



# Controllable assemblies of Cd(II) supramolecular coordination complexes based on a versatile tripyridyltriazole ligand and halide/pseudoalide anions



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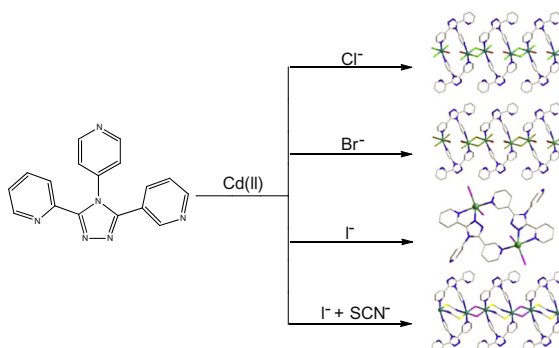
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## HIGHLIGHTS

- Four Cd(II) supramolecular complexes are constructed based on a tripyridyltriazole tecton.
- The coordination architectures can be well regulated by the halide/thiocyanate anions.
- Solid state fluorescent emissions are available at room temperature.

## GRAPHICAL ABSTRACT

Four interrelated coordination supramolecular complexes have been assembled from  $CdX_2$  ( $X = Cl^-$ ,  $Br^-$ ,  $I^-$  or  $I^-/SCN^-$ ) and 3-(2-pyridyl)-4-(4-pyridyl)-5-(3-pyridyl)-1,2,4-triazole, in which the anions and organic linker take diverse coordination modes. All these complexes show solid-state fluorescent emissions at room temperature.



## ARTICLE INFO

### Article history:

Received 20 March 2015  
Received in revised form 27 April 2015  
Accepted 28 April 2015  
Available online 6 May 2015

### Keywords:

Cd(II) complexes  
Controllable assemblies  
Crystal structures  
Halide and pseudoalide anions  
Tripyridyltriazole ligand

## ABSTRACT

Three Cd(II) complexes  $[Cd(L)(H_2O)Cl_2]_n$  (**1**),  $[Cd(L)(H_2O)Br_2]_n$  (**2**), and  $[Cd(L)_2]_2$  (**3**) have been assembled from  $CdX_2$  (**1**,  $X = Cl$ ; **2**,  $X = Br$ ; **3**,  $X = I$ ) and a tripyridyltriazole ligand 3-(2-pyridyl)-4-(4-pyridyl)-5-(3-pyridyl)-1,2,4-triazole (**L**). Complexes **1** and **2** are isostructural and exhibit 1-D loop-like chain, while complex **3** has a distinct dimeric macrocyclic motif. Interestingly, another 1-D chain  $[Cd(L)(SCN)]_n$  (**4**) can be achieved when  $NH_4SCN$  is introduced into the assembled system of **3**. Structural analysis of **1–4** illustrates that the halide and thiocyanate anions in these coordination complexes behave as not only the counteranions, but also the structure directing agents. The fluorescent and thermal properties of **1–4** have also been investigated.

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## Introduction

As a rising class of hybrid materials, metal–organic supramolecular complexes have attracted considerable attention during the past decade for their intriguing structures and potential applications [1–4]. The ingenious design and sophisticated

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selection of organic ligands are critical to produce the targeted structures with desired properties, via interlinking the suited metal ions or clusters. As a great sort of organic linkers, the derivatives of *N*-heterocyclic categories involving pyridyl [5], imidazolyl [6], and triazolyl [7] components, are of growing research interests and used to construct a great variety of coordination architectures. Recently, a novel type of tripyridyltriazole ligands have been developed, which possess multiple potential coordination sites and multifunctional possible conformations to be versatile in the construction of various coordination architectures [8].

On the other hand, anions may play a critical role in the structural direction of supramolecular complexes in the assembled processes [9], especially for those with metal halides and neutral ligands [10]. Herein, we synthesized four coordination complexes, [Cd(L)(H<sub>2</sub>O)Cl<sub>2</sub>]<sub>n</sub> (**1**), [Cd(L)(H<sub>2</sub>O)Br<sub>2</sub>]<sub>n</sub> (**2**), [Cd(L)I<sub>2</sub>]<sub>2</sub> (**3**) and [Cd(L)(SCN)]<sub>n</sub> (**4**) (L = 3-(2-pyridyl)-4-(4-pyridyl)-5-(3-pyridyl)-1,2,4-triazole), in which the ligand L or halide anions display different binding modes, influenced by the nature of halide anions for **1–3** and the synergistic effect of halide/thiocyanate anions for **4**. Their thermal stability and fluorescence are also explored.

## Experimental

### Material and methods

All analytical grade chemicals and solvents were obtained from commercial sources and used without further purification. The L ligand was obtained according to the literature method [11]. Fourier transform (FT) IR spectra (KBr pellets) were recorded on an AVATAR-370 (Nicolet) spectrometer in the range of 400–4000 cm<sup>-1</sup>. Elemental analyses of C, H, and N were performed on a CE-440 (Leemanlabs) analyzer. Powder X-ray diffraction (PXRD) data were obtained on a D8 Advance diffractometer at 40 kV and 30 mA for Cu-target tube ( $\lambda = 1.54056 \text{ \AA}$ ). The calculated PXRD patterns were obtained from the single-crystal diffraction data with PLATON [12] (see Fig. S1). Thermogravimetric analysis experiments were carried out on a TGA Q500 thermal analyzer in 25–800 °C at a heating rate of 10 °C/min under N<sub>2</sub> atmosphere with an empty Al<sub>2</sub>O<sub>3</sub> crucible as the reference. All fluorescence measurements in solid state were taken on a Cary Eclipse spectrofluorometer (Varian) at room temperature.

### Synthesis and characterization

Typical synthesis of **1–4**. The ligand L (15.0 mg, 0.05 mmol) was dissolved in CH<sub>3</sub>OH (5 mL), to which an aqueous solution of (5 mL) of CdCl<sub>2</sub>·2.5H<sub>2</sub>O (11.4 mg, 0.05 mmol), CdBr<sub>2</sub>·4H<sub>2</sub>O (17.2 mg, 0.05 mmol), CdI<sub>2</sub> (18.3 mg, 0.05 mmol) or CdI<sub>2</sub> (18.3 mg, 0.05 mmol)/NH<sub>4</sub>SCN (3.6 mg, 0.05 mol), respectively, for **1–4** was added with stirring. After ca. 20 min, the solution was filtered and left to stand under room temperature. Upon slow evaporation of the solvents, colorless block crystals of complexes **1–4** were produced over about one week.

For **1**: 52% yield (13.0 mg, based on L). Anal. Calcd for C<sub>17</sub>H<sub>14</sub>CdN<sub>6</sub>OCl<sub>2</sub>: C, 40.70; H, 2.81; N, 16.76%. Found: C, 40.81; H, 2.93; N, 16.65%. IR (KBr, cm<sup>-1</sup>): 3436b, 3057w, 1601s, 1599s, 1506s, 1477m, 1444vs, 1420s, 1346w, 1217w, 1196m, 1163w, 1048w, 1006m, 840s, 793m, 730w, 693m, 633m, 610s.

For **2**: 58% yield (17.1 mg, based on L). Anal. Calcd for C<sub>17</sub>H<sub>14</sub>CdN<sub>6</sub>OBr<sub>2</sub>: C, 34.57; H, 2.39; N, 14.23%. Found: C, 34.65; H, 2.50; N, 14.22%. IR (KBr, cm<sup>-1</sup>): 3437b, 3055w, 1600s, 1571m, 1507s, 1477m, 1443s, 1420m, 1335w, 1216w, 1196w, 1101w, 1047w, 1006m, 839m, 793m, 730m, 693m, 611s.

For **3**: 76% yield (25.3 mg, based on L). Anal. Calcd for C<sub>17</sub>H<sub>12</sub>CdN<sub>6</sub>I<sub>2</sub>: C, 30.63; H, 1.81; N, 12.61%. Found: C, 30.82; H, 1.91; N, 12.50%. IR (KBr, cm<sup>-1</sup>): 1597s, 1580s, 1497s, 1473s, 1457vs, 1404s, 1283m, 1201m, 1131w, 1052m, 1000m, 838m, 791m, 696s, 642s.

For **4**: 39% yield (11.6 mg, based on L). Anal. Calcd for C<sub>18</sub>H<sub>12</sub>CdN<sub>7</sub>SI: C, 36.17; H, 2.02; N, 16.41%. Found: C, 36.05; H, 2.13; N, 16.30%. IR (KBr, cm<sup>-1</sup>): 2116vs, 1976m, 1601s, 1574m, 1507s, 1476m, 1444s, 1421s, 1357w, 1217m, 1197m, 1163w, 1047w, 1006m, 837m, 827m, 793m, 744w, 702s, 636m, 611m.

### X-ray crystallography

Single crystal X-ray diffraction data for **1–4** were collected on a Bruker APEX II CCD diffractometer equipped with a graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at room temperature. The structures were solved by direct methods and refined anisotropically on *F*<sup>2</sup> for all non-hydrogen atoms by full-matrix least-squares methods with the SHELXTL software [13]. All hydrogen atoms of the organic ligands were geometrically generated with assigned isotropic thermal parameters, whereas those of

**Table 1**  
Crystallographic data and structure refinement summary for **1–4**.

Compound reference	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Chemical formula	C <sub>17</sub> H <sub>14</sub> CdCl <sub>2</sub> N <sub>6</sub> O	C <sub>17</sub> H <sub>14</sub> Br <sub>2</sub> CdN <sub>6</sub> O	C <sub>17</sub> H <sub>12</sub> CdI <sub>2</sub> N <sub>6</sub>	C <sub>18</sub> H <sub>12</sub> CdIN <sub>7</sub> S
Formula mass	501.64	590.56	666.53	597.71
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
<i>a</i> (Å)	8.0625(6)	8.199(2)	8.0637(12)	8.4050(11)
<i>b</i> (Å)	8.4698(6)	8.627(2)	11.1779(16)	8.8142(11)
<i>c</i> (Å)	3.727(1)	13.805(4)	11.6603(17)	13.8983(18)
$\alpha$ (°)	92.846(1)	92.390(4)	79.509(2)	91.106(2)
$\beta$ (°)	90.059(1)	90.564(4)	79.964(2)	90.331(2)
$\gamma$ (°)	108.110(1)	107.267(5)	82.363(2)	109.230(2)
Unit cell volume (Å <sup>3</sup> )	889.72(11)	931.4(4)	1012.1(3)	971.9(2)
Temperature (K)	296(2)	296(2)	296(2)	296(2)
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
No. of formula units per unit cell, <i>Z</i>	2	2	2	2
Absorption coefficient ( $\mu$ /mm <sup>-1</sup> )	1.549	5.483	4.142	2.838
No. of reflections measured	4582	4800	5231	5010
No. of independent reflections	3120	3271	3566	3404
<i>R</i> <sub>int</sub>	0.0116	0.0139	0.0167	0.0104
Final <i>R</i> <sub>i</sub> values ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0285	0.0280	0.0304	0.0248
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0698	0.0660	0.0680	0.0599
Final <i>R</i> <sub>i</sub> values (all data)	0.0330	0.0362	0.0376	0.0291
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values (all data)	0.0725	0.0702	0.0718	0.0623
Goodness of fit on <i>F</i> <sup>2</sup>	1.040	1.045	1.035	1.039

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