



# Three distinct cadmium coordination polymers with a multidentate tripyridyl-substituted triazole tecton regulated by halide anions



Jing Chen, Na Wu, Cheng-Peng Li\*

College of Chemistry, Tianjin Key Laboratory of Structure and Performance for Functional Molecules, MOE Key Laboratory of Inorganic–Organic Hybrid Functional Material Chemistry, Tianjin Normal University, Tianjin 300387, PR China

## HIGHLIGHTS

- Three diverse 1D coordination polymers are constructed from a versatile tripyridyltriazole ligand and Cd(II) halides.
- Different binding features of halide ions are observed to direct the structural assemblies.
- Solid state fluorescent emissions of the complexes can also be regulated.

## ARTICLE INFO

### Article history:

Received 9 July 2013

Received in revised form 13 August 2013

Accepted 13 August 2013

Available online 20 August 2013

### Keywords:

Halide effect

Controlled coordination assemblies

Tripyridyltriazole ligand

Structural diversity

Fluorescence

## ABSTRACT

Three distinct Cd(II) coordination polymers  $[\text{Cd}_3(\text{L}^{434})_2\text{Cl}_6]_n$  (**1**),  $[\text{Cd}(\text{L}^{434})_2\text{Br}_2]_n$  (**2**), and  $[\text{Cd}_2(\text{L}^{434})_2\text{I}_4(\text{H}_2\text{O})_2]_n$  (**3**) have been designed and synthesized with a versatile building block 3,5-bis(4-pyridyl)-4-(3-pyridyl)-1,2,4-triazole ( $\text{L}^{434}$ ) by altering the Cd(II) halides of reaction systems. Single crystal X-ray diffraction reveals that **1–3** display different zigzag, box-like, and ladder-like 1D polymeric motifs, respectively. Moreover, aromatic stacking interactions are observed in all these structures to extend and/or stabilize the supramolecular lattices. Their thermal stabilities and fluorescent properties have also been explored. Significantly, the regular variation in structural patterns and photoluminescence properties of **1–3** can be properly ascribed to the diversification of halide anions.

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## 1. Introduction

Crystal engineering is of great significance since it can provide a rational strategy for creating multifarious crystalline materials, rearranged by the building blocks with appropriate structure-directing groups for intermolecular contacts, such as the most familiar coordination and H-bonding interactions [1,2]. Coordination polymers, as an essential topic of crystal engineering, evoke increased interests in view of their fascinating structural features and promising applications as new crystalline materials [3–6]. In general, the sophisticated strategy for constructing coordination polymers is largely dependent on the design of organic or inorganic building units with desired connected features. The organic tectons with suited functional groups and molecular skeletons have been demonstrated to be most critical to fine-tune the coordination motifs. On the other hand, elaborate selection of reaction parameters such as pH conditions [7], solvents [8], anions [9], and additives [10], may also well regulate the final products.

In this context, we select herein a novel tripyridyl-substituted 1,2,4-triazole building block 3,5-bis(4-pyridyl)-4-(3-pyridyl)-1,2,4-triazole ( $\text{L}^{434}$ ), with adaptable conformations and binding fashions as well as potential capability for participating in secondary aromatic stacking interactions, to assemble with different  $\text{CdX}_2$  salts ( $X = \text{Cl}, \text{Br}, \text{and I}$ ). As a result, three different 1D coordination polymers, namely  $[\text{Cd}_3(\text{L}^{434})_2\text{Cl}_6]_n$  (**1**),  $[\text{Cd}(\text{L}^{434})_2\text{Br}_2]_n$  (**2**), and  $[\text{Cd}_2(\text{L}^{434})_2\text{I}_4(\text{H}_2\text{O})_2]_n$  (**3**) can be obtained, which demonstrate the significant influence of halide anions on their structural assemblies. In addition, thermal stability and solid-state fluorescent emissions of these polymeric complexes have also been explored.

## 2. Experimental

### 2.1. Materials and general methods

All analytical grade chemicals and solvents were purchased and used as received. The ligand  $\text{L}^{434}$  was synthesized according to a comparable literature procedure [11]. Fourier transform (FT) IR spectra (KBr pellets) were recorded on an AVATAR-370 (Nicolet) spectrometer. Elemental analyses of C, H, and N were taken on a

\* Corresponding author. Tel.: +86 2223766556.

E-mail address: [tjnulicp@gmail.com](mailto:tjnulicp@gmail.com) (C.-P. Li).

**Table 1**  
Crystallographic data for **1–3**.

Compound reference	<b>1</b>	<b>2</b>	<b>3</b>
Chemical formula	C <sub>34</sub> H <sub>24</sub> Cd <sub>3</sub> Cl <sub>6</sub> N <sub>12</sub>	C <sub>34</sub> H <sub>24</sub> Br <sub>2</sub> CdN <sub>12</sub>	C <sub>34</sub> H <sub>28</sub> Cd <sub>2</sub> I <sub>4</sub> N <sub>12</sub> O <sub>2</sub>
Formula mass	1150.58	872.87	1369.08
Crystal system	Triclinic	Triclinic	Monoclinic
Crystal size (mm)	0.28 × 0.22 × 0.20	0.14 × 0.13 × 0.11	0.28 × 0.22 × 0.20
<i>a</i> (Å)	8.479(6)	8.2982(9)	18.816(4)
<i>b</i> (Å)	10.886(7)	8.5691(9)	11.581(2)
<i>c</i> (Å)	11.768(8)	13.100(2)	19.253(4)
$\alpha$ (°)	69.618(10)	99.701(2)	90.00
$\beta$ (°)	81.802(11)	97.348(2)	94.168(4)
$\gamma$ (°)	80.239(12)	113.7130(10)	90.00
Unit cell volume (Å <sup>3</sup> )	999.4(12)	820.68(18)	4183.9(14)
Temperature (K)	296(2)	173(2)	296(2)
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>Z</i>	1	1	4
<i>D</i> <sub>calc</sub> (Mg m <sup>-3</sup> )	1.912	1.766	2.173
$\mu$ (mm <sup>-1</sup> )	2.026	3.146	4.014
<i>F</i> (000)	558	430	2560
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.6008, 0.6874	0.6671, 0.7235	0.3994, 0.5007
Range of <i>h</i> , <i>k</i> , <i>l</i>	−8/10, −12/12, −13/13	−6/9, −10/10, −15/9	−21/22, −12/13, −15/22
$\theta$ range (°)	1.85–25.03	1.62–25.01	1.46–25.03
No. of reflections measured	4989	4163	20,889
No. of independent reflections	3463	2862	7383
<i>R</i> <sub>int</sub>	0.0498	0.0155	0.1062
Final <i>R</i> <sub>1</sub> values ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0977	0.0243	0.0736
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.2820	0.0640	0.1666
Final <i>R</i> <sub>1</sub> values (all data)	0.1135	0.0275	0.1753
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values (all data)	0.3023	0.0660	0.2109
Goodness of fit on <i>F</i> <sup>2</sup>	1.198	1.049	1.037
Largest diff. peak and hole (e Å <sup>-3</sup> )	3.187, −1.337	0.794, −0.646	1.889, −1.389

**Table 2**  
Selected bond distances (Å) and angles (°) for **1–3**.<sup>a</sup>

<b>1</b>			
Cd1–Cl1	2.969(3)	Cd1–N5A	2.159(15)
Cd1–Cl2	3.026(3)	Cd2–Cl1	2.587(3)
Cd2–N1	2.35(2)	Cd2–Cl3	2.469(3)
Cd2–Cl2	2.620(3)		
Cl1–Cd1–N5A	89.8(4)	Cl2–Cd1–N5A	90.5(4)
Cl1–Cd1–Cl2	85.7(7)	N1–Cd2–Cl3	106.0(5)
N1–Cd2–Cl1	101.6(5)	Cl3–Cd2–Cl1	123.13(8)
N1–Cd2–Cl2	94.1(5)	Cl3–Cd2–Cl2	122.87(9)
Cl1–Cd2–Cl2	103.12(8)		
<b>2</b>			
Cd1–N5A	2.436(2)	Cd1–N6	2.506(2)
Cd1–Br1	2.6727(3)		
N5A–Cd1–N6	82.79(7)	N5A–Cd1–Br1	91.27(5)
N6–Cd1–Br1	87.81(5)		
<b>3</b>			
Cd1–N5	2.369(11)	Cd1–N7	2.376(11)
Cd1–O1	2.439(11)	Cd1–I2	2.822(2)
Cd1–I1A	2.9813(18)	Cd1–I1	3.173(2)
Cd2–N1B	2.340(11)	Cd2–N11	2.371(12)
Cd2–O2	2.436(12)	Cd2–I4	2.749(2)
Cd2–I3	2.8417(17)		
N5–Cd1–N7	166.2(5)	N5–Cd1–O1	83.9(4)
N7–Cd1–O1	88.7(4)	N5–Cd1–I2	97.5(3)
N7–Cd1–I2	94.5(3)	O1–Cd1–I2	93.1(3)
N5–Cd1–I1A	90.6(3)	N7–Cd1–I1A	94.9(3)
O1–Cd1–I1A	170.0(3)	I2–Cd1–I1A	95.89(6)
N5–Cd1–I1	83.4(3)	N7–Cd1–I1	84.1(3)
O1–Cd1–I1	82.2(3)	I2–Cd1–I1	175.09(6)
I1A–Cd1–I1	88.92(5)	N1B–Cd2–N11	148.3(5)
N1B–Cd2–O2	82.3(4)	N11–Cd2–O2	78.1(4)
N1B–Cd2–I4	104.0(4)	N11–Cd2–I4	104.4(3)
O2–Cd2–I4	102.3(3)	N1B–Cd2–I3	96.1(3)
N11–Cd2–I3	86.5(3)	O2–Cd2–I3	145.4(3)
I4–Cd2–I3	111.54(6)		

<sup>a</sup> Symmetry codes for **1**: A:  $-x+1, -y+1, -z$ ; for **2**: A:  $x-1, y-1, z$ ; for **3**: A:  $-x+1, -y+2, -z+1$ ; B:  $x, y-2, z-1$ .

CE-440 (Leemanlabs) analyzer. Thermogravimetric analysis experiments were performed on a TGA Q500 thermal analyzer in 25–800 °C (heating rate: 10 °C/min) under N<sub>2</sub> atmosphere with an empty Al<sub>2</sub>O<sub>3</sub> crucible as the reference. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 Advance diffractometer at 40 kV and 100 mA for a Cu-target tube ( $\lambda = 1.5406$  Å). The calculated PXRD patterns were obtained from the single-crystal X-ray diffraction data by using PLATON (see Fig. S1).

## 2.2. Synthesis and characterization

Typical syntheses of **1–3**. The ligand **L**<sup>434</sup> (0.1 mmol) was dissolved in CH<sub>3</sub>OH (10 mL), to which an aqueous solution (5 mL) of CdX<sub>2</sub> (0.1 mmol) was added with stirring. After ca. 30 min, the solution was filtered and left to stand under room temperature. Upon slow evaporation of the solvents, colorless block crystals of complexes **1–3** were produced after ca. 10 days.

For **1**: 53% yield (20.2 mg, based on CdCl<sub>2</sub>). Anal. Calcd for C<sub>34</sub>H<sub>24</sub>Cd<sub>3</sub>N<sub>12</sub>Cl<sub>6</sub>: C, 35.49; H, 2.10; N, 14.61%. Found: C, 35.43; H, 2.13; N, 14.64%. IR (KBr, cm<sup>-1</sup>): 1610m, 1598m, 1477m, 1466m, 1438s, 1203w, 998w, 843w, 828w, 737w, 700m, 620m.

For **2**: 58% yield (25.3 mg, based on **L**<sup>434</sup>). Anal. Calcd for C<sub>34</sub>H<sub>24</sub>CdN<sub>12</sub>Br<sub>2</sub>: C, 46.78; H, 2.77; N, 19.26%. Found: C, 46.74; H, 2.78; N, 19.28%. IR (KBr, cm<sup>-1</sup>): 1604s, 1460s, 1437vs, 1221w, 1202w, 1129w, 1065w, 1002m, 841w, 821w, 795w, 700m, 622m.

For **3**: 42% yield (28.6 mg). Anal. Calcd for C<sub>34</sub>H<sub>28</sub>Cd<sub>2</sub>N<sub>12</sub>I<sub>4</sub>O<sub>2</sub>: C, 32.50; H, 2.25; N, 13.37%. Found: C, 32.45; H, 2.27; N, 13.41%. IR (KBr, cm<sup>-1</sup>): 3400b, 1653s, 1638s, 1617s, 1484w, 1466m, 1438w, 828w, 742w, 707w, 624m.

## 2.3. X-ray crystallography

Single crystal X-ray diffraction data for complexes **1–3** were collected on a Bruker APEX II CCD diffractometer equipped with a graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at room temperature. The structures were solved by direct methods

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