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A Series of Cadmium(II) Coordination Polymers Synthesized at different pH Values

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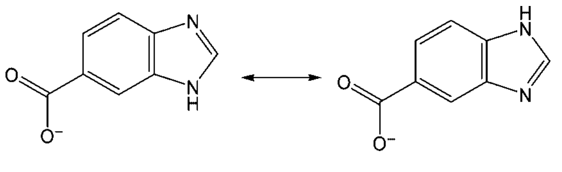
A new family of cadmium(II) coordination polymers, $\{[Cd(Hbic)_2{\cdot}(H_2O)_2]{\cdot}2H_2O\}_n$ (**1**), $[Cd(Hbic)_2]_n$ (**2**), $[Cd(Hbic)_2{\cdot}(H_2O)]_n$ (**3**), H_2bic = 1H-benzimidazole-5-carboxylic acid, has been hydrothermally prepared by the assembly of Cd^{II} with H_2bic. A change in the pH values resulted in a series of compounds with different compositions and dimensionalities. Formed at the lowest pH, compound **1** has a two-dimensional supramolecular structure, which contains 1D chains extended by hydrogen bonds. At a slightly higher pH, compound **2** is synthesized with a higher number of deprotonated carboxylate groups per cadmium atom. A further increase in the pH leads to 3D dinuclear compound **3** with yellow-green emitting fluorescence.

Introduction

The rational design and synthesis of metal–organic frameworks (MOFs) has undergone tremendous development owing to their structural and functional motifs,[1] which include magnetism,[2] catalysis,[3] luminescence,[4] and gas sorption.[5] The utilization of organic aromatic moieties containing carboxylic and nitrogen donor groups, for example imidazolecarboxylate or pyridylcarboxylate groups, can result in many intriguing polymers.[6] To obtain designed and predictable frameworks with potential properties, the observation of coordination polymers constructed from organic ligands and metal ions through a self-assembly route has been explored intensively, but it is still a challenge to date. The aromatic organic ligands with carboxy groups and nitrogen donors, on one hand, have been extensively employed in the construction of inorganic/organic hybrid materials for thermal stability and, on the other hand, can result in structures with high dimensions because of the multifunctional coordination sites.[7] The structure chemistry of functional groups such as carboxylates and nitrogen-donor groups are sensitive to pH values and the protonation states of these ligands. The formation of novel coordination compounds markedly depends on the metal ions.[8]

In order to have a better understanding of the effects of the pH value on the aromatic nitrogen-donor ligands, the reaction system of H_2bic (H_2bic = 1H-benzimidazole-5-carboxylic acid) and $Cd(NO_3)_2{\cdot}4H_2O$ was studied. As a hybrid ligand, $Hbic^-$ possesses two kinds of resonance structures (Scheme 1). The conformation of polymorphism is worthy to explore.[9] Furthermore, there are four potentially coordinating sites: two oxygen atoms of the carboxylate group and two nitrogen atoms of the imidazole ring. Two protons, one from the carboxylate and the other from the nitrogen donor, should play an important role in the process of assembly. Consequently, H_2bic is a good candidate for the investigation of the relation between the pH value and the coordination geometry. The diverse geometries of different metal ions may play critical roles in the assembly of metal–organic frameworks with various structures. The choice of metal ions in the systems is very important.[10] In the present work, we have selected cadmium(II) as metal nodes because of the luminescent characteristics. Other factors of the system such as the temperature, the amount of distilled water, and the type of stainless steel reactor are kept critically constant. Herein, we report the syntheses and characterizations of a new family of cadmium(II) coordination polymers: compounds $\{[Cd(Hbic)_2{\cdot}(H_2O)_2]{\cdot}2H_2O\}_n$ (**1**), $[Cd(Hbic)_2]_n$ (**2**), and $[Cd(Hbic)_2{\cdot}(H_2O)]_n$ (**3**), built from the aromatic nitrogen-donor ligands H_2bic and $Cd(NO_3)_2{\cdot}4H_2O$. The three compounds have been characterized by IR



Scheme 1. Resonance structures of $Hbic^-$ ligand.

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spectra, elemental analysis, thermogravimetric analysis, and fluorescent spectroscopy, as well as single-crystal X-ray diffraction analysis.[11–12] Discussion of the subtleties is addressed below.

Results and Discussions

Syntheses

Our aim is to investigate the effects of the pH value on the coordination behavior of aromatic nitrogen-donor ligands and the structures of the compounds thus formed. H_2bic and $Cd(NO_3)_2\cdot 4H_2O$ were selected as starting materials in our study. We first carried out the reaction at a pH value of 5.0, compound **1** with a 2D supramolecular assembly was obtained, in which the carboxylic proton was deprotonated and Hbic$^-$ adopted a single coordination mode (Figure S1, a). We raised the pH value to 6.5 and compound **2** with a 4^4 rhombus network structure was obtained, in which Hbic$^-$ adopted two different coordination modes (Figure S1, b and c). If the pH value was raised to 7.2, compound **3** with a 3D architecture was isolated, in which Hbic$^-$ also adopted two different coordination modes (Figure S1, d and e). The results illustrate that the pH value plays a crucial role on the coordination mode of Hbic$^-$ and the structures of the products. To confirm this, the reaction was carried out at a pH value between 5.0 and 6.5, a mixture of compounds **1** and **2** was obtained. If the reaction was carried out at a pH value between 6.5 and 7.2, a mixture of **2** and **3** was obtained. However, our efforts to obtain a compound constructed from bic^{2-}, in which both nitrogen atoms of H_2bic were deprotonated, at high pH values was unsuccessful. Among the three compounds, only compound **1** has coordinated water molecules which formed at the lowest pH value. The higher the pH value, the more difficult it is for water molecules to coordinate to the metal ions.

Structural Descriptions

$\{[Cd(Hbic)_2\cdot(H_2O)_2]\cdot 2H_2O\}_n$ (1)

Structure determination shows that compound **1** crystallizes in the monoclinic space group C_2/c and has a 1D chain architecture with guest water molecules. The coordination environment of the metal ion and the coordination mode of Hbic$^-$ are shown in Figure 1 and Figure S1, respectively. The Cd^{II} ion is coordinated by two nitrogen atoms, two water molecules and two *syn* carboxylate oxygen atoms in a distorted octahedral environment. The bond lengths of Cd–N1, Cd–OW1, and Cd–O2B are 2.280(3), 2.325(4), and 2.338(3) Å, respectively, which are the typical distances of Cd–N and Cd–O bonds. Linked by two Hbic$^-$ ligands, these metal nodes are extended into 1D chains along the [010] direction (Figure 2, a). In addition, each guest water is hydrogen bonded to one coordinated water molecule [OW2–OW1A distance: 2.702 Å; symmetry code: A: $x + 1/2, -y + 1/2, z - 1/2$] and two monodentate carboxylate oxygen atoms: one from the same polymeric chain with the coordinated water molecule [OW2–O2 distance 2.751 Å; symmetry code: B: $-x + 1/2, y + 1/2, -z - 1/2$] and the other from a neighboring polymeric chain [OW2–O1 distance: 2.795 Å] (Figure 2, b). The hydrogen bonds lead the 1D

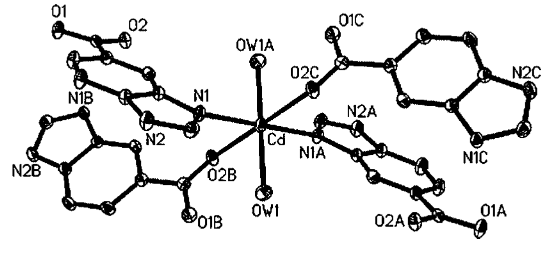


Figure 1. The coordination environment around Cd^{II} in compound **1** with the thermal ellipsoids drawn at the 30% probability level. The guest water molecules are omitted for clarity. Symmetry codes: A: $-x, -y, -z$; B: $-x, y, -z-1/2$.

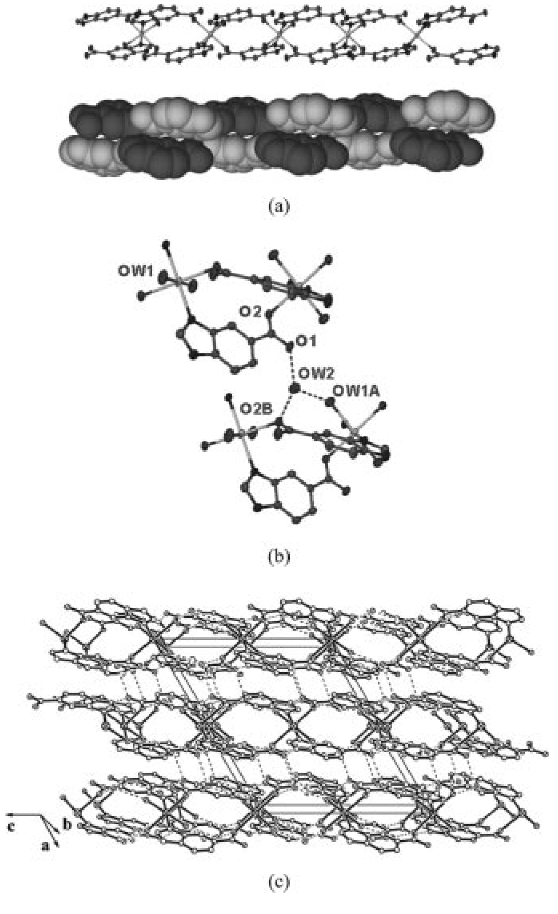


Figure 2. The 1D polymeric chain architecture in compound **1** (a). View of the supramolecular assembly along the [010] direction in compound **1** (b), the guest water molecules are omitted for clarity. Details of H-bond (dotted lines) for compounds **1** (c), hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 50% probability level. Symmetry codes: A: $x + 1/2, -y + 1/2, z - 1/2$; B: $-x + 1/2, y + 1/2, -z - 1/2$.

chains to a supramolecular architecture (Figure 2, c).[13] Ping Liu and coworkers have synthesized a Co compound that is isostructural to compound **1**.[14]

[Cd(Hbic)$_2$]$_n$ (2)

Single-crystal X-ray diffraction analysis reveals that compound **2** crystallizes in the orthorhombic space group *Pbcn* and is composed of a 2D coordination network. The asymmetric unit of compound **2** is shown in Figure 3, which contains one Cd^{II} and two Hbic$^-$ ligands showing two different coordination modes (Figure S1). Similar to compound **1**, the central Cd^{II} ions in **2** are six-coordinate in a distorted octahedral coordination geometry. The equatorial plane is defined by one nitrogen atom, a chelating carboxylate group, and one oxygen atom from another chelating carboxylate group. One nitrogen atom and one oxygen atom from the chelating carboxylate group occupy the axial positions of the octahedron with an O2–Cd–N1B bond angle of 146.96(10)°. The bond lengths of Cd–O1, Cd–O2, and Cd–N3 are 2.330(3), 2.335(3), and 2.278(3) Å, respectively, which are all within the normal ranges. The ligands link adjacent Cd^{II} nodes into the formation of a 4^4 rhombus network, which is different from other square-grid frameworks (Figure 4, a).[15] Furthermore, the distance between benzene rings is 3.585 Å, which indicates that there are weak face-to-face π–π stacking interactions between the neighboring layers (Figure 4, b and c).[16] We have reported a weak antiferromagnetic coordination polymer synthesized from $Ni(NO_3)_2 \cdot 6H_2O$ and H$_2$bic,[17] which is an allomer of **2**.

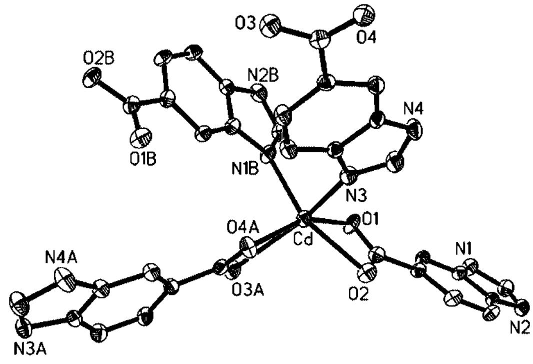


Figure 3. Perspective view of the asymmetric unit of compound **2** (30% probability ellipsoids). Symmetry codes: A: x, $-y$, $z-1/2$; B: $-x+3/2$, $y-1/2$, z.

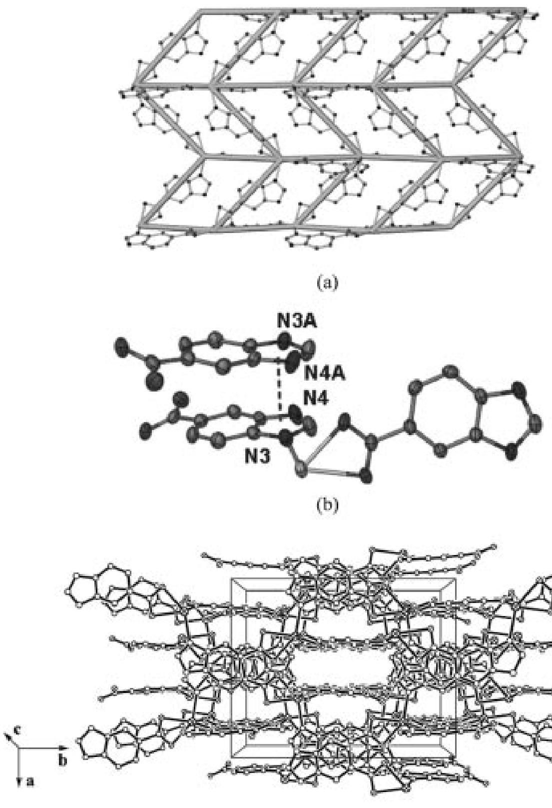


Figure 4. The 4^4 rhombus network (a) along the [100] direction. Details of π–π stacking interactions (dotted lines) for compound **2** (b), hydrogen atoms are omitted for clarity, and the thermal ellipsoids are drawn at the 50% probability level. Symmetry code: A: $2-x$, y, $1/2-z$. Packing of the 2D framework of compound **2** (c) along the [001] direction.

[Cd(Hbic)$_2$·(H$_2$O)]$_n$ (3)

The framework of compound **3** crystallizes in the monoclinic space group *P21/c* and has a 3D architecture with guest water molecules. The structure is built up of dinuclear units in which the cadmium atoms are joined by two oxygen atoms from the chelating/bridging carboxylate groups (Figure 5). Each cadmium atom is six-coordinate through two nitrogen atoms of Hbic$^-$ at apical positions and four oxygen atoms in the equatorial basal plane: one from monodentate carboxylate group and three from two chelating/bridging carboxylate groups (Cd–N, Cd–O). The coordination geometries for Hbic$^-$ are shown in Figure S1 and act as bridging and chelating/bridging ligands, respectively. With a head-to-head aggregation, four Hbic$^-$ ligands link Cd^{II} centers into a [Cd(Hbic$^-$)]$_4$ ring, in which four metal ions and four ligands are approximately coplanar. On the basis of Cd^{II} distances, the ring is 7.922 × 10.259 Å^2. In addition, every couple of neighboring Cd^{II} ions is involved in another kind of building unit which consists of two metal joints and two oxygen atoms from chelating/bridging carboxylate groups. Two types of rings form the butterfly framework (Figure 6, a). Interestingly, each [Cd(Hbic$^-$)]$_4$ is surrounded by four other perpendicular [Cd(Hbic$^-$)]$_4$ rings through sharing Cd^{II} joints, which may be due to the proper geometry of the metal ion. The 3D network can be classified as a 4^{28} topological-type based on eight connected nodes. As hydrogen bonding donors, the water molecules are involved in interactions with the nitrogen atoms and chelating carboxylate oxygen atoms to stabilize the framework furthermore [OW–N1, 2.825 Å; OW–O2A, 3.009 Å; symmetry code: A: $-x+1$, $-y+2$, $-z-1$].[13] Finally, the weak face-to-face π–π stacking interactions between adjacent Hbic$^-$ ligands (distance, 3.600 Å) stabilize the whole framework further (Figure 6, b and c).[16]

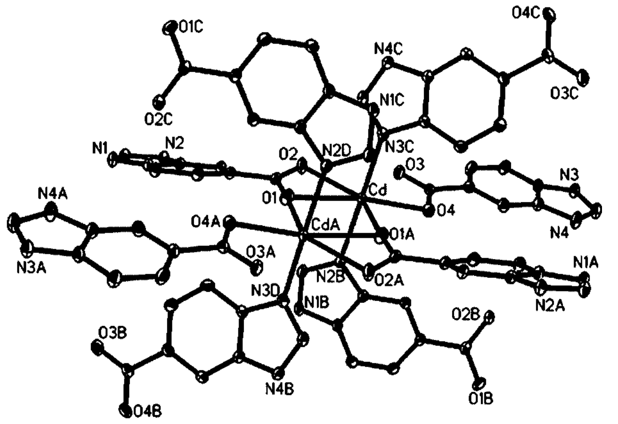
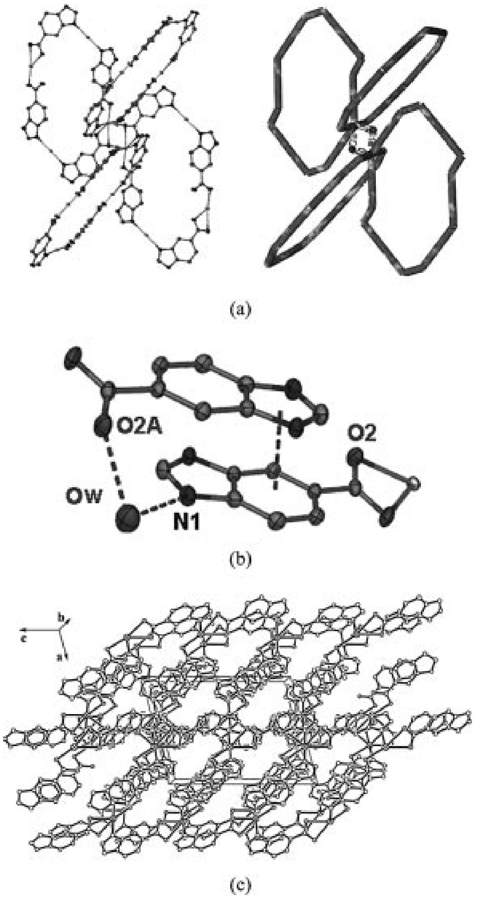


Figure 5. The coordination environment around Cd^{II} in compound **3** with the thermal ellipsoids drawn at the 30% probability level. The guest water molecules are omitted for clarity. Symmetry codes: A: $-x+2$, $y+1/2$, $-z+1/2$; B: x, $-y+3/2$, $z+1/2$.


(a)

(b)

(c)

Figure 6. View of the butterfly framework generated from four $[Cd(Hbic^{-})]_4$ rings (a). Details of H-bond and π–π stacking interactions (dotted lines) for compound **3** (b), hydrogen atoms are omitted for clarity, and the thermal ellipsoids are drawn at the 50% probability level. Symmetry code: A: $-x+1$, $-y+2$, $-z-1$. Packing of the 3D framework of compound **3** along the [010] direction (c), the guest water molecules are omitted for clarity.

Characterization of Vibrational Spectra

In the IR spectrum of compound **1**, a strong and broad peak at 3467 cm^{-1} indicates the presence of water molecules. The antisymmetric and symmetric stretching vibrations of carboxylate group at 1530 cm^{-1} and 1384 cm^{-1}, respectively, show that all $Hbic^{-}$ ligands adopt a monodentate coordination mode that is consist with the crystal structure. The IR spectrum of compound **2** shows typical chelating carboxylate antisymmetric and symmetric stretching bands at 1530 cm^{-1} and 1417 cm^{-1}, respectively. The IR spectrum of compound **3** shows a broad peak at 3451 cm^{-1} that also testifies to the existence of guest water molecules. The antisymmetric and symmetric stretching vibrations at 1532 cm^{-1} and 1418 cm^{-1}, and at 1383 cm^{-1}, respectively, show that the carboxylate groups employ the chelating and monodentate coordination geometry.[18]

Thermogravimetric Analysis

To access the thermal stability of the three compounds, thermogravimetric analyses were carried out with a NETZSCH STA 449C unit, at a heating rate of 10 °C/min under an air atmosphere. As shown in Figure S2, the TGA curve of compound **1** exhibits two significant weight losses. The first weight loss occurs between 81 °C and 185 °C, which can be attributed to the loss of guest water molecules. The observed weight loss of 6.79% is in good agreement with the calculated value (7.11%). From 304 °C to 631 °C, the weight loss of 65.74% suggests the decomposition of compound **1**. The residue weight (24.55%) is ascribed to CdO (calculated 25.34%). The TGA curve of compound **2** indicates only one weight loss stage. The weight loss of 70.2% covers a temperature range from 251 °C to 545 °C, which is possibly due to the collapse of compound **2**. The TGA curve of compound **3** indicates two obvious weight loss stages: 4.04% between 94 °C and 148 °C, and 66.02% between 296 °C and 647 °C. The former is in accordance with the loss of the guest water molecules (calculated 3.98%). The latter suggests the chemical decomposition of compound **3**. The residue weight (27.8%) is attributed to CdO (calculated 28.3%).

Fluorescent Properties

At room temperature, the luminescent spectra of compounds **1**–**3** and the H_2bic ligand in solid state are shown in Figure 7. The fluorescence spectrum of compound **1** is shown in Figure 7 and exhibits one emission maxima at 443 nm. The emission spectrum of compound **2**, shown in Figure 7 and redshifted relative to **1**, appears at 572 nm. Also shown in Figure 7, the emission spectrum of compound **3** is redshifted compared with those of compounds **1** and **2** to 576 nm. As previously reported, the emission of compound **1** may be attributed to σ-donation from the coordination environment of the Cd^{II} centers, and may be assigned to a ligand-to-metal charge-transfer (LMCT).[19] To ascertain the adscription of the emission spectra, the photoluminescence of pure H_2bic is measured with one emission maxima at 550 nm under the same conditions (Figure 7, ligand). We speculate that the maximum emissions bands of compounds **2** and **3** may be caused by the intraligand π–π* transition. Owing to the yellow-green emissions of compounds **2** and **3**, the remarkable feature demonstrates that they may be potential candidates for yellow-green emitting fluorescent materials.[20]

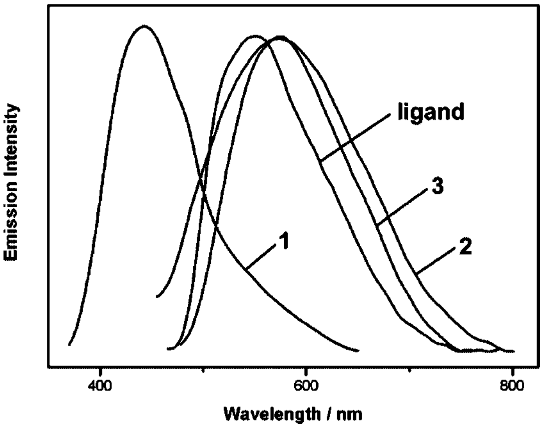


Figure 7. Solid-state emission spectra for compounds **1**–**3** and the H_2bic ligand at room temperature.

Conclusions

A new family of compounds, $\{[Cd(Hbic)_2\cdot(H_2O)_2]\cdot 2H_2O\}_n$ (**1**), $[Cd(Hbic)_2]_n$ (**2**), $[Cd(Hbic)_2\cdot(H_2O)]_n$ (**3**), has been synthesized hydrothermally and characterized during our investigation of the $Cd(NO_3)_2\cdot 4H_2O/H_2bic/NaOH$ reaction system. The pH values played an important role in the formation of these compounds. At 165 °C, the reaction at a pH value of 5.0 led to the formation of compound **1** with a 2D supramolecular assembly consisting of one-dimensional chains and hydrogen bonded water molecules. When the pH value was raised to 6.5, the reaction gave rise to the formation of compound **2** with a 4^4 rhombus network structure. Further increase in the pH to a value of 7.2 led to the formation of compound **3** with a 3D architecture based on dinuclear cadmium units. With yellow-green emissions, compounds **2** and **3** may be good candidates for fluorescent materials.

Experimental Section

Materials and General Methods: H_2bic = 1H-benzimidazole-5-carboxylic acid was purchased from Acros and used without further purification; all other reagents are commercially available and used as purchased. IR spectra as KBr pellets were recorded with a Magna 750 FTIR spectrophotometer. Elemental analysis of C, H, and N were determined by using a Perkin–Elmer 240C elemental analyzer. Fluorescence spectroscopy was performed with an Edinburgh Analytical instrument FLS920.

Synthesis: A mixture of $Cd(NO_3)_2\cdot 4H_2O$ (0.25 mmol, 77.1 mg), H_2bic (0.25 mmol, 40.5 mg), NaOH (0–0.37 mmol, 0–14.8 mg), and distilled water (12 mL) was sealed in a 18 mL stainless steel vessel with a Teflon liner and heated at 165 °C for 72 h. After cooling at a rate of 3 °C/h to 25 °C, the crystals were obtained and washed with water and ethanol. Optimized syntheses of compounds **1**, **2**, and **3** are given below.

Synthesis of $\{[Cd(Hbic)_2\cdot(H_2O)_2]\cdot 2H_2O\}_n$ (1): A mixture of $Cd(NO_3)_2\cdot 4H_2O$ (0.25 mmol, 77.1 mg), H_2bic (0.25 mmol, 40.5 mg), and H_2O (12 mL) was placed in a Teflon-lined stainless steel vessel then heated at 165 °C for 72 h. After cooling the reac-

Table 1. Crystal data and structure determination summary for **1**, **2**, and **3**.

	1	2	3
Formula	$C_{16}H_{18}CdN_4O_8$	$C_{16}H_{10}CdN_4O_4$	$C_{16}H_{12}CdN_4O_5$
Fw	506.74	434.68	452.70
Crystal size [mm]	0.15 × 0.10 × 0.05	0.15 × 0.10 × 0.05	0.50 × 0.33 × 0.25
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	*C2/c*	*Pbcn*	*P21/c*
a [Å]	16.338(4)	12.542(4)	10.834(3)
b [Å]	9.157(1)	15.743(5)	10.743(3)
c [Å]	14.328(3)	15.190(5)	14.456(4)
β [°]	120.079(5)		104.343(3)
V [Å^3]	1854.9(6)	2999(2)	1630.1(7)
Z	8	8	4
$D_{calcd.}$ [g cm^{-3}]	1.815	1.925	1.845
μ [mm^{-1}]	1.232	1.488	1.377
$F(000)$	1016	1712	896
T [K]	173(2)	173(2)	173(2)
λ(Mo-K_a) [Å]	0.71073	0.71073	0.71073
Reflections collected	6907	21949	12063
Unique reflections	2119	3440	3725
R_{int}	0.0468	0.0470	0.0136
Parameters	133	228	235
S on F^2	1.118	1.213	1.100
R_1 [$I > 2\sigma(I)$][a]	0.0511	0.0481	0.0219
wR_2 [$I > 2\sigma(I)$][b]	0.0816	0.0786	0.0544
R_1 (all data)	0.0758	0.0628	0.0234
wR_2 (all data)[b]	0.0913	0.0831	0.0554
$\Delta\rho_{min}$ and $\Delta\rho_{max}$ [e Å^3]	0.479 and –0.487	0.610 and –0.385	0.999 and –0.437

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

tion system to 25 °C over 48 h, yellow prism crystals of **1** were obtained and washed with water and ethanol. The final pH value of the reaction medium was 5.0. Yield: 15.8 mg, 25% (based on Cd). IR (KBr): 3467 (bs), 1625 (s), 1530 (m), 1458 (s), 1384 (m), 1283 (w), 848 (w), 782 (w), 730 (w), 697 (w) cm^{-1}. $C_8H_9Cd_{0.5}N_2O_4$ (253.37): calcd. C 37.92, H 3.58, N 11.05; found C 37.87, H 3.61, N 11.00.

Synthesis of [Cd(Hbic)$_2$]$_n$ (2): A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.25 mmol, 77.1 mg), H_2bic (0.25 mmol, 40.5 mg), H_2O (12 mL), and NaOH (0.27 mmol, 10.8 mg) was placed in a Teflon-lined stainless steel vessel then heated at 165 °C for 72 h. After cooling the reaction system to 25 °C over 48 h, light yellow block crystals of **2** were obtained and washed with water and acetone. The final pH value of the reaction medium was 6.5. Yield: 44.5 mg, 41% (based on Cd). IR (KBr): 3451 (bs), 1626 (s), 1530 (s), 1417 (m), 1382 (s), 967 (w), 777 (m), 671 (w), 539 (w) cm^{-1}. $C_{16}H_{10}CdN_4O_4$ (434.67): calcd. C 44.21, H 2.31, N 12.89; found C 44.16, H 2.48, N 12.81.

Synthesis of [Cd(Hbic)$_2$·(H$_2$O)]$_n$ (3): A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.25 mmol, 77.1 mg), H_2bic (0.25 mmol, 40.5 mg), H_2O (12 mL), and NaOH (0.37 mmol, 14.8 mg) was placed in a Teflon-lined stainless steel vessel then heated at 165 °C for 72 h. After cooling at a rate of 3 °C/h to room temperature, yellow prism crystals of **3** were obtained. The final pH value of the reaction medium was 7.2. The resulting product was recovered by filtration, washed with ethanol, and dried in air. Yield: 39.6 mg, 35% (based on Cd). IR (KBr): 3451 (bs), 1626 (s), 1532 (s), 1418 (m), 1383 (s), 936 (w), 776 (s), 623 (s), 539 (w) cm^{-1}. $C_{16}H_{12}CdN_4O_5$ (452.68): calcd. C 42.45, H 2.67, N 12.38; found C 42.39, H 2.72, N 12.29.

Table 2. Selected bond lengths [Å] and angles [°] for **1**–**3**.[a]

Compound **1**			
Cd–N1	2.280(3)	Cd–OW1	2.325(4)
Cd–O2B	2.338(3)		
N1A–Cd–N1	180.0(2)	N1A–Cd–O2B	95.1(1)
N1–Cd–O2B	84.9(1)	OW1–Cd–O2B	86.4(1)
N1–Cd–OW1A	97.6(1)	O2B–Cd–O2C	180.0(2)
N1–Cd–OW1	82.4(1)	OW1–Cd–O2C	93.6(1)
OW1A–Cd–OW1	180.0(2)		
Compound **2**			
Cd–O4A	2.239(3)	Cd–O1	2.330(3)
Cd–N1B	2.269(4)	Cd–O2	2.335(3)
Cd–N3	2.278(3)	Cd–O3A	2.561(3)
O4A–Cd–N1B	102.5(1)	N3–Cd–O2	89.6(1)
O4A–Cd–N3	94.8(1)	O1–Cd–O2	55.8(1)
N1B–Cd–N3	94.7(1)	O4A–Cd–O3A	54.2(1)
O4A–Cd–O1	154.5(1)	N1B–Cd–O3A	91.0(1)
N1B–Cd–O1	91.7(1)	N3–Cd–O3A	148.9(1)
N3–Cd–O1	105.3(1)	O1–Cd–O3A	105.1(1)
O4A–Cd–O2	109.9(1)	O2–Cd–O3A	102.0(1)
N1B–Cd–O2	147.0(1)		
Compound **3**			
Cd–O4	2.279(1)	Cd–O2	2.349(2)
Cd–N3A	2.299(2)	Cd–O1C	2.387(1)
Cd–N2B	2.298(2)	Cd–O1	2.576(2)
O4–Cd–N3A	88.9(1)	N2BCd–O1C	86.1(1)
O4–Cd–N2B	92.6(1)	O2–Cd–O1C	135.3(1)
N3A–Cd–N2B	176.9(1)	O4–Cd–O1	167.4(1)
O4–Cd–O2	139.5(1)	N3A–Cd–O1	94.8(1)
N3A–Cd–O2	88.7(1)	N2B–Cd–O1	83.2(1)
N2B–Cd–O2	92.0(1)	O2–Cd–O1	52.7(1)
O4–Cd–O1C	85.2(1)	O1C–Cd–O1	82.8(1)
N3A–Cd–O1C	91.3(1)		

[a] Symmetry codes: **1**: A: –*x*, –*y*, –*z*; B: –*x*, *y*, –*z* – 1/2; C: *x*, –*y*, *z* + 1/2. **2**: A: *x*, –*y*, *z* – 1/2; B: –*x* + 3/2, *y* – 1/2, *z*. **3**: A: –*x* + 2, *y* + 1/2, –*z* + 1/2; B: *x*, –*y* + 3/2, *z* + 1/2; C: –*x* + 1, –*y* + 2, –*z*.

X-ray Crystallographic Studies: Measurements of compounds **1**, **2**, and **3** were collected with a Rigaku CCD. The absorption corrections were performed with the procedure contained within the CrystalClear software package.[11] The structures were solved by direct methods with the SHELXL-97 program package.[12] All data were refined by full-matrix least-squares minimizations of $\sum(F_o - F_c)^2$ with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were generated geometrically (C–H 0.95 Å). The crystallographic data and structure determination summaries for compounds **1**, **2**, and **3** are listed in Table 1. Selected bond lengths and angles for the three compounds are listed in Table 2. CCDC-609811, CCDC-609812, and CCDC-609813 for compounds **1**, **2**, and **3**, 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): The coordination modes of Hbic$^-$ and TGA curves for compounds **1**–**3**.

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