DOI: 10.1002/ejic.200600713

Cadmium(II) and Zinc(II) Coordination Polymers with 1D Ladder and 2D Basket Weave Layer Structures Constructed from a New T-Shaped Ligand

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Keywords: Pyridinones / Polymers / T-shaped ligands / Luminescence / Coordination modes

A novel imidazo[1,2-*a*]pyridin-2-one ligand, 3,3-bis(carboxymethyl)imidazo[1,2-*a*]pyridin-2-one (H_2L), was conveniently synthesized and acts as a three-connecting T-shaped building block. Hydrothermal treatment of the H_2L ligand with $Cd(ClO_4)_2{\cdot}6H_2O$ or $Zn(ClO_4)_2{\cdot}6H_2O$ gives two new coordination polymers, $[CdL(H_2O)_2]_n$ (**1**) or $[ZnL(H_2O)]_n$ (**2**). Compound **1** consists of a rare 1D ladder-like chain and **2** is the first example of a polymer with a 2D basket weave network. Solid-state photoluminescent analyses of **1** and **2** show that they display strong fluorescent emissions.

Introduction

In the past decades, coordination polymers have been subjected to a vast number of studies owing to their potential applications in catalysis, molecular adsorption, magnetism, nonlinear optics, luminescence, and molecular sensing,[1,2] as well as their intriguing structural motifs.[3] Recently, increasing investigations have been focused on the construction of coordination polymers with the use of heterocyclic carboxylic acids such as pyridine-,[4] pyrazole-,[5] and imidazolecarboxylic acids[6] as building blocks. These building blocks contain multioxygen and nitrogen atoms and can coordinate with metal ions in different ways, which results in the formation of various metal–organic frameworks with specific topologies and useful properties. It is well-known that organic ligands play crucial roles in the design and construction of desirable frameworks because changes in the flexibility, length, and symmetry of the organic ligands can result in a remarkable class of coordination polymers bearing diverse architectures and functions.[7] Our previous work had shown that the N-containing polycarboxylate ligands could be used to construct novel coordination polymers.[8] Herein, we turn our attention to a novel N-containing polycarboxylate ligand, 3,3-bis(carboxymethyl)imidazo[1,2-*a*]pyridin-2-one (H_2L). This ligand consists of a rigid imidazo[1,2-*a*]pyridin-2-one ring and flexible diacetic acid moieties; it is possible that the combination of these specialties may lead to the formation of interesting topologies.

A number of infinite ladder-like coordination polymers have been reported;[9] however, most of them were constructed with two-connecting ligands such as 4,4′-bipy. In principle, it is difficult to obtain a T-shaped geometry around the metal center, which is essential for the ladder structure, by using two-connecting ligands.[10] One strategy that can be used to overcome this difficulty is to use three-connecting T-shaped ligands as building units.[11] Hitherto, only a few ladder-like compounds containing T-shaped ligands have been reported.[10–12] Comparatively, less effort has been made in the construction of 2D layers by using three-connecting T-shaped ligands.[11b,13] According to the definition of Wells,[14] five types of 2D architectures (brick wall, herringbone, bilayer, basket weave, and long and short brick) can be expected for a T-shaped geometry, but only the first three types have already been realized so far.[3c]

During our research on the H_2L ligand, we have obtained two new coordination polymers, $[CdL(H_2O)_2]_n$ (**1**) and $[ZnL(H_2O)]_n$ (**2**). The ladder-like chain built from the T-shaped ligand as found in **1** is rare. To the best of our knowledge, compound **2** is the first example of a coordination polymer whose 2D basket weave network is constructed from the combination of metal centers with a T-shaped geometry and ligands with T-shaped structure simultaneously. Herein, we report the syntheses, X-ray single-crystal analyses, and photoluminescent properties of **1** and **2**.

Results and Discussion

Synthesis of 3,3-Bis(carboxymethyl)imidazo[1,2-*a*]pyridin-2-one (H_2L)

Imidazo[1,2-*a*]pyridine derivatives have been attracting considerable interest because of their significant pharmaceutical importance.[15] They are also versatile intermediates

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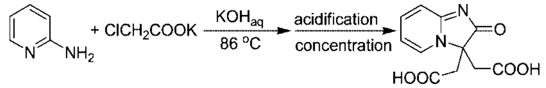
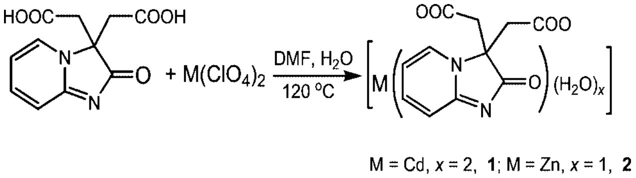
for synthetic transformations.[16] However, less effort has been made in the synthesis of imidazo[1,2-*a*]pyridin-2-one derivatives. We exploit a novel and facile synthetic method for these imidazo[1,2-*a*]pyridin-2-one derivatives (Scheme 1). 3,3-Bis(carboxymethyl)imidazo[1,2-*a*]pyridin-2-one (H_2L) was obtained as a free acid from the reaction of potassium chloroacetate and 2-aminopyridine in aqueous alkaline solution heated at 86 °C, followed by acidification of the mixture with aqueous HCl and concentration under boiling conditions. After cooling of the mixture to remove the precipitated KCl (ice bath), the desired acid was precipitated and removed by filtration. The negative ion electrospray mass spectrum (H_2O) of H_2L shows the characteristic molecular ion peak around m/z = 248.97, which provides strong evidence for the formula $C_{11}H_{10}N_2O_5$. The molecular structure is also supported by microanalysis, IR, and NMR spectroscopic results.



Scheme 1. Synthesis of 3,3-bis(carboxymethyl)imidazo[1,2-*a*]pyridin-2-one.

Syntheses of Compounds 1 and 2

Compounds **1** and **2** were readily obtained in good yields (Scheme 2) by treating the corresponding metal perchlorate salts and H_2L in a mixture of DMF and H_2O at 120 °C for two days. Their formulations are supported by IR, microanalysis and thermogravimetric analysis (TGA) results. The phase purities were revealed by powder diffraction patterns of the bulk samples, which are consistent with the theoretical patterns generated from their single-crystal X-ray diffraction data (see Supporting Information).



Scheme 2. Syntheses of compounds **1** and **2**.

Description of Crystal Structure

$[CdL(H_2O)_2]_n$ (1)

Compound **1** has a 1D infinite ladder structure that is assembled through metal–nitrogen and metal–oxygen coordination bonds. The coordination geometry of each Cd^{II} ion is a distorted octahedron, in which the Cd^{II} ion is coordinated to two water oxygen atoms, three carboxylate oxygen atoms, and one nitrogen atom from three L^{2-} ligands (Figure 1). The five Cd–O bond lengths range from 2.234(2) to 2.508(2) Å, and the Cd–N bond length is 2.264(2) Å (Table 1).

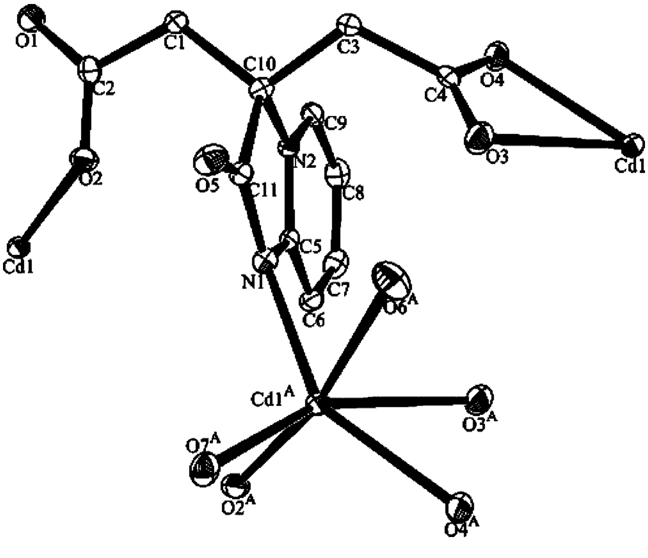


Figure 1. ORTEP drawing at the 50% probability level showing the Cd^{II} coordination environment and T-shaped ligand in **1**. Hydrogen atoms are omitted for clarity. Symmetry code: A: $-x$, $-y$, $-z$.

Table 1. Selected bond lengths [Å] and angles [°] for compounds **1** and **2**.

1[a]		**2**[b]	
Cd1–O2	2.234(2)	Zn1–O2#2	1.980(2)
Cd1–O3	2.508(2)	Zn1–O3#3	2.075(2)
Cd1–O4	2.296(2)	Zn1–O6	2.034(2)
Cd1–O6	2.423(2)	Zn1–N1	2.010(2)
Cd1–O7	2.253(2)		
Cd1–N1#3	2.264(2)		
O2–Cd1–O3	96.59(7)	O2#2–Zn1–O3#3	125.43(8)
O2–Cd1–O4	104.72(6)	O2#2–Zn1–O6	99.54(10)
O2–Cd1–O6	169.89(7)	O2#2–Zn1–N1	114.13(8)
O2–Cd1–O7	89.80(7)	O3#3–Zn1–O6	94.20(9)
O2–Cd1–N1#3	89.11(7)	O3#3–Zn1–N1	116.62(9)
O3–Cd1–O4	54.83(6)	O6–Zn1–N1	95.72(10)
O3–Cd1–O6	89.50(7)		
O3–Cd1–O7	152.41(6)		
O3–Cd1–N1#3	93.37(7)		
O4–Cd1–O6	85.39(7)		
O4–Cd1–O7	97.59(6)		
O4–Cd1–N1#3	146.02(7)		
O6–Cd1–O7	88.49(8)		
O6–Cd1–N1#3	82.45(7)		
O7–Cd1–N1#3	113.61(7)		

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

As a rail and rung simultaneously, each L^{2-} ligand bridges three Cd atoms through its two carboxylate groups and one nitrogen atom to form a ladder extending along the *a* axis, as shown in Figure 2. As a result, the L^{2-} ligand can be described as a three-connecting T-shaped building block. The Cd atom can be taken as a three-connecting node with a T-shaped geometry if two coordinated water molecules are disregarded. The T-shaped configurations of both the Cd^{II} center and the L^{2-} ligand have thus accommodated the formation of a 1D ladder. Interestingly, the two flexible acetate groups bridge two Cd atoms in the monodentate and chelating fashion, respectively, to form the side rail of the ladder, while one nitrogen atom is linked to the third Cd atom. As a result, the rigid imidazo[1,2-*a*]pyridin-2-one ring acts as the rung. Because of the distorted T-joints and the unequal separations between the Cd1 and C10 atoms across the adjacent carboxylate groups, the 1D ladder is composed of two kinds of alternating rhombic rings with step lengths of 4.78 and 5.16 Å, respectively. The structure of **1** is a rare ladder motif consisting of two kinds of step lengths.[17]

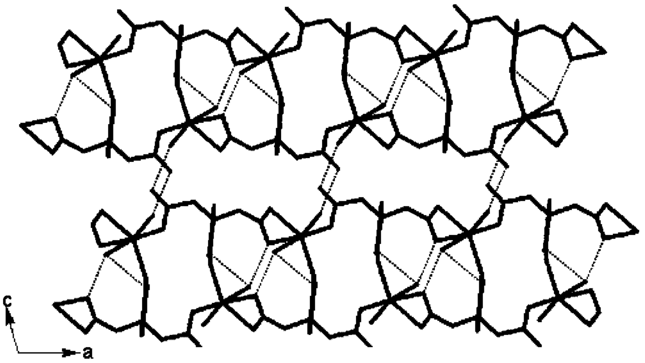


Figure 2. View along the *b* axis of the 2D hydrogen bonding network (dotted lines) of **1**.

As shown in Figure 2, the ladders extending along the *a* axis are organized by the O7···O1 [2.700(2) Å] hydrogen bonds that exist between two adjacent chains to form a layer that lies in the *a*,*c* plane. There are also intra-chained hydrogen bonding interactions [O6···O5 2.856(3) and O6···O3 2.807(3) Å] between coordinating water molecules, carbonyl oxygen atoms, and carboxylate oxygen atoms (Table 2). It is interesting to note that the stack of undulating 2D hydrogen bonding layers through the O···O hydrogen bonding interactions [O7···O5 2.739(3) Å] gives rise to a 3D supramolecular network with rhombic channels occupied by the pendent pyridine rings of the L^{2-} ligands (see Supporting Information).

Table 2. Hydrogen bond geometries for compounds **1** and **2**.

	D–H···A	*d*(D···A) [Å]	<(D–H···A) [°]
1[a]	O6–H01···O3^{i}	2.807(3)	153(4)
	O6–H02···O5^{i}	2.856(3)	149(4)
	O7–H03···O5^{ii}	2.739(3)	173(4)
2[b]	O6–H02···O1^{i}	2.615(3)	178(4)
	O6–H01···O5^{ii}	2.688(3)	168(4)

[a] Symmetry codes for **1**: ^{i}: $-x, -y, -z$; ^{ii}: $-x, y+1/2, -z+1/2$. [b] Symmetry codes for **2**: ^{i}: $x-1/2, -y-1/2, z-1/2$; ^{ii}: $-x+1/2, y+1/2, -z+1/2$.

[ZnL(H$_2$O)]$_n$ (2)

Compound **2** possesses a 2D basket weave network based on the three-connecting T-shaped ligand. As shown in Figure 3, each Zn^{II} ion adopts a distorted tetrahedral coordination environment by coordinating one water molecule, two carboxylate oxygen atoms, and one nitrogen atom from three L^{2-} ligands with the Zn–O bond lengths ranging from 1.980(2) to 2.075(2) Å, and the Zn–N bond length of 2.010(2) Å (Table 1).

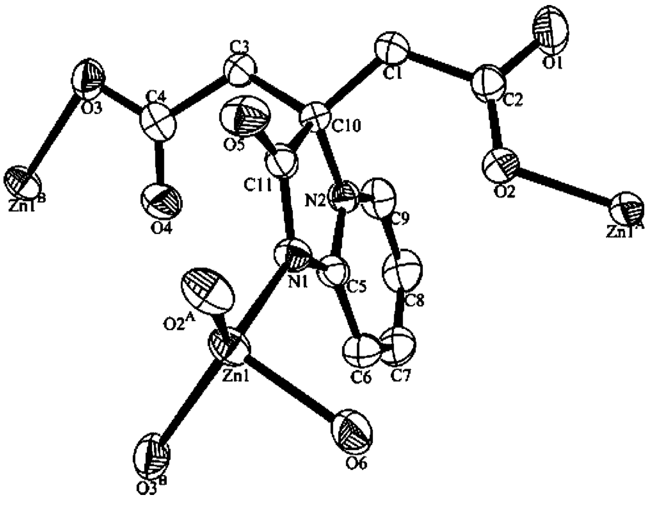


Figure 3. ORTEP drawing at the 50% probability level showing the Zn^{II} coordination environment and T-shaped ligand in **2**. Hydrogen atoms are omitted for clarity. Symmetry code: A: $-x+1/2$, $y+1/2$, $-z+1/2$; B: $-x$, $-y$, $-z$.

The L^{2-} ligand also acts as a three-connecting T-shaped building block, bridging three Zn atoms through its two monodentate carboxylate groups and one nitrogen atom. The Zn atom can also be taken as a three-connecting node with a T-shaped geometry if one coordinated water molecule is disregarded (the aqua ligand does not bridge). Interestingly, four arms (two acetate groups and two imidazo[1,2-*a*]pyridin-2-one rings) from two different L^{2-} ligands bridge two Zn atoms to form a four-membered metallacycle with four three-connecting nodes (two C10 atoms and two Zn1 atoms). Such metallacycles are further extended to form not a ladder as observed in **1**, but a 2D basket weave network lying in the *a*,*b* plane, as shown in Figure 4. In principle, the transformation from the 1D ladder of **1** to the 2D basket weave network of **2** only requires the alternate breaking of opposite side rails of one ladder and then the connection to the neighboring parallel ladders (see Supporting Information). Thus, the present case is the first coordination network having a 2D basket weave architecture that is constructed from the combination of metal ions with T-shaped geometries and ligands with T-shape structures simultaneously. There are intralayered hydrogen bonding interactions [O6···O5 2.688(3) Å] between coordinating water molecules and carbonyl oxygen atoms. It is very interesting to notice that the 2D basket weave network of **2** exhibits beautiful sinusoidal 2D layers extending along the *a*,*c* plane, which further assemble into a 3D supramolecular network through the interlayered hydrogen bonding interactions [O6···O1 2.615(3) Å] (see Supporting Information).

It is worthy to note that the structural differences between **1** and **2** with the same L^{2-} ligands and the same synthetic conditions may mainly be attributed to the radii of the metal atoms with the Cd atom having a larger atomic radius than the Zn atom, which results in different coordi-

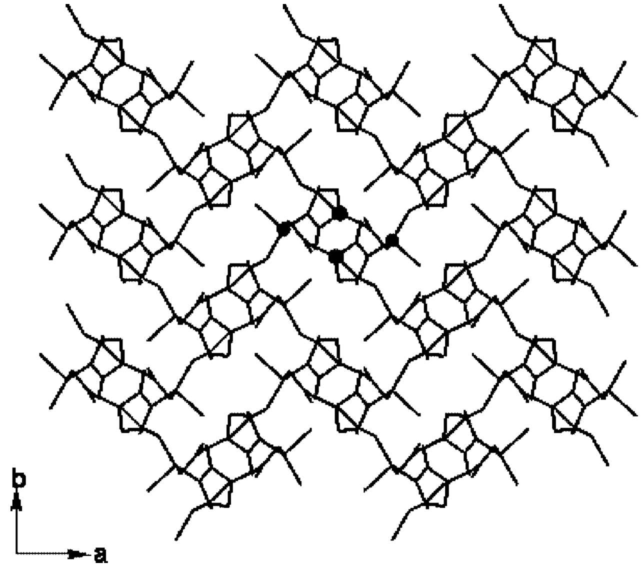


Figure 4. View of the 2D basket weave network lying in the *a,b* plane of **2**. Pyridine rings are omitted for clarity, and the black spheres represent three-connecting nodes.

nation environments (Cd^{II} with octahedron geometry and Zn^{II} with tetrahedron geometry).[18]

Thermogravimetric Analyses

TG analysis of **1** reveals that its first weight loss appears at ca. 152 °C due to the loss of two coordinating water molecules (calcd. 9.1%; found 9.2%). The second weight loss occurs between 252 °C and 550 °C and is characteristic of the decomposition of the organic moiety. Coordination polymer **2** shows the first weight loss at ca.168 °C with the loss of one coordinating water molecule (calcd. 5.4%; found 5.1%), and the second weight loss occurs between 355 °C and 472 °C and is characteristic of the decomposition of the organic moiety (see Supporting Information).

Photoluminescent Properties

The emission spectra of **1** and **2** in the solid state at room temperature are depicted in Figure 5. Compounds **1** and **2** display similar shoulder peaks, and their maximum emission peaks occur at 400 nm upon excitation at 210 nm and 250 nm, respectively. The emissions of **1** and **2** can probably be assigned to intraligand fluorescent emission,[19] since the free H_2L ligand reveals the same maximum emission band (400 nm) upon excitation at 313 nm (see Supporting Information). These results imply that the coordination of the L^{2-} ligand with the Cd^{II} and Zn^{II} ions, although yielding different topological structures, has no influence on the emission mechanism of the metal coordination polymer.[20] Compared to that of the free H_2L ligand, **1** and **2** show significantly stronger photoluminescence, probably due to the coordination of the H_2L ligand to the metal ions, which increases the ligand conformational rigidity;[21] the nonradiative decay of the intraligand excited state is thereby reduced. The metallacycles of **1** and **2** built by T-shaped L^{2-} ligands probably cause significant enhancement to the rigidity of the ligand. The difference in the emission intensities of **1** and **2** is probably due to the differences in the metal ions and the coordination environment around them.[22] These observations suggest that compounds **1** and **2** may be excellent candidates for potential photoactive materials,[23] since these condensed materials are thermally stable and insoluble in water and common organic solvents.

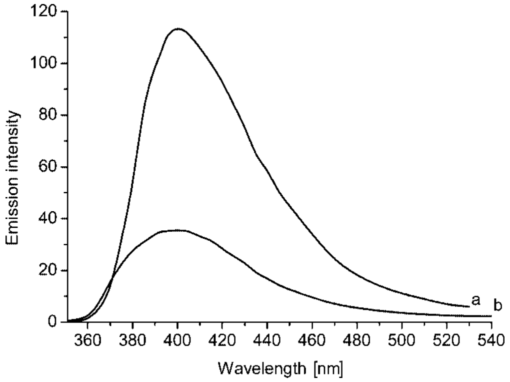


Figure 5. Solid-state emission spectra of a) **1** and b) **2** at room temperature.

Conclusions

A novel imidazo[1,2-*a*]pyridin-2-one derivative (H_2L) was conveniently synthesized and characterized. By a combination of the different coordination environments of the metal ions and the T-shaped coordination mode of the L^{2-} ligand, we have successfully synthesized two new coordination polymers, of which **1** has a rarely reported ladder motif and **2** is the first example having a 2D basket weave network. Toward the synthesis and design of 1D ladder chains or 2D basket weave networks, we think that T-shaped ligands are very suitable and promising for the syntheses of compounds with novel structures such as ladders, brickwalls, herringbones, bilayers, basket weaves, and long and short bricks.

Experimental Section

General Methods: All reagents are commercially available and used as purchased without further purification. Elemental analysis was carried out with an Elementar Vario EL III microanalyser. The FTIR spectra were recorded with a Bruker Vector 22 spectrophotometer in the 4000–400 cm^{-1} region. Mass spectra were obtained by negative ion electrospray (H_2O solution) with a LCQ Advantage Max mass spectrometer. ^1H- and ^{13}C NMR spectra were recorded with a Bruker AV300 and AV400 spectrometer, respectively. The emission spectra for the solid samples were recorded at room temperature with a Hitachi 850 fluorescence spectrophotometer. Thermogravimetric analyses were performed under air with a heating rate of 10 $°C\,min^{-1}$ with a Shimadzu TGA-50H TG analyzer. Powder X-ray diffraction (PXRD) patterns were obtained with a MXPAHF rotation anode X-ray diffractometer. ***Caution:*** Cd-

$(ClO_4)_2{\cdot}6H_2O$ and $Zn(ClO_4)_2{\cdot}6H_2O$ are potentially explosive and should be used with care!!

Synthesis of 3,3-Bis(carboxymethyl)imidazo[1,2-*a*]pyridin-2-one (H_2L): A solution of KOH (33.6 g, 0.6 mol) in water (75 mL) was added dropwise to an ice-bath cooled solution of chloroacetic acid (28.4 g, 0.3 mol) in water (75 mL). To the resulting alkaline solution, 2-aminopyridine (9.4 g, 0.1 mol) was slowly added, and the mixture was heated under reflux at 86 °C for 30 h. HCl (6 N, 53 mL) was added to neutralize the solution, which was concentrated under boiling conditions and then cooled (ice-bath) to remove KCl. After the mother liquor (pH = 2–3) was allowed to stand in the refrigerator for three days, the desired acid (H_2L) was separated out and collected by filtration. The solid was recrystallized from hot ethanol/water (1:1), and the colorless product was then collected by filtration and air-dried. Yield: 5.75 g (23%, based on 2-aminopyridine). $C_{11}H_{10}N_2O_5$ (250.21): calcd. C 52.80, H 4.03, N 11.20; found C 52.48, H 4.05, N 10.93. MS (ES–, H_2O): m/z = 250 $[M]^+$. ^1H NMR (300 MHz, D_2O, 25 °C): δ = 8.77 (d, $^3J_{H,H}$ = 6.8 Hz, 1 H, 5-H), 8.48 (dd, $^3J_{H,H}$ = 6.8, 8.4 Hz, 1 H, 6-H), 7.67 (m, 2 H, 7-H, 8-H), 3.44 (s, 4 H, CH_2) ppm. ^{13}C NMR (100 MHz, D_2O, 25 °C): δ = 175.5 (C-2), 172.0 (*C*OOH), 153.2 (C-9), 147.9 (C-5), 136.2 (C-7), 120.4 (C-8), 111.6 (C-6), 69.8 (C-3), 42.5 (CH_2) ppm. IR (KBr pellet): $\tilde{\nu}$ = 3434 (m), 3077(m), 2972(m), 2876(w), 2792(w), 2683(w), 1771(s), 1708(m), 1649(s), 1580(m), 1519(s), 1414(m), 1185(s), 807(m), 598(m), 440(m) cm^{-1}.

Synthesis of $[CdL(H_2O)_2]_n$ (1): A mixture of $Cd(ClO_4)_2{\cdot}6H_2O$ (0.15 mmol) and H_2L (0.15 mmol) was placed in a heavy-walled Pyrex tube containing DMF (0.3 mL) and H_2O (0.3 mL). The tube was frozen in liquid N_2, sealed under vacuum, and then heated at 120 °C for two days. The colorless crystals were collected and washed with ethanol. Yield: 0.042 g [70%, based on $Cd(ClO_4)_2{\cdot}6H_2O$]. $C_{11}H_{12}CdN_2O_7$ (396.63): calcd. C 33.28, H 3.02, N 7.06; found C 33.54, H 2.69, N 7.07. IR (KBr pellet): $\tilde{\nu}$ = 3333 (s), 3053(w), 2967(w), 1709(s), 1653(s), 1593(s), 1559(s), 1496(s), 1440(m), 1391(s), 1348(m), 1297(w), 1227(m), 1162(w), 1140(m), 1089(w), 1026(w), 934(w), 920(m), 839(m), 771(s), 701(m), 606(m), 508(m) cm^{-1}.

Synthesis of $[ZnL(H_2O)]_n$ (2): A mixture of $Zn(ClO_4)_2{\cdot}6H_2O$ (0.15 mmol) and H_2L (0.15 mmol) was placed in a heavy-walled Pyrex tube containing DMF (0.3 mL) and H_2O (0.3 mL). The tube was frozen in liquid N_2, sealed under vacuum, and then heated at 120 °C for two days. The colorless crystals were collected and washed with ethanol. Yield 0.027 g [54%, based on $Zn(ClO_4)_2{\cdot}6H_2O$]. $C_{11}H_{10}N_2O_6Zn$ (331.58): calcd. C 39.81, H 3.01, N 8.44; found C 39.71, H 2.77, N 8.42. IR (KBr pellet): $\tilde{\nu}$ = 3322 (s), 3051(w), 2971(w), 1710(s), 1630(s), 1567(w), 1497(s), 1408(s), 1346(s), 1293(m), 1238(m), 1167(m), 1143(m), 1085(w), 1024(w), 943(w), 916(m), 866(w), 769(s), 703(m), 625(m), 524(m) cm^{-1}.

X-ray Crystallographic Study: Diffraction intensities for **1** and **2** were collected at 293 K with a Bruker P4 diffractometer by employing graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Empirical absorption correction was applied with the use of the SADABS program.[24] The structures were solved by direct methods and refined by full-matrix least-squares on F^2 by using the SHELXS-97 and SHELXL-97 programs, respectively.[25] All non-hydrogen atoms were refined anisotropically. The C–H hydrogen atoms were placed in geometrically calculated positions; the O–H hydrogen atoms were located from Fourier difference maps and kept fixed in that position. The selected bond lengths and bond angles for **1** and **2** are listed in Table 1, and the crystallographic data are summarized in Table 3.

Table 3. Crystal data and structure refinement parameters for compounds **1** and **2**.

	1	2
Chemical formula	$C_{11}H_{12}CdN_2O_7$	$C_{11}H_{10}N_2O_6Zn$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
Formula weight	396.63	331.58
a [Å]	9.124(2)	11.669(2)
b [Å]	14.398(3)	8.101(2)
c [Å]	9.844(2)	12.733(3)
α [°]	90.00	90.00
β [°]	99.66(3)	94.82(3)
γ [°]	90.00	90.00
V [Å^3]	1274.7(4)	1199.4(4)
Z	4	4
F(000)	784	672
D_c [g cm^{-3}]	2.067	1.836
T [K]	293(2)	293(2)
θ range [°]	2.26–28.46	2.27–28.29
μ [mm^{-1}]	1.751	2.077
GOF	1.065	0.887
Reflections collected	6857	6797
Independent reflections (R_{int})	3001 (0.0188)	2832 (0.0305)
Observed reflections	2740	2102
R_1, wR_2 [$I > 2\sigma(I)$]	0.0251, 0.0588	0.0382, 0.0715
R_1, wR_2 [all data]	0.0283, 0.0599	0.0538, 0.0763

CCDC-260674 and -260675 for **1** and **2**, respectively, 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.

Supporting Information (see footnote on the first page of this article): Luminescent curve of H_2L. Additional figures, PXRD patterns and TGA curves of **1** and **2**.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 20472078) and the Foundation of Education Department of Anhui Province (2002kj330ZD).

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[1] a) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319–330; b) O. R. Evans, W. B. Lin, *Acc. Chem. Res.* **2002**, *35*, 511–522; c) S. Kitagawa, R. Kitaura, S.-i. Noro, *Angew. Chem. Int. Ed.* **2004**, *43*, 2334–2375; d) D. Maspoch, D. Ruiz-Molina, J. Veciana, *J. Mater. Chem.* **2004**, *14*, 2713–2723.

[2] a) N. G. Pschirer, D. M. Ciurtin, M. D. Smith, U. H. F. Bunz, H. C. zur Loye, *Angew. Chem. Int. Ed.* **2002**, *41*, 583–585; b) G. S. Papaefstathiou, Z. Zhong, L. Geng, L. R. MacGillivray, *J. Am. Chem. Soc.* **2004**, *126*, 9158–9159; c) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982–986; d) Z. Ni, A. Yassar, T. Antoun, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 12752–12753; e) S. N. Wang, H. Xing, Y. Z. Li, J. F. Bai, Y. Pan, M. Scheer, X. Z. You, *Eur. J. Inorg. Chem.* **2006**, 3041–3053.

[3] a) S. R. Batten, R. Robson, *Angew. Chem. Int. Ed.* **1998**, *37*, 1460–1494; b) A. J. Blake, N. R. Champness, P. Hubberstey, W. S. Li, M. A. Withersby, M. Schröder, *Coord. Chem. Rev.* **1999**, *183*, 117–138; c) B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629–1658.

[4] a) P. Ayyappan, O. R. Evans, W. B. Lin, *Inorg. Chem.* **2001**, *40*, 4627–4632; b) M. L. Tong, S. Hu, J. Wang, S. Kitagawa, S. W. Ng, *Cryst. Growth Des.* **2005**, *5*, 837–839; c) Y. Xu, L. Han, Z. Z. Lin, C. P. Liu, D. Q. Yuan, Y. F. Zhou, M. C. Hong, *Eur.*

J. Inorg. Chem. **2004**, 4457–4462; d) B. Zhao, P. Cheng, Y. Dai, C. Cheng, D. Z. Liao, S. P. Yan, Z. H. Jiang, G. L. Wang, *Angew. Chem. Int. Ed.* **2003**, *42*, 934–936.

[5] L. Pan, N. Ching, X. Y. Huang, J. Li, *Chem. Eur. J.* **2001**, *7*, 4431–4437.

[6] a) Y. L. Liu, V. Kravtsov, R. D. Walsh, P. Poddar, H. Srikanth, M. Eddaoudi, *Chem. Commun.* **2004**, 2806–2807; b) M. T. Caudle, J. W. Kampf, M. L. Kirk, P. G. Rasmussen, V. L. Pecoraro, *J. Am. Chem. Soc.* **1997**, *119*, 9297–9298; c) E. Shimizu, M. Kondo, Y. Fuwa, R. P. Sarker, M. Miyazawa, M. Ueno, T. Naito, K. Maeda, F. Uchida, *Inorg. Chem. Commun.* **2004**, *7*, 1191–1194; d) P. Angaridis, J. W. Kampf, V. L. Pecoraro, *Inorg. Chem.* **2005**, *44*, 3626–3635; e) P. Mahata, S. Natarajan, *Eur. J. Inorg. Chem.* **2005**, 2156–2163; f) J. Y. Lu, Z. H. Ge, *Inorg. Chim. Acta* **2005**, *358*, 828–833; g) Z. F. Fei, D. B. Zhao, T. J. Geldbach, R. Scopelliti, P. J. Dyson, S. Antonijevic, G. Bodenhausen, *Angew. Chem. Int. Ed.* **2005**, *44*, 5720–5725; h) W. G. Lu, L. Jiang, X. L. Feng, T. B. Lu, *Cryst. Growth Des.* **2006**, *6*, 564–571.

[7] a) X. H. Bu, W. Chen, S. L. Lu, R. H. Zhang, D. Z. Liao, W. M. Bu, M. Shionoya, F. Brisse, J. Ribas, *Angew. Chem. Int. Ed.* **2001**, *40*, 3201–3203; b) D. N. Dybtsev, H. Chun, K. Kim, *Angew. Chem. Int. Ed.* **2004**, *43*, 5033–5036.

[8] a) G. P. Yong, S. Qiao, Z. Y. Wang, Y. Cui, *Inorg. Chim. Acta* **2005**, *358*, 3905–3913; b) G. P. Yong, Z. Y. Wang, Y. Cui, *Eur. J. Inorg. Chem.* **2004**, 4317–4323.

[9] a) K. Biradha, M. Fujita, *Chem. Commun.* **2002**, 1866–1867; b) A. J. Barton, A. R. J. Genge, W. Levason, G. Reid, *J. Chem. Soc., Dalton Trans.* **2000**, 2163–2166; c) M. Fujita, Y. J. Kwon, O. Sasaki, K. Yamaguchi, K. Ogura, *J. Am. Chem. Soc.* **1995**, *117*, 7287–7288; d) L. Carlucci, G. Ciani, D. Proserpio, *Coord. Chem. Rev.* **2003**, *246*, 247–289; e) M. Fujita, O. Sasaki, K. Y. Watanabe, K. Ogura, K. Yamaguchi, *New J. Chem.* **1998**, *22*, 189–191.

[10] P. Gamez, P. de Hoog, M. Lutz, A. L. Spek, J. Reedijk, *Inorg. Chim. Acta* **2003**, *351*, 319–325.

[11] a) P. Gamez, P. de Hoog, O. Roubeau, M. Lutz, W. L. Driessen, A. L. Spek, J. Reedijk, *Chem. Commun.* **2002**, 1488–1489; b) M. S. Wang, G. C. Guo, M. L. Fu, L. Xu, L. Z. Cai, J. S. Huang, *Dalton Trans.* **2005**, 2899–2907.

[12] a) P. Ayyappan, O. R. Evans, B. M. Foxman, K. A. Wheeler, T. H. Warren, W. B. Lin, *Inorg. Chem.* **2001**, *40*, 5954–5961; b) B. W. Sun, Z. M. Wang, S. Gao, *Inorg. Chem. Commun.* **2001**, *4*, 79–81.

[13] M. S. Wang, G. C. Guo, L. Z. Cai, W. T. Chen, B. Liu, A. Q. Wu, J. S. Huang, *Dalton Trans.* **2004**, 2230–2236.

[14] A. F. Wells, *Three-dimensional Nets and Polyhedra*, Wiley, New York, **1977**.

[15] a) M. Anderson, J. F. Beattie, G. A. Breault, J. Breed, K. F. Byth, J. D. Culshaw, R. P. A. Ellston, S. Green, C. A. Minshull, R. A. Norman, R. A. Pauptit, J. Stanway, A. P. Thomas, P. J. Jewsbury, *Bioorg. Med. Chem. Lett.* **2003**, *13*, 3021–3026; b) A. Gueiffier, S. Mavel, M. Lhassani, A. Elhakmaoui, R. Snoeck, G. Andrei, O. Chavignon, I. C. Teulade, M. Witvrouw, J. Balzarini, E. De Clercq, J. P. Chapat, *J. Med. Chem.* **1998**, *41*, 5108–5112; c) G. Trapani, A. Latrofa, M. Franco, A. Carrieri, S. Cellamare, M. Serra, E. Sanna, G. Biggio, G. Liso, *Eur. J. Pharm. Sci.* **2003**, *18*, 231–240; d) L. Almirante, L. Polo, A. Mugnaini, E. Provinciali, P. Rugarli, A. Biancotti, A. Gamba, W. Murmann, *J. Med. Chem.* **1965**, *8*, 305–312; e) S. Z. Langer, S. Arbilla, J. Benavides, B. Scatton, *Adv. Biochem. Psychopharmacol.* **1990**, *46*, 61–72.

[16] a) M. E. Baumann, H. Bosshard, W. Breitenstein, G. Rihs, T. Winkler, *Helv. Chim. Acta* **1984**, *67*, 1897–1905; b) J. C. Teulade, G. Grassy, R. Escale, J.-P. Chapat, *J. Org. Chem.* **1981**, *46*, 1026–1030.

[17] Y. Zou, W. L. Liu, S. Gao, J. L. Xie, Q. J. Meng, *Chem. Commun.* **2003**, 2946–2947.

[18] a) O. R. Evans, W. B. Lin, *Chem. Mater.* **2001**, *13*, 3009–3017; b) A. Q. Wu, Y. Li, F. K. Zheng, G. C. Guo, J. S. Huang, *Cryst. Growth Des.* **2006**, *6*, 444–450.

[19] a) S. T. Wang, Y. Hou, E. B. Wang, Y. G. Li, L. Xu, J. Peng, S. X. Liu, C. W. Hu, *New J. Chem.* **2003**, *27*, 1144–1147; b) X. D. Chen, M. Du, T. C. W. Mak, *Chem. Commun.* **2005**, 4417–4419.

[20] a) M. P. Clares, J. Aguilar, R. Aucejo, C. Lodeiro, M. T. Albelda, F. Pina, J. C. Lima, A. J. Parola, J. Pina, S. de Melo, C. Soriano, E. García-España, *Inorg. Chem.* **2004**, *43*, 6114–6122; b) F. Bolletta, I. Costa, L. Fabbrizzi, M. Licchelli, M. Montalti, P. Pallavicini, L. Prodi, N. Zaccheroni, *J. Chem. Soc., Dalton Trans.* **1999**, 1381–1385; c) S. A. Zabin, C. R. Jejurkar, *J. Polym. Mater.* **1997**, *14*, 239–243.

[21] a) S. L. Zheng, J. H. Yang, X. L. Yu, X. M. Chen, W. T. Wong, *Inorg. Chem.* **2004**, *43*, 830–838; b) L. Y. Zhang, J. P. Zhang, Y. Y. Lin, X. M. Chen, *Cryst. Growth Des.* **2006**, *6*, 1684–1689.

[22] a) L. Y. Zhang, G. F. Liu, S. L. Zheng, B. H. Ye, X. M. Zhang, X. M. Chen, *Eur. J. Inorg. Chem.* **2003**, 2965–2971; b) Q. R. Fang, G. S. Zhu, M. Xue, J. Y. Sun, F. X. Sun, S. L. Qiu, *Inorg. Chem.* **2006**, *45*, 3582–3587.

[23] J. C. Dai, X. T. Wu, Z. Y. Fu, S. M. Hu, W. X. Du, C. P. Cui, L. M. Wu, H. H. Zhang, R. Q. Sun, *Chem. Commun.* **2002**, 12–13.

[24] Bruker, *SMART, SAINT and SADABS*, Bruker AXS Inc., Madison, Wisconsin, USA, **2002**.

[25] G. M. Sheldrick, *SHELXTL-97*, *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

Received: August 1, 2006