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### Three isomeric copper(II) coordination polymers based on a bis-triazole-bis-amide ligand: Assembly, structures, and luminescent properties

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# Three isomeric copper(II) coordination polymers based on a bis-triazole-bis-amide ligand: Assembly, structures, and luminescent properties

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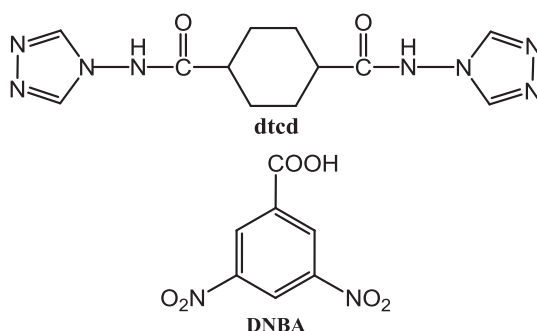
Three copper(II) isomers,  $[\text{Cu}(\text{dtd})(\text{DNBA})_2]_n$  (**1–3**) (HDNBA = 3,5-dinitrobenzoic acid, dtd = *N,N'*-di(4*H*-1,2,4-triazole)cyclohexane-1,4-dicarboxamide), were synthesized in a one-pot reaction, and structurally characterized. Polymer **1** shows a 1-D single chain in which dtd connect adjacent  $\text{Cu}^{2+}$  ions, while  $\text{DNBA}^-$  is monodentate. In **2**, every two  $\text{Cu}^{2+}$  ions are linked by carboxylate of a  $\text{DNBA}^-$  in a chelate-bridging mode into a binuclear unit, which is further connected by dtd ligands into a 1-D double chain. In **3**, dtd connect  $\text{Cu}^{2+}$  ions via triazole nitrogens to generate 1-D single chains, which are further extended into a 2-D network by the amide oxygens of a dtcb from an adjacent chain. The pH plays an important role in product distribution of **1–3**. The coordination behaviors of dtd and  $\text{DNBA}^-$  also influence the final structures. Luminescent properties of **1–3** have been investigated.

*Keywords:* Coordination polymer; Isomer; One-pot reaction; Crystal structure; Luminescent property

## 1. Introduction

Coordination polymers attract interest due to their intriguing architectures and applications in magnetism, gas separation, luminescence, and catalysis [1–8]. It is a challenge to obtain targeted coordination polymers. In the course of syntheses, many synthetic parameters have crucial effects on the final structures, such as ligands, metal, pH, temperature, and solvent [9–13]. In crystal engineering, supramolecular isomerism is an interesting subject [14, 15], useful in exploring the structure–property relationship of coordination polymers and factors influencing crystal growth, such as ligand conformation, pH, and template molecules [16–20]. However, design and controllable synthesis of supramolecular isomers are still huge challenges [21–26]. Many supramolecular isomers have been reported, which contain the same building units or component parts which coexists with different guest molecules [27]. Supramolecular isomers based on different guest molecules are not authentic supramolecular isomers, because they have disparate chemical components [28]. It would be more suitable to classify these crystals as pseudopolymorphs, rather than authentic isomers [29]. The number of proper supramolecular isomers is limited [27].

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Scheme 1. The ligands in this work.

Ligands play an important role in constructing coordination polymers and generating multiple crystal phenomena. In previous work, we designed a flexible bis-triazole-bis-amide (*N,N'*-bis(4H-1,2,4-triazole)butanamide) and obtained two kinds of crystals in one-pot reaction [30]. In continuation of this kind of ligand, in this work we designed a semi-rigid bis-triazole-bis-amide *N,N'*-di(4H-1,2,4-triazole)cyclohexane-1,4-dicarboxamide (dtcd) (scheme 1) to construct complexes and investigated coordination behavior. The triazole and amide groups may provide more potential coordination sites [31–33], the amide group is an excellent hydrogen acceptor and donor, conducive to the formation of hydrogen bonds, further influencing final structures of target polymers, and the cyclohexane in the middle of the linker exhibits flexibility to adapt to coordination environments of metal ions. These features may allow dtcd to adopt versatile coordination modes and structures. To the best of our knowledge, use of this semi-rigid bis-triazole-bis-amide as a ligand has not been reported.

Thus, dtcd was used as the main ligand and 3,5-dinitrobenzoic acid (HDNBA) (scheme 1) as the coligand to react with copper ions under hydrothermal conditions. As a result, three supramolecular isomers **1–3** with formula  $[\text{Cu}(\text{dtcd})(\text{DNBA})_2]_n$  have been obtained in a one-pot reaction. The effect of pH on the product distribution of **1–3** and the luminescence of **1–3** were investigated.

## 2. Experimental

### 2.1. Materials and measurements

All chemicals were of reagent grade, commercially available, and used without purification. The dtcd was prepared according to the literature method [34–36]. Elemental analyzes (C, H, and N) were performed on a Perkin-Elmer 240C element analyzer. FT-IR spectra were recorded with a Varian-640 spectrometer (KBr pellets). Thermogravimetric data were measured on a Pyris Diamond thermal analyzer. Powder XRD investigations were carried out with an Ultima IV diffractometer at 40 kV and 40 mA with Cu  $K\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation. Fluorescence spectra were recorded at room temperature on a Hitachi F-4500 fluorescence/phosphorescence spectrophotometer.

### 2.2. Syntheses of **1–3**

A mixture of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (48 mg, 0.20 mmol), dtcd (30 mg, 0.10 mmol), HDNBA (32 mg, 0.15 mmol),  $\text{H}_2\text{O}$  (10.0 mL), and NaOH (2.2 mL, 0.1 M) at  $\text{pH} \approx 4$  was stirred for

an hour in air, and then sealed in a 25 mL Teflon-lined stainless-steel autoclave and heated to 120 °C for 72 h. The reaction was cooled to room temperature to afford three kinds of crystals with different colors and shapes: purple platelet crystals of **1**, green block crystals of **2**, and blue needle-like crystals of **3**. According to their different colors, three kinds of crystals suitable for single-crystal structure determination were picked from the reactor using a fine needle under the microscope. For **1**, yield: 1.77 mg, 3% (based on Cu). Anal. Calcd for C<sub>26</sub>H<sub>22</sub>CuN<sub>12</sub>O<sub>14</sub> (790.11): C, 39.53; H, 2.81; N, 21.27. Found: C, 38.98; H, 2.98; N, 21.68. IR (KBr pellet, cm<sup>-1</sup>): 3143 (w), 2360 (m), 1705 (s), 1618 (s), 1537 (s), 1458 (m), 1348 (s), 1074 (s), 788 (w), 731 (s). For **2**, yield: 11.8 mg, 20% (based on Cu). Anal. Calcd for C<sub>26</sub>H<sub>22</sub>CuN<sub>12</sub>O<sub>14</sub> (790.11): C, 39.53; H, 2.81; N, 21.27. Found: C, 39.18; H, 2.88; N, 21.73. IR (KBr pellet, cm<sup>-1</sup>): 3161 (w), 2362 (m), 1733 (m), 1697 (s), 1639 (s), 1544 (s), 1404 (m), 1344 (s), 1076 (s), 790 (w), 729 (s). For **3**, yield: 2.36 mg, 4% (based on Cu). Anal. Calcd for C<sub>26</sub>H<sub>22</sub>CuN<sub>12</sub>O<sub>14</sub> (790.11): C, 39.53; H, 2.81; N, 21.27. Found: C, 39.71; H, 3.06; N, 21.79. IR (KBr pellet, cm<sup>-1</sup>): 3161 (w), 2360 (m), 1715 (w), 1643 (s), 1542 (s), 1454 (m), 1348 (s), 1072 (s), 792 (w), 727 (s).

### 2.3. X-ray crystallography study

X-ray diffraction data for **1–3** were collected with a Bruker APEX diffractometer with Mo K $\alpha$  radiation (graphite monochromator,  $\lambda = 0.71073$  Å). The structures were solved by direct methods and refined by full-matrix least-squares with SHELXL software [37]. All non-hydrogen atoms were refined anisotropically. Hydrogens of the ligands were placed in calculated positions. The crystal data and refinement parameters are summarized in table 1. Selected bond distances and angles for **1–3** are listed in table S1. The hydrogen bonding parameters for **1–3** are summarized in tables S2–S4.

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

	<b>1</b>	<b>2</b>	<b>3</b>
Formula	C <sub>26</sub> H <sub>22</sub> CuN <sub>12</sub> O <sub>14</sub>	C <sub>26</sub> H <sub>22</sub> CuN <sub>12</sub> O <sub>14</sub>	C <sub>26</sub> H <sub>22</sub> CuN <sub>12</sub> O <sub>14</sub>
Formula weight	790.11	790.11	790.11
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	C2 <sub>1</sub> /c	P-1	P-1
<i>a</i> (Å)	12.6651(16)	10.2419(6)	12.729(2)
<i>b</i> (Å)	6.2232(8)	11.5688(7)	12.816(2)
<i>c</i> (Å)	21.107(3)	14.8155(9)	12.836(2)
$\alpha$ (°)	90	74.9510(10)	62.207(3)
$\beta$ (°)	101.871(2)	89.0700(10)	68.372(3)
$\gamma$ (°)	90	69.8160(10)	89.880(3)
<i>V</i> (Å <sup>3</sup> )	1628.0(4)	1585.91(17)	1684.9(5)
<i>Z</i>	2	2	2
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.612	1.655	1.557
$\mu$ (mm <sup>-1</sup> )	0.760	0.780	0.734
<i>F</i> (0 0 0)	806	806	806
<i>R</i> <sub>1</sub> <sup>a</sup> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0606	0.0331	0.0594
<i>wR</i> <sub>2</sub> <sup>b</sup> (all data)	0.1982	0.0880	0.1621
GOF on <i>F</i> <sup>2</sup>	1.050	1.071	1.022

$$^a R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$^b wR_2 = \left[ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

### 3. Results and discussion

#### 3.1. Synthesis

Three isomeric copper(II) coordination polymers **1–3** with different colors and morphologies were synthesized in a one-pot reaction under hydrothermal conditions (120 °C for 72 h, pH ≈ 4). Many factors influence the crystallization of products. To explore the formation of **1–3**, we carried out a series of experiments by tuning the pH of the medium, reaction time, and temperature. The pH of the reaction solution prior to addition of NaOH was about 2. When the reaction pH was tuned by the addition of NaOH to be between 3.5 and 4.5, all three complexes were obtained. When the reaction pH was between 2.5 and 3.5, the only product was **2**. When the reaction pH was between 4.5 and 6, **2** and **3** were generated. The pH of the final reaction solution was not the same as that of the initial pH. In general, the yield of **2** was always relatively high, and the yields of **1** and **3** were very low (table S5). When the reaction pH was below 2.5 or above 6, no crystalline products were observed. Thus, pH of the medium has an important effect on the formation of **1–3**. When the reaction time was less than 72 h or the reaction temperature was below 120 °C, crystalline products were not observed.

#### 3.2. Description of crystal structures

Single-crystal X-ray analysis showed that **1** is a 1-D linear chain. As shown in figure 1(a), Cu<sup>2+</sup> is square-planar coordinated by two O from two DNBA<sup>−</sup> and two N from two dtcd. The Cu–O(1) distance is 1.937(3) Å and Cu–N(1) bond distance is 1.989(4) Å (table S1), respectively, within normal ranges [38]. The dtcd exhibits bridging bidentate coordination (scheme S1a) and DNBA<sup>−</sup> is monodentate (scheme S1c), as observed in reported DNBA<sup>−</sup> metal complexes [38–41]. In **1**, Cu<sup>2+</sup> ions are bridged by triazole N of dtcd to generate a 1-D linear chain (figure 1(b)), and adjacent 1-D linear chains are further extended into a 2-D supramolecular layer by intermolecular hydrogen bonding between uncoordinated carboxylate from DNBA<sup>−</sup> and N–H of the amide group from dtcd [N(4)–H(4A)⋯O(2): 2.7482 Å] (figure 1(c) and table S2).

Polymer **2** possesses a 1-D double chain structure. Figure 2(a) shows the fundamental structural unit of **2** containing an asymmetric Cu<sub>2</sub>O<sub>2</sub> core. Each Cu<sup>2+</sup> shows a distorted octahedral coordination geometry, coordinated by four oxygens from three DNBA<sup>−</sup> and two N from two dtcd. The dtcd is bridging bidentate (scheme S1a), as in **1**. There are two types of DNBA<sup>−</sup> in **2**. One is monodentate as in **1** (scheme S1c), while the other is chelate-bridging (scheme S1d), which has not been observed in reported DNBA<sup>−</sup> metal complexes. The distortion from a pure octahedral geometry for Cu<sup>2+</sup> is undoubtedly due to the chelate angles of the carboxylates. The Cu–N bond distances are 1.9768(18) [Cu(1)–N(2)] and 1.9876(18) Å [Cu(1)–N(1)] (table S1). The bond distances of Cu(1)–O(1), Cu(1)–O(2), Cu(1)–O(8), and Cu(1)–O(2A) are 1.9487(12), 2.0362(12), 2.508(21), and 2.7289(17) Å, respectively. Bond distances of Cu(1)–O(1) and Cu(1)–O(2) are in the normal range. Although the bond distance of Cu(1)–O(2A) is longer than others, it is still in the normal range [42]. O(2) and O(2A) connect two different Cu<sup>2+</sup> ions, forming a Cu<sub>2</sub>O<sub>2</sub> core with Cu⋯Cu distance of 3.9103(4) Å. The core bond angles of O2–Cu1–O2A and Cu1A–O2–Cu1 are 70.570(54) and 109.430(63)°, respectively. The Cu<sub>2</sub>O<sub>2</sub> cores are linked by dtcd to generate double chains (figure 2(b)), which are further extended into a 2-D supramolecular network by hydrogen bonding between O of nitro of DNBA<sup>−</sup> and C–H of the triazole ring from dtcd

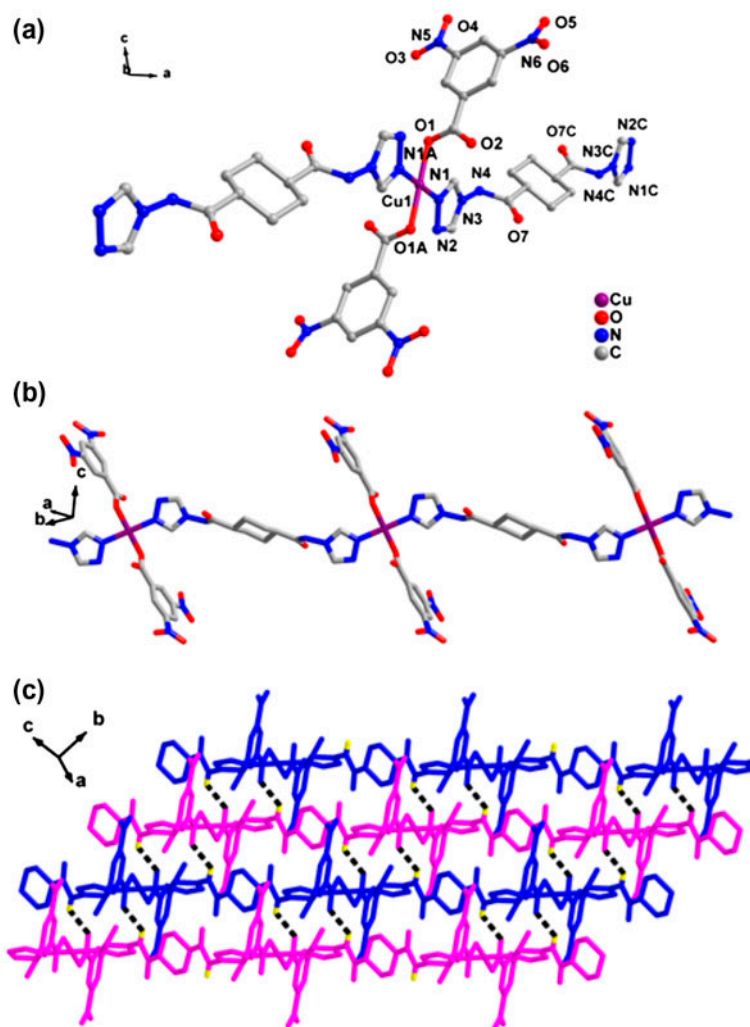


Figure 1. (a) Coordination environment of  $\text{Cu}^{2+}$  in **1**. All hydrogens are omitted for clarity. A:  $-x$ ,  $-y$ ,  $-z$ . (b) 1-D chain in **1** formed from  $\text{Cu}^{2+}$  and dtdc. (c) 2-D supramolecular sheet of **1** formed by hydrogen bonding interactions.

[C(9)–H(9A)⋯O(12): 2.9882 Å] (figure 2(c) and table S3). Adjacent 2-D supramolecular layers are further connected by hydrogen-bonding interactions between the carboxylate O from a DNBA<sup>−</sup> and the acylamino N–H from dtdc [N(8)–H(8C)⋯O(8): 2.7729 Å] to form a three-dimensional (3-D) supramolecular architecture (figure S1).

Unlike **1** and **2**, polymer **3** exhibits a 2-D network. As shown in figure 3(a), the asymmetric unit of **3** is also composed of one  $\text{Cu}^{2+}$ , one dtdc, and two DNBA<sup>−</sup>.  $\text{Cu}^{2+}$  exhibits a distorted square-pyramidal coordination geometry. The basal atoms are two N from triazole of two dtdc with Cu–N distances of 1.973(4) and 1.998(4) Å and O1 and O4 from carboxylates of two DNBA<sup>−</sup> with Cu–O distances of 1.945(3) and 1.935(3) Å, respectively. O2 is axial from the amide of a third dtdc with Cu–O distance of 2.309(4) Å (table S1). Although



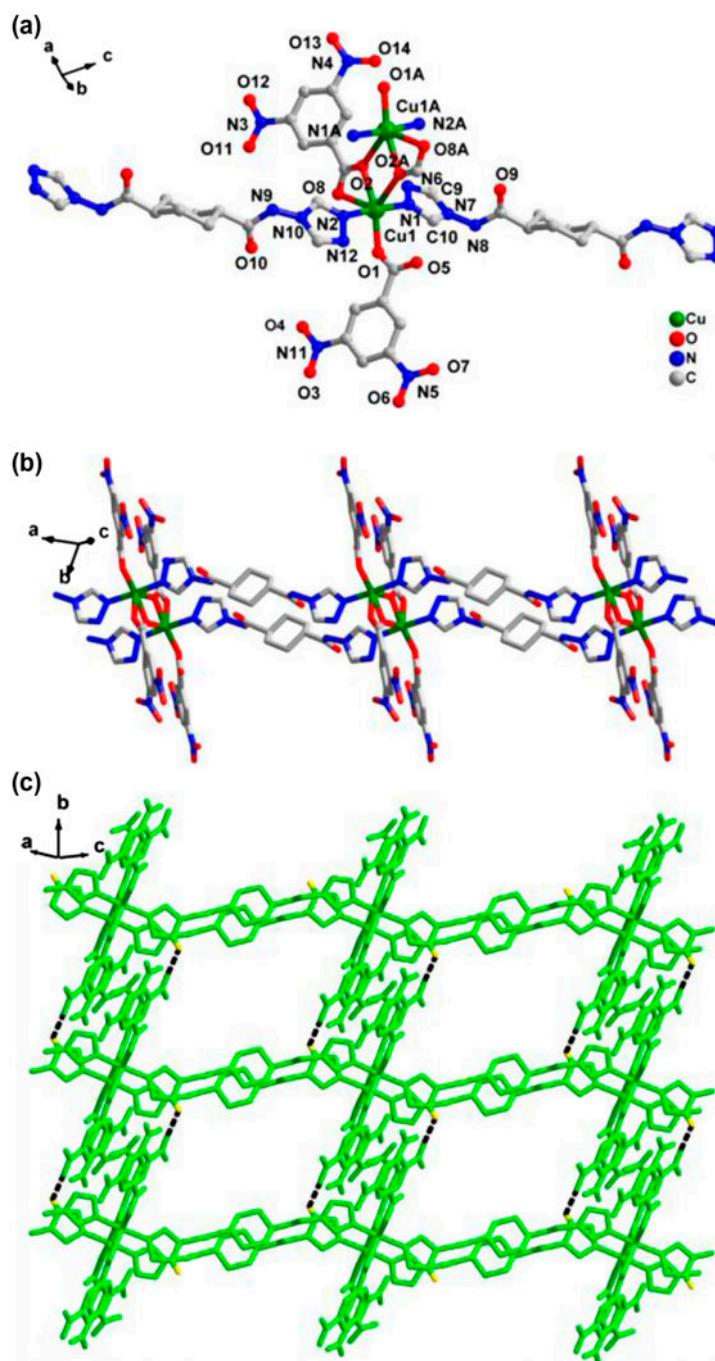


Figure 2. (a) Coordination environment of  $\text{Cu}^{2+}$  in **2**. All hydrogens are omitted for clarity. A:  $1-x, -y, 2-z$ . (b) 1-D double chain in **2** formed from  $\text{Cu}_2\text{O}_2$  units and dtcd. (c) 2-D supramolecular sheet of **2** formed by hydrogen bonding interactions.



the bond distance of Cu–O2 is longer than those of Cu–O1 and Cu–O4, all are within the normal ranges [43]. DNBA<sup>−</sup> is monodentate (scheme S1c), as in **1**. Unlike **1** and **2**, dtcd exhibits two coordination modes, a bridging bidentate coordination like that in **1** and **2** (scheme S1a), and also a bridging quadridentate coordination (scheme S1b). Cu<sup>2+</sup> ions are connected by triazole N of dtcd through bridging bidentate coordination to generate 1-D linear chains (figure 3(b)), which are further linked by amide O of dtcd through the bridging quadridentate coordination to build a 2-D sheet (figure 3(c)). The bidentate dtcd and quadridentate dtcd connect alternate Cu<sup>2+</sup> ions in the 1-D chain. The 2-D networks are further

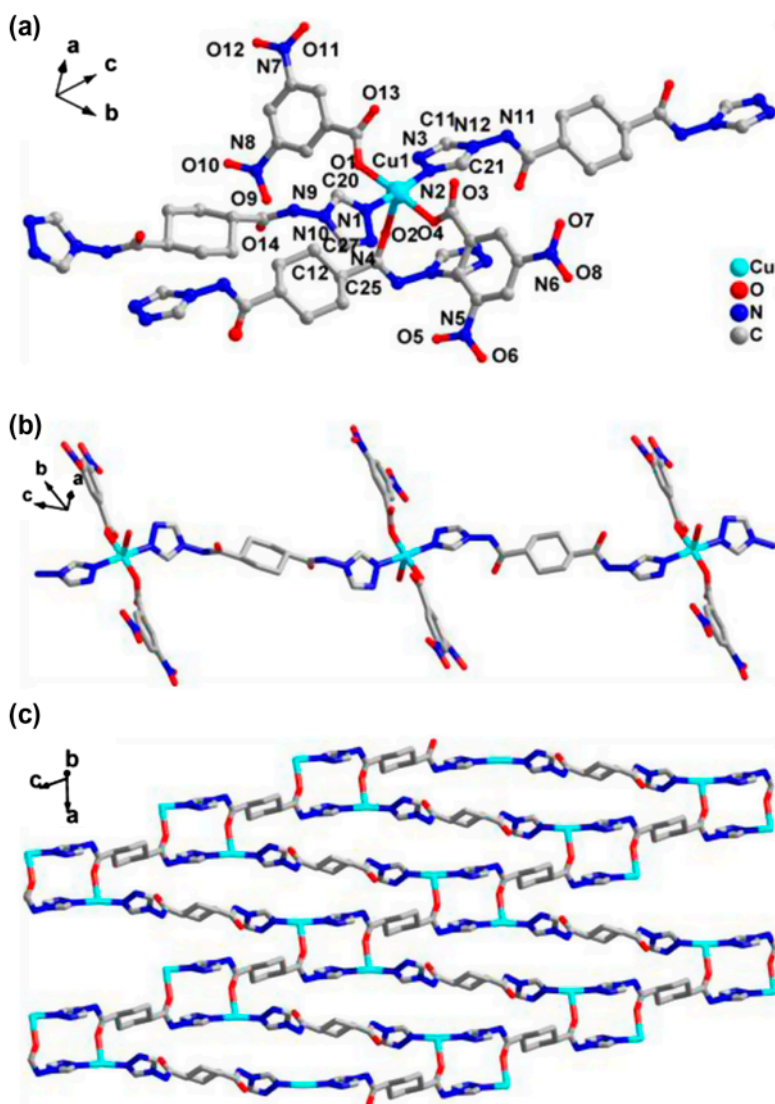


Figure 3. (a) Coordination environment of Cu<sup>2+</sup> in **3**. All hydrogens are omitted for clarity. (b) 1-D chain in **3** constructed from Cu<sup>2+</sup> and dtcd. (c) The 2-D layer of **3**.

extended into a 3-D supramolecular framework through hydrogen-bonding interactions between a nitro of DNBA<sup>-</sup> and C–H of an adjacent triazole ring [C(11)–H(11B)⋯O(10), 2.9411 Å] (figure S2 and table S4).

**1–3** present distinct structural differences. Compound **1** shows a 1-D single chain, while **2** exhibits a 1-D double chain. The difference between the 1-D structures of **1** and **2** is due to the different coordination modes of DNBA<sup>-</sup> with Cu<sup>2+</sup>. Compared with **1** and **2**, **3** exhibits a 2-D layer, attributed to different coordinations of dtcd. Coordination environments of Cu<sup>2+</sup> change from four-coordinate in **1**, to six in **2**, to five in **3**. Coordination of dtcd and DNBA<sup>-</sup>, as well as Cu<sup>2+</sup>, have significant effects on the structures of **1–3**.

There are some reports on triazole-based Cu coordination polymers [44–46]. For example, Tian and co-workers reported four copper coordination polymers based on [1,2-bis(1,2,4-triazol-1-yl)ethane] (bte), [1,3-bis(1,2,4-triazol-1-yl)propane] (btp), and [1,4-bis(1,2,4-triazol-1-yl)butane] (btb) in which all bis-triazole ligands adopted a  $\mu_2$ -bridging mode [44]. In this work, the dtcd exhibits  $\mu_4$ -bridging in **3**, which indicates that the introduction of amide gives the bis-triazole-bis-amide ligand more potential coordination sites.

### 3.3. IR spectrum of 1–3

The main feature of IR spectra for **1–3** concerns the dtcd and carboxylate of DNBA<sup>-</sup> (figure S3). No strong absorption around 1700 cm<sup>-1</sup> for –COOH is observed, which implies that carboxyl of HDNBA is completely deprotonated [47]. Strong peaks at 1348, 1537, 1618, and 1705 cm<sup>-1</sup> for **1**, 1344, 1544, 1639, and 1697 cm<sup>-1</sup> for **2**, and 1348, 1542, 1643, and 1715 cm<sup>-1</sup> for **3** may be attributed to asymmetric and symmetric vibrations of carboxylates. Separations between the symmetric and asymmetric vibrations vary, indicating different binding modes of carboxylates [48, 49]. The characteristic bands at 1458 cm<sup>-1</sup> for **1**, 1470 cm<sup>-1</sup> for **2**, and 1454 cm<sup>-1</sup> for **3** can be assigned to  $\nu_{C-N}$  of the triazole-rings of dtcd [48].

### 3.4. Thermogravimetric analysis and powder X-ray diffraction of 1–3

Thermogravimetric (TG) analysis was performed to estimate the thermal stability of **1–3** (figure S4). The TG curves of **1–3** show one weight loss step from 20 to 780 °C. The steps range from 173 to 557 °C, 268 to 553 °C, and 136 to 696 °C for **1–3**, respectively, with weight losses of 89.18% for **1**, 89.87% for **2**, and 90.21% for **3**, consistent with the decomposition of ligands (Calcd 89.65%). The remaining weight (10.82% for **1**, 10.13% for **2**, and 9.79% for **3**) corresponds to CuO (Calcd 10.35%). As shown in figures S5–S7, the crystalline phase purities of **1–3** were established by the similarity of simulated and experimental PXRD patterns. The as-synthesized patterns are in agreement with the corresponding simulated ones, indicating the phase purities of samples.

### 3.5. Fluorescent properties of 1–3

The luminescence of coordination polymers has been investigated for applications as photosensitive materials [50]. The photoluminescent properties of free dtcd and **1–3** in the solid state were investigated at room temperature. As shown in figure 4, free dtcd exhibits an intense fluorescent emission with maximum at 411 nm upon excitation at 310 nm. The

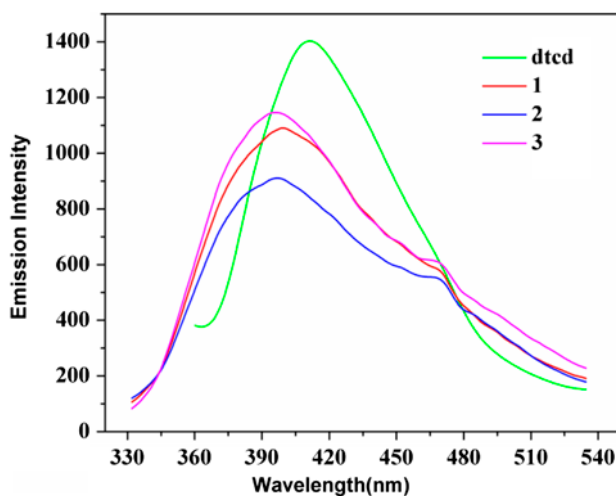


Figure 4. Solid-state fluorescent spectra of dtcd and 1–3 at room temperature.

emission peaks of 1–3 are at 400, 397, and 396 nm, respectively, upon excitation at 320 nm. Compared with free dtcd ligand, emission maxima of 1–3 are slightly blue-shifted, which may be attributed to ligand-to-metal charge transfer [51, 52]. Emission peaks of 1–3 are very similar, and only the emission intensities are slightly different, which demonstrates that 1–3 have same components.

#### 4. Conclusion

Three new isomeric bis-triazole-bis-amide-based copper(II) coordination polymers 1–3 have been synthesized in a one-pot reaction under hydrothermal conditions. The pH of the medium has a significant influence on the product distribution of 1–3. The bis-triazole-bis-amide-based ligand contributes to the generation of multiple crystal phenomena in the one-pot reaction. The coordination modes of dtcd and DNBA, as well as that of  $\text{Cu}^{2+}$  ion, have significant effects on the structures of 1–3. Isomers 1–3 exhibit good luminescence, demonstrating their potential applications in luminescent materials.

#### Supplementary material

Tables of selected bond distances and angles, hydrogen-bonding distances and angles, and effect of pH on the yields of 1–3; scheme of coordination modes of dtcd and DNBA-ligands; figures of the supramolecular networks of 2 and 3 and IR spectra, TG curves, and experimental and simulated PXRD patterns of 1–3. CCDC 900626, 900627, and 900628 for 1–3 contain the supplementary crystallographic data in 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](http://www.ccdc.cam.ac.uk/data_request/cif). Supplemental data for this article can be accessed <http://dx.doi.org/10.1080/00958972.2013.847183>.

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## References

- [1] E. Pardo, C. Train, H. Liu, L.M. Chamoreau, B. Dkhil, K. Boubekeur, F. Lloret, K. Nakatani, H. Tokoro, S. Ohkoshi, M. Verdaguer. *Angew. Chem. Int. Ed.*, **33**, 8356 (2012).
- [2] K.C. Mondal, A. Sundt, Y. Lan, G.E. Kostakis, O. Waldmann, L. Ungur, L.F. Chibotaru, C.E. Anson, A.K. Powell. *Angew. Chem. Int. Ed.*, **30**, 7550 (2012).
- [3] A.N. Khlobystov, A.J. Blake, N.R. Champness, D.A. Lemenovskii, A.G. Majouga, N.V. Zyk, M. Schröder. *J. Coord. Chem.*, **1**, 155 (2001).
- [4] S. Kitagawa, M.L. Foo, S. Horike, Y. Inubushi. *Angew. Chem. Int. Ed.*, **25**, 6107 (2012).
- [5] R.J. Kuppler, D.J. Timmons, Q.R. Fang, J.R. Li, T.A. Makal, M.D. Young, D.Q. Yuan, D. Zhao, W.J. Zhuang, H.C. Zhou. *Coord. Chem. Rev.*, **253**, 3042 (2009).
- [6] Z. Huang, J. Du, J. Zhang, X.Q. Yu, L. Pu. *Chem. Commun.*, **48**, 3412 (2012).
- [7] G. Férey. *Chem. Soc. Rev.*, **37**, 191 (2008).
- [8] Y.H. Fu, D.R. Sun, Y.J. Chen, R.K. Huang, Z.X. Ding, X.Z. Fu, Z.H. Li. *Angew. Chem. Int. Ed.*, **14**, 3364 (2012).
- [9] G. Yang, P.C. Duan, K.G. Shi, R.G. Raptis. *Cryst. Growth Des.*, **12**, 1882 (2012).
- [10] C. Pettinari, A. Tăbăcaru, I. Boldog, K.V. Domasevitch, S. Galli, N. Masciocchi. *Inorg. Chem.*, **51**, 5235 (2012).
- [11] J.X. Yang, X. Zhang, J.K. Cheng, J. Zhang, Y.G. Yao. *Cryst. Growth Des.*, **12**, 333 (2012).
- [12] M.H. Mir, S. Kitagawa, J.J. Vittal. *Inorg. Chem.*, **47**, 7728 (2008).
- [13] R. Sen, D. Saha, S. Koner. *Chem. Eur. J.*, **19**, 5979 (2012).
- [14] B. Moulton, M.J. Zaworotko. *Chem. Rev.*, **101**, 1629 (2001).
- [15] L. Han, W. Zhao, Y. Zhou, X. Li, J.G. Pan. *Cryst. Growth Des.*, **8**, 3504 (2008).
- [16] T.L. Hennigar, D.C. MacQuarrie, P. Losier, R.D. Rogers, M.J. Zaworotko. *Angew. Chem. Int. Ed.*, **36**, 972 (1997).
- [17] X.C. Huang, J.P. Zhang, X.M. Chen. *J. Am. Chem. Soc.*, **126**, 13218 (2004).
- [18] J.P. Zhang, X.C. Huang, X.M. Chen. *Chem. Soc. Rev.*, **38**, 2385 (2009).
- [19] T.A. Makal, A.A. Yakovenko, H.C. Zhou. *J. Phys. Chem. Lett.*, **2**, 1682 (2011).
- [20] B. Moulton, M.J. Zaworotko. *Chem. Rev.*, **101**, 1629 (2001).
- [21] M.J. Zaworotko. *Chem. Commun.*, **1**, 1 (2001).
- [22] J.P. Zhang, X.M. Chen. *Chem. Commun.*, **16**, 1689 (2006).
- [23] H. Abourahma, B. Moulton, V. Kravtsov, M.J. Zaworotko. *J. Am. Chem. Soc.*, **124**, 9990 (2002).
- [24] X.C. Huang, J.P. Zhang, X.M. Chen. *J. Am. Chem. Soc.*, **126**, 13218 (2004).
- [25] V.S.S. Kumar, F.C. Pigge, N.P. Rath. *Cryst. Growth Des.*, **4**, 651 (2004).
- [26] J.B. Lin, J.P. Zhang, W.X. Zhang, W. Xue, D.X. Xue, X.M. Chen. *Inorg. Chem.*, **48**, 6652 (2009).
- [27] L. Han, W.N. Zhao, Y. Zhou, X. Li, J.G. Pan. *Cryst. Growth Des.*, **8**, 3504 (2008).
- [28] Y. Wang, C.T. He, Y.J. Liu, T.Q. Zhao, X.M. Lu, W.X. Zhang, J.P. Zhang, X.M. Chen. *Inorg. Chem.*, **51**, 4772 (2012).
- [29] J.S. Hu, L. Qin, M.D. Zhang, X.Q. Yao, Y.Z. Li, Z.J. Guo, H.G. Zheng, Z.L. Xue. *Chem. Commun.*, **48**, 681 (2012).
- [30] Q.L. Lu, W. Zhao, J.W. Zhang, X.L. Wang, J. Luan. *Z. Anorg. Allg. Chem.*, **693**, 587 (2012).
- [31] E.C. Yang, Z.Y. Liu, X.J. Shi, Q.Q. Liang, X.J. Zhao. *Inorg. Chem.*, **49**, 7969 (2010).
- [32] E.C. Yang, Z.Y. Liu, L.N. Zhao, Y.L. Yang, C.H. Zhang, X.J. Zhao. *CrystEngCommun.*, **13**, 5401 (2011).
- [33] E.C. Yang, Y.L. Yang, Z.Y. Liu, K.S. Liu, X.Y. Wu, X.J. Zhao. *CrystEngCommun.*, **13**, 2667 (2011).
- [34] L. Rajput, S. Singha, K. Biradha. *Cryst. Growth Des.*, **7**, 2788 (2007).
- [35] M. Sarkar, K. Biradha. *Cryst. Growth Des.*, **6**, 202 (2006).
- [36] S.S. Sun, A.J. Lees, P.Y. Zavalij. *Inorg. Chem.*, **42**, 3445 (2003).
- [37] G.M. Sheldrick. *Acta Crystallogr. Sect. A*, **64**, 112 (2008).
- [38] X.L. Wang, W. Zhao, J.W. Zhang, Q.L. Lu. *J. Solid State Chem.*, **198**, 162 (2013).
- [39] Y. Qi, F. Luo, S.R. Batten, Y.X. Che, J.M. Zheng. *Cryst. Growth Des.*, **8**, 2806 (2008).
- [40] Y. Wang, F.H. Zhao, A.H. Shi, Y.X. Che, J.M. Zheng. *Inorg. Chem. Commun.*, **20**, 23 (2012).
- [41] Q.L. Lu, W. Zhao, J.W. Zhang, X.L. Wang, J. Luan. *Z. Anorg. Allg. Chem.*, **693**, 587 (2012).
- [42] E.C. Yang, Y.L. Yang, Z.Y. Liu, K.S. Liu, X.Y. Wu, X.J. Zhao. *CrystEngCommun.*, **13**, 2667 (2011).

- [43] X.L. Wang, H.Y. Lin, B. Mu, A.X. Tian, G.C. Liu, N.H. Hu. *CrystEngCommun.*, **13**, 1990 (2011).
- [44] L. Tian, S.Y. Zhou, M.Y. Xu, L.P. Wang. *J. Coord. Chem.*, **65**, 3792 (2012).
- [45] H.Y. Zhou, D.G. Ding, M.C. Yin, Y.T. Fan, H.W. Hou. *J. Coord. Chem.*, **64**, 2010 (2011).
- [46] G.A. Senchyk, A.B. Lysenko, H. Krautscheid, E.B. Rusanov, A.N. Chernega, K.W. Krämer, S.X. Liu, S. Decurtins, K.V. Domasevitch. *Inorg. Chem.*, **52**, 863 (2013).
- [47] X.J. Gu, D.F. Xue. *Cryst. Growth Des.*, **6**, 2551 (2006).
- [48] E.C. Yang, Y. Feng, Z.Y. Liu, T.Y. Liu, X.J. Zhao. *CrystEngCommun.*, **13**, 230 (2011).
- [49] M.X. Li, G.Y. Xie, S.L. Jin, Y.D. Gu. *Polyhedron*, **15**, 535 (1996).
- [50] K.L. Huang, X. Liu, J.K. Li, Y.W. Ding, X. Chen, M.X. Zhang, X.B. Xu, X.J. Song. *Cryst. Growth Des.*, **10**, 1508 (2010).
- [51] X.L. Wang, Y.F. Bi, H.Y. Lin, G.C. Liu. *Cryst. Growth Des.*, **7**, 1086 (2007).
- [52] F.J. Liu, H.J. Hao, C.J. Sun, X.H. Lin, H.P. Chen, R.B. Huang, L.S. Zheng. *Cryst. Growth Des.*, **12**, 2004 (2012).