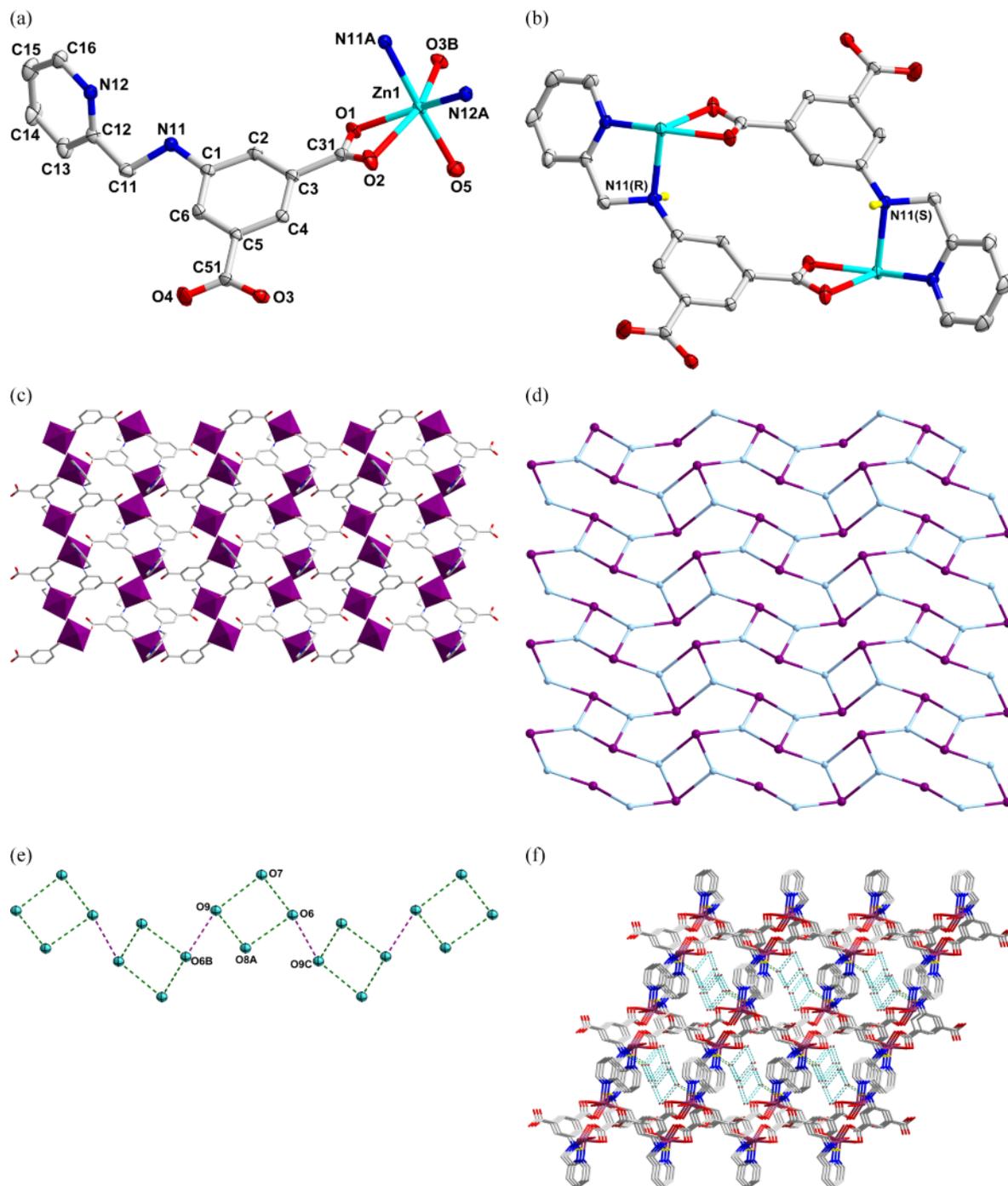


Fig. 1 (color online). (a) The coordination environment of the Zn^{2+} ions in **1** with ellipsoids drawn at the 30% probability level. The hydrogen atoms and the solvate water molecules are omitted for clarity; (b) view of a pair of enantiomerically coordinated N atoms in **1** with the position of the lone pairs at N generated geometrically (yellow); (c) the 2D network structure of **1**; (d) topological view of the 2D network of **1**; (e) view of chain-like water clusters in **1**; (f) the 3D supramolecular framework of **1** constructed through hydrogen bond interactions.

D–H···A	<i>d</i> (D···A) (Å)	∠D–H···A (deg)
[Zn(L)(H ₂ O)]·2H ₂ O (1)		
N(11)–H(4)···O(6)	3.041(10)	177
O(5)–H(11)···O(1)#1	3.035(8)	124
O(5)–H(11)···O(4)#2	3.075(7)	143
O(5)–H(12)···O(4)#3	2.793(9)	162
[Cd(L)(H ₂ O)(bpy)]·3H ₂ O (2)		
N(11)–H(4)···O(6)#1	3.102(6)	165
O(5)–H(19)···O(3)#2	2.776(4)	173
O(5)–H(20)···O(8)#3	2.658(6)	177
O(6)–H(21)···O(7)#4	2.844(5)	173
O(6)–H(22)···O(4)	2.887(4)	165
O(7)–H(23)···O(1)	3.091(5)	174
O(7)–H(24)···N(12)	2.945(6)	169

Table 2. Hydrogen bonding data for complexes **1** and **2**^a.

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

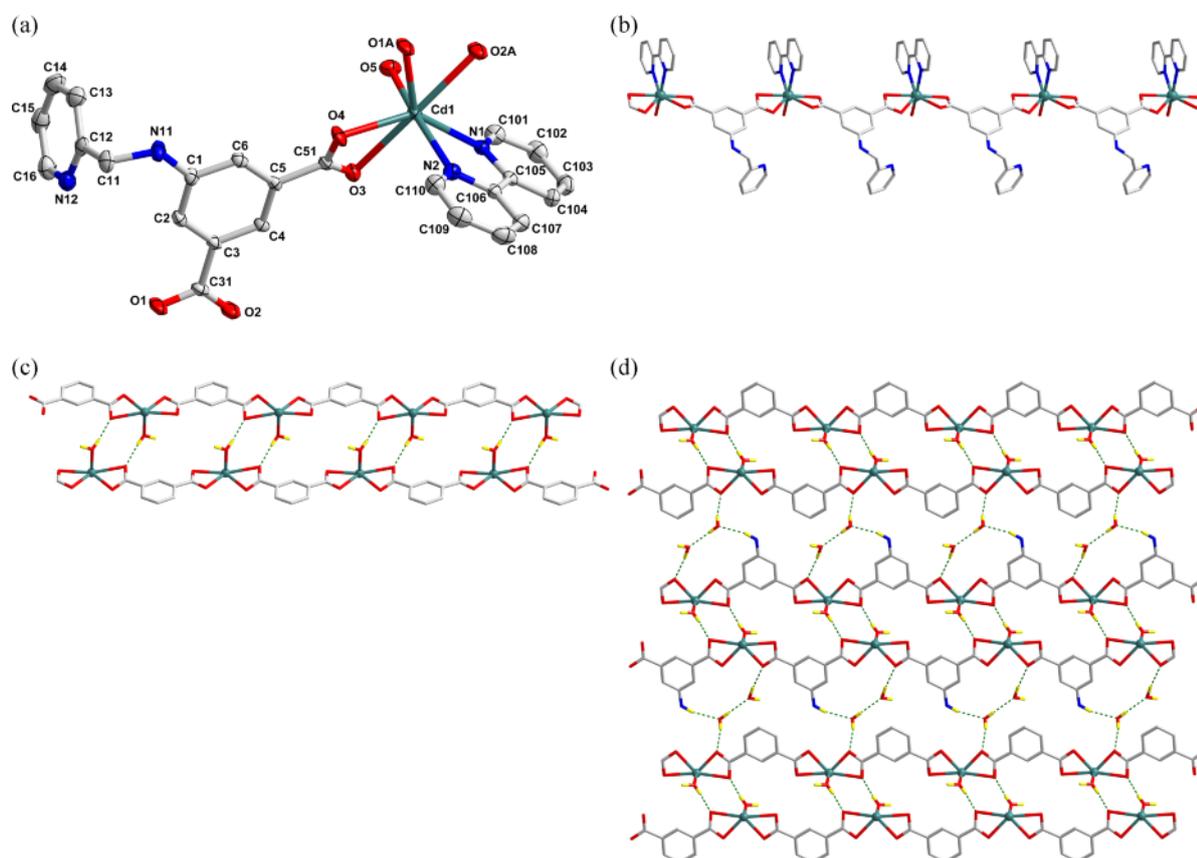


Fig. 2 (color online). (a) The coordination environment of the Cd²⁺ ions in **2** with ellipsoids drawn at the 30% probability level. The hydrogen atoms and the solvate water molecules are omitted for clarity; (b) view of the 1D structure of **2**; (c) double-chain structure in **2** extended by hydrogen bonding interactions; (d) the extended 2D network of **2**.

Zn–N bond lengths around the Zn center range between 2.059(6) and 2.392(5) Å (for Zn–O) while Zn–N amounts to 2.073(6) and 2.326(5) Å. The bond angles around Zn²⁺ cation are in the range of 57.86(17) to 170.12(17)° (Table 1). Two nitrogen atoms from the (pyridin-2-ylmethyl)amino group chelate one Zn²⁺ ion to generate a folded 5-membered *N,N*-chelated metallacycle; two L²⁻ ligands doubly bridge two Zn²⁺ cations to form a binuclear structure across the inversion center (Fig. 1b). Within this unit there exist two intrinsically chiral N atoms, which are enantiomeric to each other and thus form a meso structure. Each L²⁻ ligand bridges three Zn²⁺ ions, and every Zn²⁺ ion is coordinated by three different L²⁻ ligands. This kind of interconnection extends infinitely to fabricate a neutral 2D network (Fig. 1c). Both the Zn²⁺ ion and the L²⁻ ligand can be considered as three-connected nodes in the ratio of 1 : 1. The structure of **1** can thus be simplified as a uninodal 3-connected 2D *fes* network with (4.8²) topology (Fig. 1d) [15].

Interesting hydrogen bonding interactions N–H···O and O–H···O exist in complex **1** (Table 2). Significantly, four solvent water molecules cling to each other to generate a tetranuclear water cluster *via* the aforementioned weak interactions. Adjacent clusters

are interlinked to exhibit a water cluster chain structure (Fig. 1e). Furthermore, adjacent 2D networks are connected to give a 3D framework (Fig. 1f).

Structural description of [Cd(L)(H₂O)(bpy)]·3H₂O (**2**)

Complex **2** crystallizes in the triclinic crystal system with space group *P* $\bar{1}$ and *Z* = 2 (Table 3). The asymmetric unit of **2** consists of one Cd²⁺ cation, one L²⁻ and one bpy ligand, one coordinated and three solvate water molecules. Each Cd center is seven-coordinated by four carboxylate oxygen atoms from two L²⁻, one oxygen atom from the coordinated water molecule, and two nitrogen atoms from the bpy ligand in a distorted pentagonal-bipyramidal coordination geometry (Fig. 2a). Four carboxylate O atoms and one bpy N atom define the equatorial plane and the two apexes are occupied by another N atom and the O atom of a coordinated water molecule. The bond lengths around the Cd center vary from 2.282(3) to 2.620(3) Å, and the bond angles are in the range of 52.56(9) to 166.35(11)°, comparable to previously reported cadmium(II) complexes [11, 20]. Both carboxylate groups in L²⁻ adopt a $\mu_1\text{-}\eta^1\text{:}\eta^1$ -chelating coordination mode.

	1	2
Formula	C ₁₄ H ₁₆ N ₂ O ₇ Zn	C ₂₄ H ₂₆ N ₄ O ₈ Cd
<i>M_r</i>	389.66	610.89
Crystal size, mm ³	0.20 × 0.20 × 0.20	0.30 × 0.05 × 0.05
Crystal system	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	10.996(4)	9.5230(10)
<i>b</i> , Å	9.856(3)	10.1986(11)
<i>c</i> , Å	17.701(4)	13.4493(14)
α , deg	90	91.3730(10)
β , deg	116.715(16)	90.7620(10)
γ , deg	90	99.4040(10)
<i>V</i> , Å ³	1713.6(9)	1288.1(2)
<i>Z</i>	4	2
<i>D</i> _{calcd.} , g cm ⁻³	1.51	1.58
μ (MoK α), cm ⁻¹	1.5	0.9
<i>F</i> (000), e	800	620
<i>hkl</i> range	−6 → +13, ±11, −21 → +20	±11, ±12, −13 → +16
θ _{max} , deg	2.07–25.01	2.02–26.00
Refl. measured / unique / <i>R</i> _{int}	9214 / 3030 / 0.0388	7106 / 4974 / 0.0138
Param. refined	235	338
<i>R</i> 1(<i>F</i>) / <i>wR</i> 2(<i>F</i> ²) ^{a,b} (all reffs.)	0.0767 / 0.2212	0.0414 / 0.1159
GoF (<i>F</i> ²) ^c	1.085	1.092
$\Delta\rho$ _{fin} (max / min), e Å ⁻³	1.40 / −0.47	1.56 / −0.50

Table 3. Crystal structure data for **1** and **2**.

^a $R1 = \sum |F_o| - |F_c| / \sum |F_o|$; ^b $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2) / 3$; ^c $\text{GoF} = [\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

The flexible pyridin-2-ylmethylamino groups in L^{2-} are free of coordination. Thus the L^{2-} ligand in **2** just acts as a μ_2 -connector, linking different Cd centers to form a chain structure (Fig. 2b). Two chains are connected by hydrogen bonds to form a double-chain structure (Fig. 2c), which is further linked to a 2D network structure (Fig. 2d).

PXRD and thermal stability of complexes **1** and **2**

The phase purities of **1** and **2** could be proven by powder X-ray diffraction (PXRD). As shown in Fig. 3, each PXRD pattern of the as-synthesized sample is consistent with the simulated one.

Thermogravimetric analyses (TGA) were carried out for complexes **1** and **2**, and the results are shown in Fig. 4. For complex **1**, there is a continuous weight loss of 13.7% from 90 to 200 °C corresponding to the

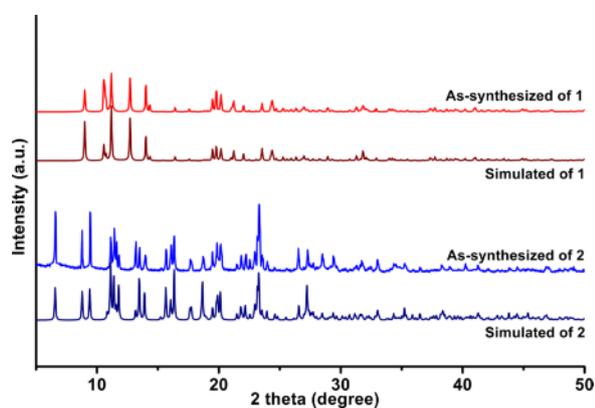


Fig. 3 (color online). The PXRD patterns of complexes **1** and **2**.

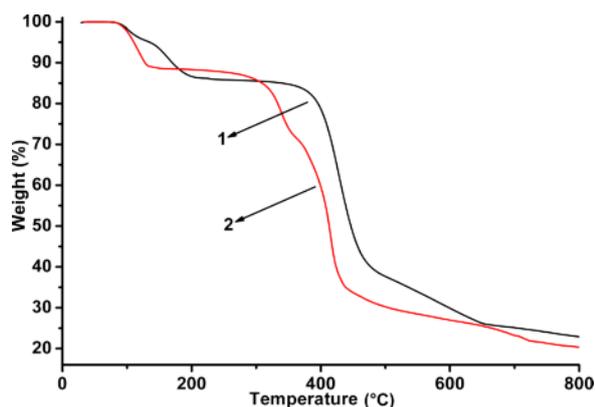


Fig. 4 (color online). TGA curves of complexes **1** and **2**.

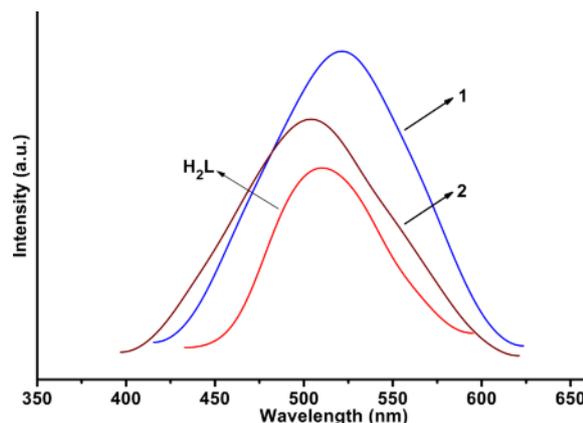


Fig. 5 (color online). Fluorescence of the complexes **1** and **2** and of the H_2L reference in the solid state at room temperature.

release of water (calcd. 13.9%). The decomposition of the framework of **1** can be observed at 358 °C. For **2**, a steep weight loss totaling 11.5% from 86 to 132 °C is attributed to the liberation of the water (calcd. 11.8%), and the subsequent collapse of the framework starts at 300 °C.

Luminescence properties

The luminescence properties of complexes with d^{10} metal centers such as Zn(II) and Cd(II) are of interest for their potential application as photoactive materials [16, 17]. Therefore, the luminescence of complexes **1** and **2** and the H_2L reference was investigated in the solid state at room temperature. As shown in Fig. 5, intense bands were observed at 520 nm ($\lambda_{ex} = 345$ nm) for **1**, 503 nm ($\lambda_{ex} = 339$ nm) for **2**, and 510 nm ($\lambda_{ex} = 330$ nm) for H_2L . As for the source of fluorescence of the complexes, it may be assigned to intra-ligand transitions of the coordinated L^{2-} ligands since a similar emission can be observed for H_2L [18, 19]. The red (or blue) shift of the emission maximum in **1** and **2**, respectively, compared with free H_2L ligand may originate from the coordination of the ligands to the metal centers [20, 21].

Experimental Section

All commercially available chemicals were of reagent grade and used as received without further purification. The H_2L ligand was synthesized *via* the experimental procedure reported in the literature [13]. Elemental analyses of C, H

and N were taken on a Perkin-Elmer 240C elemental analyzer. Infrared spectra (IR) were recorded on a Bruker Vector22 FT-IR spectrophotometer by using KBr pellets. Thermogravimetric analysis (TGA) was performed on a simultaneous SDT 2960 thermal analyzer under nitrogen atmosphere with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. The luminescence spectra for the powdered solid samples were measured on an Aminco Bowman Series 2 spectrofluorometer with a xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width was 5 nm, and all measurements were carried out under the same experimental conditions.

Preparation of $[\text{Zn}(\text{L})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$ (**1**)

A mixture of $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (59.5 mg, 0.2 mmol), H_2L (27.2 mg, 0.1 mmol) and 2 mL DMF in 8 mL H_2O was sealed in a 16 mL Teflon-lined stainless-steel container and heated at $100\text{ }^{\circ}\text{C}$ for 72 h. Then the oven was cooled down at a rate of $20\text{ }^{\circ}\text{C h}^{-1}$. After cooling to room temperature, colorless block-shaped crystals of **1** were obtained with an approximate yield of 30% based on H_2L . – $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_7\text{Zn}$ (449.90): calcd. C 43.15, H 4.14, N 7.19; found C 42.88, H 4.44, N 6.90%. – IR (KBr pellet, cm^{-1}): $\nu = 3411(\text{m}), 3262(\text{m}), 1574(\text{s}), 1548(\text{s}), 1498(\text{s}), 1417(\text{s}), 1351(\text{s}), 1322(\text{m}), 1226(\text{m}), 1086(\text{m}), 958(\text{m}), 891(\text{s}), 773(\text{m}), 726(\text{s}), 593(\text{s})$.

Preparation of $[\text{Cd}(\text{L})(\text{H}_2\text{O})(\text{bpy})]\cdot 3\text{H}_2\text{O}$ (**2**)

A mixture of $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ (61.8 mg, 0.2 mmol), H_2L (27.2 mg, 0.1 mmol), bpy (15.6 mg, 0.1 mmol), and KOH (11.2 mg, 0.2 mmol) in 10 mL H_2O was sealed in a 16 mL Teflon-lined stainless-steel container and heated at $120\text{ }^{\circ}\text{C}$ for 48 h. Then the oven was shut off and left to cool to ambient temperature. Colorless needle-like crystals of **2** were obtained with an approximate yield of 25% based on H_2L . – $\text{C}_{24}\text{H}_{26}\text{N}_4\text{O}_8\text{Cd}$ (360.62): calcd. C 47.19, H 4.29, N 9.17; found C 47.46, H 4.55, N 9.40%. – IR (KBr pellet, cm^{-1}):

$\nu = 3345(\text{m}), 1599(\text{s}), 1550(\text{s}), 1476(\text{s}), 1437(\text{s}), 1412(\text{s}), 1373(\text{s}), 1334(\text{s}), 1241(\text{m}), 1147(\text{m}), 1010(\text{m}), 814(\text{m}), 765(\text{s}), 730(\text{s})$.

X-Ray structure determinations

Powder X-ray diffraction (PXRD) patterns were measured on a Shimadzu XRD-6000 X-ray diffractometer with $\text{CuK}\alpha$ ($\lambda = 1.5418\text{ \AA}$) radiation at room temperature.

The crystallographic data collections on single crystals of complexes **1** and **2** were carried out on a Bruker Smart ApexII CCD area-detector diffractometer using graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) at 293(2) K. The diffraction data were integrated by using the program SAINT [22], which was also used for the intensity corrections and for Lorentz and polarization effects. Semi-empirical absorption corrections were applied using the program SADABS [23]. The structures of **1** and **2** were solved by Direct Methods, and all non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares techniques using the SHELXL-97 crystallographic software package [24–26]. In **1** and **2**, all hydrogen atoms at C atoms were generated geometrically. The hydrogen atoms at O5 in **1**, and O5, O6 and O7 in **2**, could be found in reasonable positions in the difference Fourier maps. Other hydrogen atoms of water molecules in **1** and **2** could not be located and thus were not included in the refinement. Two parts of the disorder solvent water molecule in **2** were restrained *via* EADP, DELU, and SIMU instructions in the refinement of the structure model.

CCDC 945780 and 945781 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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