

## Two d<sup>10</sup> Metal Coordination Polymers Based on 1*H*-1,2,4-Triazole: Synthesis, Structure and Fluorescence

Xiu-Cheng Zhang,\* Ling Xu,<sup>†</sup> Wen-Guang Liu, and Bing Liu<sup>†,‡,\*</sup>

College of Science, Northeast Forestry University, 150040 Harbin, Heilongjiang, P. R. China. \*E-mail: Xiuchengzhang@163.com

<sup>†</sup>REQUIMTE & Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal

<sup>‡</sup>Department of Chemistry, University of Aveiro, CICECO, 3810-193 Aveiro, Portugal. \*E-mail: bliu\_1203@yahoo.com.cn

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The reactions of 1*H*-1,2,4-triazole (Htr) with MX<sub>2</sub> (ZnCl<sub>2</sub> for **1**; CdBr<sub>2</sub> for **2**) resulted in two coordination polymers, [Zn(tr)Cl]<sub>n</sub> (**1**) and [Cd(Htr)<sub>2</sub>Br<sub>2</sub>]<sub>n</sub> (**2**). The structural analyses indicate that **1** and **2** feature a 2D layer and 1D triple chain, respectively. In **1**, neighbouring Zn atoms are connected by μ<sub>3</sub>-1 κN: 2 κN: 4 κN-tr<sup>-</sup> anionic ligand into 6- and 16-membered rings, further grow into a 2D sheet. Cd atoms in **2** are bonded by two μ<sub>2</sub>-Br<sup>-</sup> bridges and neutral μ<sub>2</sub>-1 κN: 2 κN-Htr to form a 1D triple chain. The fluorescent characterizations of **1**, **2** and the free Htr ligand feature similar emission peaks at 444, 446 and 423 nm respectively, which can be assigned to intra-ligand π-π\* transition of (H)tr. The energy gaps of 5.90 eV for **1**, 5.16 eV for **2**, and 5.93 eV for Htr suggest that the compounds behave as insulators.

**Key Words** : Cadmium(II), Crystal structure, Fluorescence, 1,2,4-Triazole, Zinc(II)

### Introduction

The rational design and synthesis of coordination polymers are now of great interest, not only due to the intriguing structural diversifications, but the potentiality in the novel functional materials.<sup>1</sup> The study in this field promotes the understanding of the structure-property relationship, and attributes to the purposeful design and controlled synthesis of coordination polymers with desired properties.<sup>2</sup> Though there are known numerous factors can influence the final assemblies,<sup>3</sup> the main design strategy of such materials focuses on the selection of metal ions and organic ligands.<sup>3a,4</sup> The inorganic component imparts magnetism, mechanical strength and thermal stability, etc; while the organic part offers luminescence, structural diversifications, and processability.<sup>5</sup> Therefore, the combination will integrate their advantages of organic and inorganic components in a single composite in a complementary way, thus to provide access to anticipative multifunctional coordination polymers.<sup>6</sup> Despite many efforts have been exerted, actually, it is still a great challenge to synthesize coordination polymers with predictable structures and desired properties through the selection of metal centers combining with organic building blocks.<sup>7</sup>

Heterocyclics are common candidates in the search of blue emission molecular materials, whose heterocycles can act as efficient acceptors or donor moieties with their π-deficient or π-excessive character.<sup>8</sup> The 1,2,4-triazole family, an heterocyclic 6-electrons π-excessive system, has potential applications in the heterocycle-based organic blue emission molecular materials by introducing triazole ring and selected metal center into final structures.<sup>9</sup> 1,2,4-triazole moieties have good coordinating ability to a metal centre (it presents both sp<sup>2</sup> hybridized imine- and sp<sup>3</sup>- amine-type nitrogen

atoms), whose complexes exhibit excellent luminescence and magnetic properties.<sup>9b-d,10</sup> 1*H*-1,2,4-triazole (Htr), a two-connecting neutral or three-connecting (deprotonated) anionic ligand, is helpful to produce “simple, high-symmetry” structures to study new topological networks.<sup>11</sup> In view of coordination character of 1*H*-1,2,4-triazole, our interest is in the investigation of fabricating coordination polymers. Herein, We have successfully employed Htr reacting with MX<sub>2</sub> (ZnCl<sub>2</sub> for **1**; CdBr<sub>2</sub> for **2**) to yield two new coordination polymers, [Zn(tr)Cl]<sub>n</sub> (**1**) and [Cd(Htr)<sub>2</sub>Br<sub>2</sub>]<sub>n</sub> (**2**), with the structures and fluorescent properties characterized.

### Experimental

**Materials and Physical Measurements.** The reagents and solvents were used directly as supplied commercially. The IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrometer with KBr pellets in the range 4000-400 cm<sup>-1</sup>. Elemental analyses of C, H, and N were carried out on a Vario EL III elemental analyzer. The solid-state fluorescent excitation and emission spectra were performed on a Fluoro-Max-3 spectrophotometer at room temperature with excitation and emission slits at 5.0 nm, increment 1.0 nm and integration time 0.1 s. Optical diffuse reflectance spectra were measured at room temperature with a Lambda 900 UV-vis spectrophotometer. The instrument was equipped with an integrating sphere and controlled by a personal computer. The samples were ground into fine powder and pressed onto thin glass slide holders. The BaSO<sub>4</sub> plate was used as reference. The absorption spectra were calculated from reflection spectra by the Kubelka-Munk function: α/S = (1-R)<sup>2</sup>/2R, α is the absorption coefficient, S is the scattering coefficient which is practically wavelength independent when the particle size is larger than 5 μm, and R is the reflectance.

**Table 1.** Crystal and experimental data of **1** and **2**

	<b>1</b>	<b>2</b>
Empirical formula	C <sub>2</sub> H <sub>2</sub> ClN <sub>3</sub> Zn	C <sub>2</sub> H <sub>3</sub> Br <sub>2</sub> CdN <sub>3</sub>
Color and Habit	Colorless block	Colorless prism
Crystal Size (mm <sup>3</sup> )	0.248×0.247×0.242	0.301×0.116×0.082
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P2<sub>1</sub>/n</i>	<i>Imma</i>
<i>a</i> (Å)	6.129(4)	7.316(3)
<i>b</i> (Å)	9.773(6)	7.622(3)
<i>c</i> (Å)	8.860(6)	12.202(4)
β (°)	99.520(6)	-
<i>V</i> (Å <sup>3</sup> )	523.4(6)	680.5(4)
<i>Z</i>	4	4
<i>F<sub>w</sub></i>	168.89	341.29
<i>D<sub>calcd</sub></i> (Mgm <sup>-3</sup> )	2.143	3.331
μ (mm <sup>-1</sup> )	5.060	14.850
<i>F</i> (000)	328	616
θ (°)	3.13 to 26.01	3.15 to 26.01
Reflections measured	4297	2708
Independent reflections	1029 ( <i>R<sub>int</sub></i> = 0.0265)	388 ( <i>R<sub>int</sub></i> = 0.0370)
Observed Reflection	965	333
[ <i>I</i> > 2σ( <i>I</i> )]		
Final <i>R<sub>1</sub></i> <sup><i>a</i></sup> , <i>wR<sub>2</sub></i> <sup><i>b</i></sup> [ <i>I</i> > 2σ( <i>I</i> )]	0.0161, 0.0376	0.0254, 0.0679
<i>R<sub>1</sub></i> <sup><i>a</i></sup> , <i>wR<sub>2</sub></i> <sup><i>b</i></sup> indices (all)	0.0179, 0.0383	0.0307, 0.0703
<i>GOF</i> on <i>F</i> <sup>2</sup>	1.083	1.068
(Δσ) <sub>max/min</sub>	0.001, 0.000	0.001, 0.000
Largest difference peak (e <sup>-</sup> Å <sup>-3</sup> )	0.272, -0.206	0.800, -0.942

$$R_1^a = (\sum ||F_o| - |F_c|| / \sum |F_o|), wR_2^b = [\sum (w(F_o^2 - F_c^2)^2) / \sum (w|F_o^2|)]^{1/2}$$

**Synthesis of [Zn(tr)Cl]<sub>n</sub> (1).** The 10 mL aqueous solution of ZnCl<sub>2</sub> (0.0137 g, 0.1 mmol) was dropwise to 20 mL aqueous solution of Htr (0.0139 g, 0.2 mmol). The reaction mixture was stirred at room temperature for 6 h producing a white suspension. After filtering, the natural evaporation of the mother solution yielded colorless block crystals. Yield based on Zn: 0.0096 g, 56.8%. Elemental analysis (%) for C<sub>2</sub>H<sub>2</sub>ClN<sub>3</sub>Zn, Found (calcd): C, 14.13 (14.22); H, 1.32 (1.19); N, 24.79 (24.88). IR data (in KBr, cm<sup>-1</sup>): 3454 (br, s), 3128 (m), 3105 (s), 3046 (w), 2949 (w), 1818 (w), 1799 (w), 1771 (w), 1560 (s), 1532 (s), 1441 (m), 1333 (s), 1302 (s), 1224 (s), 1179 (s), 1043 (s), 913 (s), 887 (s), 660 (s).

**Synthesis of [Cd(Htr)<sub>2</sub>Br<sub>2</sub>]<sub>n</sub> (2).** To a 20 mL aqueous solution containing Htr (0.0139 g, 0.2 mmol) was added dropwise an 10 mL aqueous solution of CdBr<sub>2</sub>·4H<sub>2</sub>O (0.0345 g, 0.1 mmol), stirring for 6 h at room temperature. The resulting white suspension was filtered, and the colorless prismatic crystals were obtained by slow evaporation of the filtrate at room temperature for a couple of weeks. Yield based on Htr: 0.0137 g, 40.2%. Elemental analysis (%) for C<sub>2</sub>H<sub>3</sub>Br<sub>2</sub>CdN<sub>3</sub>, Found (calcd): C, 6.93 (7.04); H, 0.78 (0.89); N, 12.43 (12.31). IR data (in KBr, cm<sup>-1</sup>): 3446 (br, m), 3249 (s), 3424 (s), 2362 (w), 1733 (w), 1540 (m), 1521 (s), 1504 (s), 1409 (s), 1302 (s), 1240 (w), 1209 (w), 1150 (w), 1125 (s), 1045 (s), 983 (w), 958 (w), 877 (s), 700 (s), 626 (s).

**Structural Determination and Refinement.** Data were collected on a Rigaku Mercury CCD diffractometer equip-

**Table 2.** Selected Bond Distances (Å) and Angles (°) for **1** and **2**

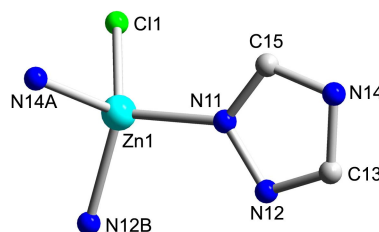
<b>1</b>			
Zn1-N11	2.0060(17)	Zn1-N12B	2.0082(18)
Zn1-N14A	2.0063(17)	Zn1-Cl1	2.2123(11)
N11-Zn1-N14A	110.19(8)	N12B-Zn1-Cl1	113.33(6)
N11-Zn1-N12B	107.05(6)	C13-N12-Zn1B	125.89(12)
N14A-Zn1-N12B	106.33(7)	N11-N12-Zn1B	128.07(12)
N11-Zn1-Cl1	113.25(6)	C13-N14-Zn1C	125.40(13)
N14A-Zn1-Cl1	106.48(6)	C15-N14-Zn1C	131.67(13)
<b>2</b>			
Cd1-N1	2.336(4)	Cd1-Br1	2.7714(8)
N1-Cd1-Br1A	92.19(8)	Br1-Cd1-Br1B	94.70(3)
N1A-Cd1-Br1A	87.81(8)	N1-Cd1-Br1C	87.81(8)
N1-Cd1-Br1	87.81(8)	N1A-Cd1-Br1C	92.19(8)
N1A-Cd1-Br1	92.19(8)	Br1A-Cd1-Br1C	94.70(3)
N1-Cd1-Br1B	92.19(8)	Br1-Cd1-Br1C	85.30(3)
N1A-Cd1-Br1B	87.81(8)	C1-N1-Cd1	133.0(4)
Br1A-Cd1-Br1B	85.30(3)	N1C-N1-Cd1	119.18(10)
		Cd1-Br1-Cd1C	82.60(3)

Symmetry codes: **1** *A* = -*x*+1/2, *y*-1/2, -*z*+3/2; *B* = -*x*+1, -*y*+1, -*z*+2; *C* = -*x*+1/2, *y*+1/2, -*z*+3/2; **2** *A* = -*x*+1/2, -*y*+3/2, -*z*+3/2; *B* = *x*-1/2, *y*, -*z*+3/2; *C* = -*x*+1, -*y*+3/2, *z*.

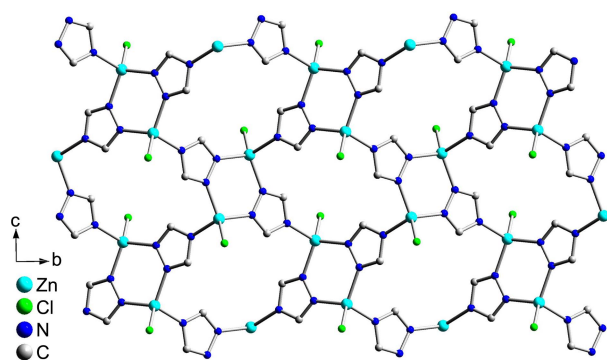
ed with a graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293(2) K. The intensity data were collected by the  $\omega$  scan technique. The intensity data were reduced using CrystalClear program.<sup>12</sup> The structures were solved by direct method using SHELXTL<sup>TM</sup> package of crystallographic software<sup>13</sup> and refined by full-matrix least-squares technique on *F*<sup>2</sup>. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to C atoms were located at geometrically calculated positions to their carrier atoms and refined with isotropic thermal parameters included in the final stage of the refinement. A summary of the structural determination and refinement for **1** and **2** is listed in Table 1. Selected bond distances and angles of **1** and **2** are shown in Table 2.

## Results and Discussion

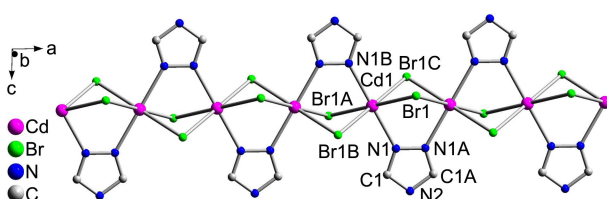
**Structural Description of [Zn(tr)Cl]<sub>n</sub> (1).** The single crystallographic analysis reveals **1** is a 2D layered coordination polymer, in whose asymmetric unit there exist one Zn(II), one deprotonated tr<sup>-</sup> and one Cl<sup>-</sup> anions. Each Zn(II) center has a slightly distorted tetrahedron geometry with the



**Figure 1.** The coordination geometry of Zn(II) in **1**. Symmetry codes: *A* = -*x*+1/2, *y*-1/2, -*z*+3/2; *B* = -*x*+1, -*y*+1, -*z*+2; *C* = -*x*+1/2, *y*+1/2, -*z*+3/2.



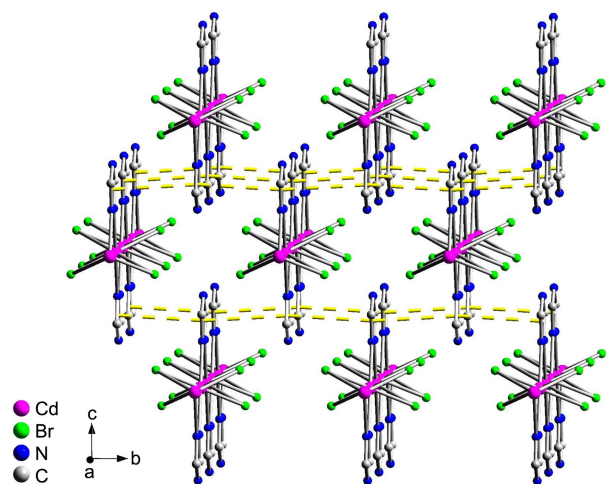
**Figure 2.** The 2D layer of **1**. Hydrogen atoms are omitted for clarity.



**Figure 3.** The 1D chain of **2** with atom-labelling scheme along the  $a$ -direction. Hydrogen atoms are omitted for clarity. Symmetry codes:  $A = 0.5-x, 1.5-y, 1.5-z$ ;  $B = x-0.5, y, 1.5-z$ ;  $C = 1-x, 1.5-y, z$ .

three basal sites occupied by N11, N14A, and N12B atoms ( $A = -x+1/2, y-1/2, -z+3/2$ ;  $B = -x+1, -y+1, -z+2$ ) from three  $\text{tr}^-$  ligands with Zn-N distances ranging from 2.0060(17)-2.0082(18) Å, and the last apical position occupied by  $\text{Cl}^-$  (Figure 1).  $\text{Tr}^-$  adopts  $\mu_3-1 \kappa\text{N}: 2 \kappa\text{N}: 4 \kappa\text{N}$  coordination mode to link three  $\text{Zn}^{2+}$  centers. With two pyrazole bridges (1,2-positioned N), two Zn1 atoms are connected into a planar hexagonal ring. Four imidazole bridges (1,4- or 2,4-positioned N) link four Zn1 atoms to fabricate a 16-membered non-planar ring. By the fuse of the 6- and 16-membered rings, a 2D polymeric network is formed along the  $bc$  plane (Figure 2).

#### Structural Description of $[\text{Cd}(\text{Htr})_2\text{Br}_2]_n$ (**2**). $[\text{Cd}(\text{Htr})_2\text{Br}_2]_n$

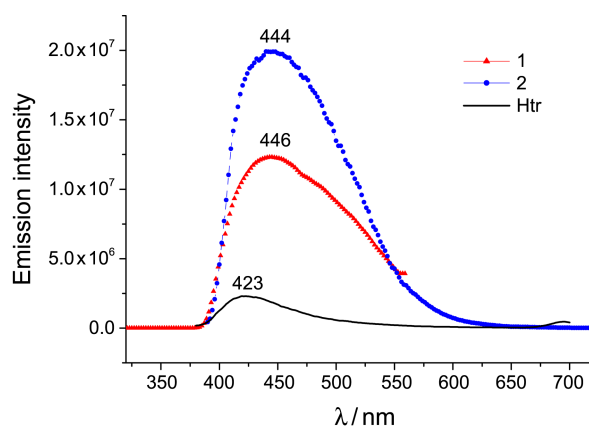


**Figure 4.** The 3D supramolecular architecture of **2** constructed from the 1D chains interconnected by  $\pi\cdots\pi$  stacking interactions viewed along the  $a$ -direction.

(**2**) crystallizes in the orthorhombic group  $Imma$ . Figure 3 shows the principal structural features of **2** with the atom-labelling scheme relevant to the coordination sphere of Cd1. The asymmetrical unit consists of a quarter Cd(II), a half neutral Htr (cutting the Htr ligand through the middle N2 atom), and a half  $\text{Br}^-$  anion. 0.5 positive charge on the Cd(II) of a quarter occupancy is balanced by  $\text{Br}^-$  of a half occupancy. Six-coordinated Cd1 center, lying in a crystallographic inversion center, exhibits a slightly distorted octahedron geometry, whose equatorial plane occupied by Br1 and its three symmetry-related atoms Br1A, Br1B, Br1C ( $A = 0.5-x, 1.5-y, 1.5-z$ ;  $B = x-0.5, y, 1.5-z$ ;  $C = 1-x, 1.5-y, z$ ), and the two apical positions by N1 and N1B atoms (Figure 3).

The neighboring Cd(II) centers are connected by two ways to generate Cd $\cdots$ Cd separations of 3.658 Å. *i*) The  $\mu_2$ -Br adopts symmetry mode to bind two neighboring Cd(II) centers with Cd1-Br1 bond being 2.7714(8) Å. With the linkage of  $\mu_2$ -Br, an inorganic skeleton zigzag double chain  $[\text{CdBr}_2]_n$  was formed along the  $a$ -direction; *ii*) Htr ligand binding two neighboring Cd(II) with its 1,2-positioned nitrogen atoms anchors on the both sides of the inorganic skeleton like wing to form the final triple chain (Figure 3). The minimum distance between the centroids of triazole rings being 3.818 Å, indicates very weak  $\pi\cdots\pi$  stacking interactions are formed among the neighboring chains. By the connections, a 3-D supramolecular architecture is shaped (Figure 4).

Compounds **1** and **2** were yielded under the fixed reaction conditions, metal salts induce significant differences. Besides the difference in the coordination capabilities of Zn(II) and Cd(II), the stronger acidity of  $\text{CdBr}_2$  aqueous solution in **2** restrains the deprotonation of Htr to keep Htr in the neutral form. H atom carried on N11 moves to N14 of the triazole ring, making Htr adopt  $\mu_2-1 \kappa\text{N}: 2 \kappa\text{N}$  coordination fashion. While in **1**, the coordination of Zn(II) to N11 is enough to deproton Htr under weaker acid environment, thus to enable  $\text{tr}^-$  ligand to adopt  $\mu_3-1 \kappa\text{N}: 2 \kappa\text{N}: 4 \kappa\text{N}$  mode to form 2D sheet. Based on the search about the metal-triazole system, it can be easily found that the triazoles adopting  $\mu_2-1 \kappa\text{N}: 2 \kappa\text{N}$  are apt to form linear trinuclear arrangements



**Figure 5.** The solid-state emission spectra of **1** ( $\lambda_{\text{ex}} = 370$  nm), **2** ( $\lambda_{\text{ex}} = 290$  nm), and free Htr ( $\lambda_{\text{ex}} = 368$  nm) recorded at room temperature.

$[M_3(\text{trz})_6(\text{H}_2\text{O})_6]_n$ ,<sup>14</sup> and 1-D chains.<sup>11c,15</sup> In the case of  $\mu_3$ -1  $\kappa\text{N}$ : 2  $\kappa\text{N}$ : 4  $\kappa\text{N}$  mode, the structures usually are three or two dimensional frameworks. Therefore, the coordination modes of 1,2,4-triazoles have essential effect on the dimensionality of the final frameworks. 2D polymer **1** under mild solution conditions also adopts the same  $\mu_3$ -mode as those in 3D frameworks obtained in hydrothermal reactions, indicating the reaction temperature is an important factor. Compared to Zn/Cu-triazole systems, the structural studies in Cd-triazole system are relatively limited with eight examples reported,<sup>5,11c,16</sup> two of which are 1D Cd-(H)tr chains.<sup>11c</sup>

**Optical Properties.** Compounds **1** and **2** reported here show luminescent features in the solid-state electronic emission spectra at room temperature (Figure 5). **1** produces a bright blue fluorescence with a broad emission at around 446 nm excited at 370 nm. The emission spectrum for **2** shows a bright blue fluorescence at *ca.* 444 nm with  $\lambda_{\text{ex.}} = 290$  nm. Compared to the free ligand Htr (emission at 423 nm with  $\lambda_{\text{ex.}} = 368$  nm), the emissions at 446 and 444 nm with small red-shifts of 23 and 21 nm can be assigned to the  $\pi$ - $\pi^*$  intra-ligand transitions. It also exhibits the coordination of metal centers have a subtle effect on the emission bands. When compared their excitation spectra ( $\lambda_{\text{ex.}}$ ), the effect of the metal is clearer. Zn(II) coordinating with  $\text{tr}^-$  ring has a small effect on the energy level of  $\text{tr}^-$  ring; while for Cd(II), maximal wavelength of the excitation spectrum ( $\lambda_{\text{ex.}}$ ) blue shifts 78 nm from 368 to 290 nm, indicating Cd(II) coordinating with Htr decreases the electronic density of the ring. This similar metal's effect also can be found in the Eg calculations assessed by their diffuse reflectance spectra. It also leaves space to tune emission bands through adjusting the metal centers for the further systematic experiments. Due to the emission peaks of **1** and **2** locating in the region of blue ray (435-480 nm), it may suggest that **1** and **2** can be regarded as a potential candidate for organic blue emission materials.

The observation in our previous work focusing on 3-(1,2,4-triazolyl-4-yl)-1*H*-1,2,4-triazole (trtr), (*m*-phenol)-1,2,4-triazole (ptr), 4,4'-bi-1,2,4-triazole (4,4'-trtr) and 3-

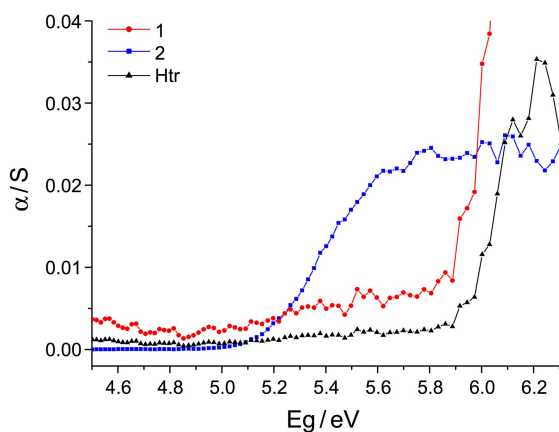
amino-1*H*-1,2,4-triazole (Atr), presents some hints. Compared emission bands of the free ligands (423 nm for Htr and Atr, 427 nm for trtr, and 426 nm for 4,4'-trtr), it indicates that the emissions originate from the intra-ligand charge transfer of the triazole ring. It also suggests that the substituted groups of  $-\text{NH}_2$ , and triazole have not obviously affect the emission of triazole ring. While for ptr ligand with the emission at 450 nm red-shifting *ca.* 27 nm compared to Htr, it relates with the formation of the delocalization  $\pi$ -conjugated system between triazole and phenol. Besides the effect of the substituted group, more importantly, the effect of metal adjusting the emissions can be found. For example, the emissions of ptr-Zn complexes locate in 524-530 nm,<sup>14c,15g,17</sup> for ptr-Cd complex, the emission red-shifts to 580 nm. While when metals are Hg, Cu and Ag, the emissions approach to that of ptr.<sup>15g,14d,18</sup> The similar phenomena can be found in other ligands. In trtr-M series, the emissions of trtr-Zn/Mn are around 350 nm;<sup>19</sup> for trtr-Cd, it is at 454 nm.<sup>19a</sup> Additionally, there should be other factors in determination of the emissions, such as structural features and compositions. In Atr series, three Zn-Atr complexes contain same coordination mode, but the emissions are significantly different: 416 nm for  $[\text{Zn}(\text{atr})\text{Cl}]_n$ ,<sup>20</sup> 334 and 462 nm for  $[\text{Zn}(\text{atr})(\text{OAc})]_n$ ,<sup>21</sup> and 443 nm for  $[\text{Zn}_2(\text{trr})_2(\text{OAc})_2]_n$ .<sup>22</sup>

The optical properties of **1** and **2** were assessed by their optical diffuse reflectance data.<sup>23</sup> The Kubelka-Munk (or remission,  $F$ ) functions converted from the diffuse reflectance data were plotted according to the diffuse reflectance data (Figure 6). Optical absorption spectra indicate the optical gaps  $E_g = 5.90$  eV for **1**, 5.16 eV for **2**, and 5.93 eV for Htr, suggesting that the compounds behave as insulators.

## Conclusion

In this work, we synthesized two coordination polymers, 2D layer  $[\text{Zn}(\text{tr})\text{Cl}]_n$  (**1**) and 1D triple chain  $[\text{Cd}(\text{Htr})_2\text{Br}_2]_n$  (**2**). Because of the different acidities of  $\text{ZnCl}_2$  and  $\text{CdBr}_2$ , the (H)tr ligands adopt different coordination modes: in **1**, deprotonated anionic  $\text{tr}^-$  ligand takes  $\mu_3$ -1  $\kappa\text{N}$ : 2  $\kappa\text{N}$ : 4  $\kappa\text{N}$  mode to connect neighbouring Zn atoms into 6- and 16-membered rings, and further fuse into a 2D layered structure; while in **2**, stronger acidity of  $\text{CdBr}_2$  restrains the deprotonation of Htr, thus to make Htr adopt  $\mu_2$ -1  $\kappa\text{N}$ : 2  $\kappa\text{N}$  coordination fashion to form a 1D triple chain with the connections of  $\text{Br}^-$  between Cd centers. Though with different structures, **1** and **2** show very similar pale blue fluorescence at 444 and 446 nm respectively. Compared to that of free Htr ligand ( $\lambda_{\text{em}} = 423$  nm), 21 and 23 nm red-shifts indicating their fluorescence can be assigned to intra-ligand  $\pi$ - $\pi^*$  transition of (H)tr. The optical gaps ( $E_g = 5.90$  eV for **1**, 5.16 eV for **2**, and 5.93 eV for Htr) assessed from the diffuse reflectance spectra suggest the compounds behave as insulators.

**Supplementary Material.** Crystallographic data for the structure reported here has been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC: 810185–810186). That data can be obtained free of charge



**Figure 6.** The band gaps of **1**, **2** and free Htr estimated to be 5.90, 5.16, and 5.93 eV were assessed by the optical diffuse reflectance data.

via <http://www.ccdc.cam.ac.uk/perl/catreq.cgi> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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## References

- (a) Whitesides, G. M.; Ismagilov, R. F. *Science* **1999**, *284*, 89. (b) Lehn, J. M. *Science* **2002**, *295*, 2400. (c) Cahill, C. L.; De Lill, D. T.; Frisch, M. *Cryst. Eng. Comm.* **2007**, *9*, 15. (d) Maspocho, D.; Ruiz-Molina, D.; Veciana, J. *Chem. Soc. Rev.* **2007**, *36*, 770. (e) Robin, A. Y.; Fromm, K. M. *Coord. Chem. Rev.* **2006**, *250*, 2127. (f) James, S. L. *Chem. Soc. Rev.* **2003**, *32*, 276.
- (a) Coronado, E.; Galan-Mascaros, J. R.; Gomez-Garcia, C. J.; Laukhin, V. *Nature* **2000**, *408*, 447. (b) Noro, S.; Kitagawa, S.; Kondo, M.; Seki, K. *Angew. Chem. Int. Ed.* **2000**, *39*, 2082. (c) Zhang, J.; Chen, S. M.; Valle, H.; Wong, M.; Austria, C.; Cruz, M.; Bu, X. H. *J. Am. Chem. Soc.* **2007**, *129*, 14168.
- (a) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629. (b) Matsuda, R.; Kitaura, R.; Kitagawa, S.; Kubota, Y.; Belosludov, R. V.; Kobayashi, T. C.; Sakamoto, H.; Chiba, T.; Takata, M.; Kawazoe, Y.; Mita, Y. *Nature* **2005**, *436*, 238. (c) Sun, W. W.; Cheng, A. L.; Jia, Q. X.; Gao, E. Q. *Inorg. Chem.* **2007**, *46*, 5471. (d) Du, M.; Jiang, X. J.; Zhao, X. J. *Inorg. Chem.* **2006**, *45*, 3998.
- (a) Carlucci, L.; Ciani, G.; Proserpio, D. M. *Coord. Chem. Rev.* **2003**, *246*, 247. (b) Hagrman, P. J.; Hagrman, D.; Zubietta, J. *Angew. Chem. Int. Ed.* **1999**, *38*, 2638. (c) Fujita, M.; Tominaga, A. M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 371. (d) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (e) Melanie, A. P.; Darren, W. J. *Chem. Soc. Rev.* **2007**, *36*, 1441.
- (a) Ouellette, W.; Hudson, B. S.; Zubietta, J. *Inorg. Chem.* **2007**, *26*, 4887. (b) Mitzi, D. B. *Dalton Trans.* **2001**, 1.
- (a) Kitaura, R.; Kitagawa, S.; Kubota, Y.; Kobayashi, T. C.; Kindo, K.; Mita, Y.; Matsuo, A.; Kobayashi, M.; Chang, H. C.; Ozawa, T. C.; Suzuki, M.; Sakata, M.; Takata, M. *Science* **2002**, *298*, 2358. (b) Halder, G. J.; Kepert, C. J.; Moubaraki, B.; Murray, K. S.; Cashion, J. D. *Science* **2002**, *298*, 1762. (c) Maiti, D. K.; Chatterjee, N.; Pandit, P.; Hota, S. K. *Chem. Commun.* **2010**, *46*, 2022. (d) Wang, H. Y.; Cheng, J. Y.; Ma, J. P.; Dong, Y. B.; Huang, R. Q. *Inorg. Chem.* **2010**, *49*, 2416.
- (a) Martinez-Manez, R.; Sancenon, F. *Chem. Rev.* **2003**, *103*, 4419. (b) Clapp, A. R.; Medintz, I. L.; Mauro, J. M.; Fisher, B. R.; Bawendi, M. G.; Mattoussi, H. *J. Am. Chem. Soc.* **2004**, *126*, 301.
- Abbotto, A.; Beverina, L.; Bozio, R.; Facchetti, A.; Ferrante, C.; Pagani, G. A.; Pedron, D.; Signorini, R. *Org. Lett.* **2002**, *4*, 1495.
- (a) Liu, J. C.; Fu, D. G.; Zhuang, J. Z.; Duan, C. Y.; X. Z. You, J. *Chem. Soc. Dalton Trans.* **1999**, 2337. (b) Browne, W. R.; O'Connor, C. M.; Hughes, H. P.; Hage, R.; Walter, O.; Doering, M.; Gallagher, J. F.; Vos, J. G. *J. Chem. Soc. Dalton Trans.* **2002**, 4048. (c) Tang, S.; Liu, M. R.; Lu, P.; Xia, H.; Li, M.; Xie, Z. Q.; Shen, F. Z.; Gu, C.; Wang, H. P.; Yang, B. *Adv. Funct. Mater.* **2007**, *17*, 2869. (d) Chen, H. Y.; Chi, Y.; Liu, C. S.; Yu, J. K.; Cheng, Y. M.; Chen, K. S.; Chou, P. T.; Peng, S. M.; Lee, G. H.; Carty, A. J. *Adv. Funct. Mater.* **2005**, *15*, 567.
- (a) Garcia, Y.; Ksenofontov, V.; Mentior, S.; Dîrtu, M. M.; Gieck, C.; Bhatthacharjee, A.; Gätlich, P. *Chem. Eur. J.* **2008**, *14*, 3745. (b) Kitchen, J. A.; Brooker, S. *Coord. Chem. Rev.* **2008**, *252*, 2072. (c) Bronisz, R. *Inorg. Chem.* **2005**, *44*, 4463. (d) Bhatthacharjee, A.; Ksenofontov, V.; Sugiyarto, K. H.; Goodwin, H. A.; Gütlich, P. *Adv. Funct. Mater.* **2003**, *13*, 877. (e) Shao, P.; Li, Z.; Qin, J. G.; Gong, H. M.; Ding, S.; Wang, Q. Q. *Aust. J. Chem.* **2006**, *59*, 49.
- (a) Li, J. R.; Yu, Q.; Sañudo, E. C.; Tao, Y.; Bu, X. H. *Chem. Commun.* **2007**, 2602. (b) Zhai, Q. G.; Lu, S. M.; Chen, C. Z.; Xu, X. J.; Yang, W. B. *Cryst. Growth Des.* **2006**, *6*, 1393. (c) Zhai, Q. G.; Wu, X. Y.; Chen, S. M.; Lu, C. Z.; Yang, W. B. *Cryst. Growth Des.* **2006**, *6*, 2126. (d) Ren, H.; Song, T. Y.; Xu, J. N.; Jing, S. B.; Yu, Y.; Zhang, P.; Zhang, L. R. *Cryst. Growth Des.* **2009**, *9*, 105. (e) Zhang, J. P.; Lin, Y. Y.; Huang, X. C.; Chen, X. M. *J. Am. Chem. Soc.* **2005**, *127*, 5495.
- Rigaku, CrystalClear 1.3.6, Software User's Guide for the Rigaku R-Axis, Mercury and Jupiter CCD Automated X-ray Imaging System. Rigaku Molecular Structure Corporation, 2002, Utah, USA.
- Siemens, SHELXTLTM Version 5 Reference Manual, Siemens Energy & Automation Inc. Madison, Wisconsin, 1994, USA.
- (a) Kolnaar, J. J. A.; van Dijk, G.; Kooijman, H.; Spek, A. L.; Ksenofontov, V. G.; Gütlich, P.; Haasnoot, J. G.; Reedijk, J. *Inorg. Chem.* **1997**, *36*, 2433. (b) Garcia, Y.; Guionneau, P.; Bravic, G.; Chasseau, D.; Howard, J. A. K.; Khan, O.; Ksenofontov, V.; Reiman, S.; Gütlich, P. *Eur. J. Inorg. Chem.* **2000**, 1531. (c) Liu, B.; Xu, L.; Guo, G. C.; Huang, J. S. *J. Mol. Struct.* **2006**, *825*, 79. (d) Zhang, X. C.; Chen, Y. H.; Liu, B. *Bull. Korean Chem. Soc.* **2008**, *29*, 511.
- (a) Drabent, K.; Ciunik, Z. *Chem. Commun.* **2001**, 1254. (b) Garcia, Y.; Koningsbruggen, P. J.; Bravic, G.; Chasseau, D.; Kahn, O. *Eur. J. Inorg. Chem.* **2003**, 356. (c) Garcia, Y.; van Koningsbruggen, P. J.; Bravic, G.; Guionneau, P.; Chasseau, D.; Cascarano, G. L.; Moscovici, J.; Lambert, K.; Michalowicz, A. *Inorg. Chem.* **1997**, *36*, 6357. (d) He, X.; Lu, C. Z.; Wu, C. D.; Chen, L. J. *Eur. J. Inorg. Chem.* **2006**, 2491. (e) Ouellette, W.; Prosvirin, A. V.; Chieffo, V.; Dunbar, K. R.; Hudson, B.; Zubietta, J. *Inorg. Chem.* **2006**, *45*, 9346. (f) Zhai, Q. G.; Wu, X. Y.; Chen, S. M.; Zhao, Z. G.; Lu, C. Z. *Inorg. Chem.* **2007**, *46*, 5046. (g) Liu, B.; Guo, G. C.; Huang, J. S. *J. Solid. State. Chem.* **2006**, *179*, 3136.
- (a) Haasnoot, J. G.; De Keyser, G. C. M.; Verschoor, G. C. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *39*, 1207. (b) Wang, X. L.; Qin, C.; Lan, Y. Q.; Shao, K. Z.; Su, Z. M.; Wang, E. B. *Chem. Commun.* **2009**, 410. (c) Chen, X. M.; Wang, D. S.; Luo, Q. Z.; Wang, R. Z. *Naturforsch., B: Chem. Sci.* **2008**, *63*, 489. (d) Lu, Y. C.; Li, X. R.; Zhang, Z. H.; Du, M. *Chin. J. Struct. Chem.* **2007**, *26*, 15. (e) Zhai, Q. G.; Lu, C. Z.; Wu, X. Y.; Batten, S. R. *Cryst. Growth Des.* **2007**, *7*, 2332. (f) Ellsworth, J. M.; Seward, K. L.; Smith, M. D.; zur Loye, H. C. *Solid State Sciences* **2008**, *10*, 267.
- Liu, B.; Li, B.; Zhang, X. C. *Bull. Korean Chem. Soc.* **2006**, *27*, 1677.
- Liu, B.; Xu, L.; Guo, G. C.; Huang, J. C. *Inorg. Chem. Commun.* **2006**, *9*, 687.
- (a) Liu, B.; Zhang, X. C.; Wang, Y. F. *Inorg. Chem. Commun.* **2007**, *10*, 199. (b) Liu, B.; Zhang, X. C.; Chen, Y. H. *Inorg. Chem. Commun.* **2007**, *10*, 498.
- Liu, B.; Zhou, Z. Q.; Zhang, X. C.; Zhang, X. Y. *Inorg. Chem. Commun.* **2007**, *10*, 1095.
- Liu, B.; Zhang, X. C. *Inorg. Chem. Commun.* **2008**, *11*, 1162.
- Chen, Y. H.; Liu, B. *Bull. Korean Chem. Soc.* **2008**, *29*, 2517
- (a) Wendlandt, W. W.; Hecht, H. G. *Reflectance Spectroscopy*; Interscience Publishers: New York, 1966. (b) Kotuem, G. *Reflectance Spectroscopy*; Springer-Verlag: New York, 1969.