



## Four Zn(II)/Cd(II)-3-amino-1,2,4-triazolate frameworks constructed by in situ metal/ligand reactions: Structures and fluorescent properties

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### ABSTRACT

Four Cd(II) and Zn(II) complexes with the in situ-generated ligand of 3-amino-1,2,4-triazolate ( $\text{AmTAZ}^-$ ) were isolated from the solvothermal reactions of the corresponding Cd(II) or Zn(II) salts with 5-amino-1H-1,2,4-triazole-3-carboxylic acid ( $\text{AmTAZAc}$ ). Their structures were determined by single-crystal X-ray diffraction analysis.  $[\text{Zn}(\text{AmTAZ})(\text{CH}_3\text{COO})]$  (**1**) presents a two-dimensional framework constructed from Zn(II) ions and  $\mu_3$ - $\text{AmTAZ}^-$  ligands. A remarkable feature of  $[\text{Zn}_4(\text{AmTAZ})_4(\text{SO}_4)(\text{OH})(\text{C}_2\text{O}_4)_{0.5}] \cdot 2\text{H}_2\text{O}$  (**2**) is the construction of the building units of octagonal cylinders which interact with each other by sharing one face or overlapping, resulting in the formation of a three-dimensional framework with three kinds of 1D channels.  $[\text{Cd}(\text{AmTAZ})\text{Br}]$  (**3**) crystallizes in a chiral space group  $P2_12_12_1$ , giving a homochiral three-dimensional framework with two types of helical channels (left- and right-handed). Different from the others, the 3-amino-1,2,4-triazole molecules in  $[\text{Cd}(\text{AmTAZ})\text{SO}_4]$  (**4**) behave as neutral  $\mu_2$ -2,4-bridges to connect the two-dimensional  $\text{CdSO}_4$  sheets into a three-dimensional framework. Of all, **2** and **3** display different fluorescent properties probably due to different metal ions, coordination environments and structural topologies.

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### 1. Introduction

The design and synthesis of metal-organic framework (MOF) coordination polymers are of great interest due to their intriguing architectures [1–6] and potential applications in heterogeneous catalysis, non-linear optics, magnetism, and gas storage [7–17]. A large number of compounds with various topologies ranging from 1D chains [18,19] and ladders [20–22], 2D grids [23,24], 3D microporous networks [25–27], interpenetrated modes [28–30], and helical frameworks [31–36] have been obtained by careful selection of organic ligands and secondary building units. Most commonly used organic ligands are carboxylic acids and polypyridines because the former can exhibit flexible coordination modes, while the latter can afford more predictable coordination modes. In recent years, 1,2,4-triazole and its derivatives, typical members of polyazaheteroaromatic N-donor ligands, have gained more and more attention as ligands in constructing appealing MOFs because of their potential  $\mu_{1,2}$ -,  $\mu_{2,4}$ -, and  $\mu_{1,2,4}$ -bridging fashions and the fact that they unite the coordination of both pyrazole and imidazole, but with a smaller extent of electron donation due to the inductive effect of the additional non-bridging N atoms [37–45].

Two approaches have been reported to be able to yield MOF coordination polymers with 1,2,4-triazole and its derivatives as ligands. Direct reaction using metal salt and triazole ligands under either conventional solution or hydro(solvo)thermal conditions is the most commonly reported ones. By this way, the triazoles act usually as neutral ligands when the reaction was carried out under mild conditions [46–48], while the deprotonated fashion of triazole was obtained under solvothermal conditions [49–59]. The counterions and the substituents on the triazole ring are found to affect profoundly the structures and the topologies of the products. Another route to obtain metal-triazolate coordination polymers is the in situ metal/ligand reactions. It was reported that the reaction of Cu(II) ion with organonitriles and ammonia or hydrazine under solvothermal conditions led to the isolation of copper-triazolate polymers with diverse structures and the formation of supramolecular isomers, where triazolate ligands were in situ prepared by the copper-mediated oxidative cycloaddition of organonitriles and ammonia or hydrazine [60–67]. The in situ-generated triazole-containing ligand can also be achieved via the transformation of the triazole derivative in the process of metal/ligand reaction. For example, reaction of copper(II) salt with 3,5-diacetylamino-1,2,4-triazole and 3-acetylamino-5-amino-1,2,4-triazole in water afforded a heptanuclear copper compound with a new triazole-derived macrocyclic ligand, which was generated in situ from the condensation of simple triazole derivatives [68]. Solvothermal reaction of Zn(II) salt with 3-amino-1,2,4-triazole-5-carboxylic acid gave a three-dimensional

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zinc-organic framework displaying open-ended, hollow nanotubular channels,  $[\text{ZnF}(\text{AmTAZ})] \cdot \text{solvents}$  ( $\text{AmTAZ}^- = 3\text{-amino-1,2,4-triazolate}$ ). The  $\text{AmTAZ}^-$  ligand was derived from the decarboxylation of 3-amino-1,2,4-triazole-5-carboxylic acid in the solvothermal process [69]. Up to now, construction of metal–triazole coordination polymers via the route of the transformation of triazole derivative has been studied only rarely.

Herein, we wish to present the synthesis, structure, and luminescent properties of four Zn(II) and Cd(II) coordination polymers with 3-amino-1,2,4-triazolate ligand transformed from the decarboxylation of 5-amino-1H-1,2,4-triazole-3-carboxylic acid ( $\text{AmTAZAc}$ ) under solvothermal reactions. Anion-dependent structural diversity in the isolated polymers was observed. The use of Zn(II) and acetate ions gave a two-dimensional framework. When the  $\text{ZnSO}_4$  was applied, an open three-dimensional structure with three kinds of channels was obtained. In the Cd(II) series, the solvothermal reactions gave a three-dimensional framework containing two types of helical channels (left- and right-handed) with the coordination of anions of bromide, and a three-dimensional framework built from the two-dimensional  $\text{CdSO}_4$  sheets and  $\mu_2$ -2,4-bridges when the anion was changed into  $\text{SO}_4^{2-}$ . The fluorescent properties of **2** and **3** were tested. It was shown that they exhibit different fluorescent emissions probably due to different metal ions, coordination environments, and the structure topologies.

## 2. Experimental sections

### 2.1. Materials and methods

All chemicals were used as obtained without further purification. Infrared spectra were recorded as KBr pellet using a Nicolet 360 FT-IR spectrometer. Elemental analyses (C, H, and N) were performed on a Vario EL analyzer. Luminescence spectra were recorded on an Edinburgh Analytical Instrument FLS920 Luminescence spectrometer at room temperature.

### 2.2. Preparation of compounds

#### 2.2.1. Synthesis of $[\text{Zn}(\text{AmTAZ})(\text{CH}_3\text{COO})] (\mathbf{1})$

A mixture of  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (0.2148 g, 1 mmol), 5-amino-1H-1,2,4-triazole-3-carboxylic acid (0.1145 g, 0.9 mmol), NaOH (0.0393 g, 1 mmol), ethanol (2 mL) and water (12 mL) was sealed in a 23 mL Teflon-lined autoclave, heated at 140 °C for 168 h, and cooled over a period of 48 h. Colorless crystals of **2** were collected in a yield of 74% (0.1382 g).  $\text{C}_4\text{H}_6\text{N}_4\text{O}_2\text{Zn}$  (207.50): calcd. C 23.15, H 2.91, N 27.00; found C 23.14, H 2.88, N, 27.08. IR (KBr pellet): 3406(vs), 3335(s), 1626(s), 1595(vs), 1556(m), 1526(m), 1427(w), 1401(m), 1336(w), 1328(w), 1225(w), 1155(w), 1100(w), 1073(m), 1026(m), 937(w), 778(w), 751(w), 681(m), 650(m), 490(w)  $\text{cm}^{-1}$ .

#### 2.2.2. Synthesis of $[\text{Zn}_4(\text{AmTAZ})_4(\text{SO}_4)(\text{OH})(\text{C}_2\text{O}_4)_{0.5}] \cdot 2\text{H}_2\text{O} (\mathbf{2})$

A mixture of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (0.1436 g, 0.5 mmol), 5-amino-1H-1,2,4-triazole-3-carboxylic acid (0.1147 g, 0.9 mmol) and water (12 mL) was sealed in a 23 mL Teflon-lined autoclave, heated at 170 °C for 168 h, and cooled over a period of 48 h. Colorless crystals of **3** were separated in a yield of 62% (0.0610 g).  $\text{C}_9\text{H}_{17}\text{N}_4\text{O}_5\text{SZn}_4$  (786.93): calcd. C 14.40, H 1.74, N 29.84; found C 14.38, H 1.72, N 29.80. IR (KBr pellet): 3404(vs.), 3221(s), 1651(vs.), 1632(s), 1569(m), 1551(s), 1523(m), 1429(w), 1383(w), 1311(w), 1314(w), 1286(w), 1222(m), 1106(s), 1068(s), 1051(s), 1012(m), 988(w), 876(w), 801(w), 774(w), 746(w), 654(w), 617(w), 531(w), 499(w), 480(w)  $\text{cm}^{-1}$ .

#### 2.2.3. Synthesis of $[\text{Cd}(\text{AmTAZ})\text{Br}] (\mathbf{3})$

Hydrothermal treatment (160 °C, 168 h) of  $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$  (0.3442 g, 1 mmol), 5-amino-1H-1,2,4-triazole-3-carboxylic acid (0.1145 g, 0.9 mmol), NaOH (0.0393 g, 1 mmol) and water (12 mL) produced **6** as colorless crystals in a yield of 77% (0.1908 g).  $\text{C}_2\text{H}_3\text{N}_4\text{BrCd}$  (275.39): calcd. C 8.72, H 1.10, N 20.34; found C 8.79, H 1.08, N 20.69. IR (KBr pellet): 3445(m), 3290(m), 3219(m), 1635(w), 1573(s), 1510(s), 1483(s), 1456(m), 1391(m), 1288(m), 1210(m), 1071(m), 972(m), 873(w), 711(m), 667(m)  $\text{cm}^{-1}$ .

#### 2.2.4. Synthesis of $[\text{Cd}(\text{AmTAZH})\text{SO}_4] (\mathbf{4})$

Hydrothermal treatment (170 °C for 168 h) of  $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$  (0.1764 g, 0.5 mmol), 5-amino-1H-1,2,4-triazole-3-carboxylic acid (0.1145 g, 0.9 mmol), triethylamine and water (12 mL) yielded colorless crystals of **7** in a yield of 75% (0.1097 g).  $\text{C}_2\text{H}_4\text{N}_4\text{O}_4\text{CdS}$  (292.55): C 8.21, H 1.38, N 19.15; found C 8.31, H 1.32, N 19.54. IR (KBr pellet): 3427(s), 3345(s), 3267(m), 3206(m), 3146(m), 2997(m), 2873(w), 1646(s), 1587(m), 1526(m), 1360(m), 1281(m), 1244(m), 1115(vs), 1057(vs), 1040(vs), 976(m), 885(w), 646(m), 599(m), 471(m), 433(w), 414(w)  $\text{cm}^{-1}$ .

### 2.3. X-ray crystallography

The crystal of **1–4** was put in a fine-focus-sealed tube and the measurement was performed on a Stoe IPDS diffractometer at 183 K (**3**) or on a Bruker-AXS SMART-CCD diffractometer at 293 K (**1**, **2** and **4**) using graphite-monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Absorption corrections were applied by using the multi-scan program SADABS (**1**, **2** and **4**) [70] or numerical method (**3**). The structures were solved by direct methods (**1**, **2** and **4**) or with patterson method (**3**) of SHELXS-97 and were refined by full-matrix least-squares against  $F^2$  using the SHELXL-97 program [71] or the corresponding programs in the SHELXTL package [72]. After all of the non-H atoms were located, the model was refined again, initially using isotropic and later anisotropic thermal displacement parameters. The H atoms of aqua, hydroxyl, and amino groups of **1–4** were located from difference maps and refined with isotropic temperature factors.

The structure of **3** was difficult to solve because of space group ambiguity. All trials with possible orthorhombic space group  $C222$  and  $Pnma$  and monoclinic space groups  $P2_1/n$ ,  $P2_1/m$ ,  $P2/m$ ,  $P2_1$ ,  $Pn$ ,  $P2$ , and  $Pm$  were not successful. Thus, weak reflections were neglected by using programs XYZ and RECIPE (Stoe software). The resulting unit cell is that of this final result in the cif-file. A merohedric twin-refinement was applied (twin ratio 0.45:0.55). For the numerical absorption correction, nine crystal faces were indexed and measured. Six light atoms (compared to Cd and Br) in the  $\text{AmTAZ}^-$  ligand were set to equal anisotropic displacement parameters (EADP) to achieve esthetic ORTEP plots. The positions of H-atoms at N4 and C1 were calculated after each refinement cycle. A secondary extinction correction was also applied during refinement with SHELXL-97. The structure was solved with Patterson method of SHELXS-97. Due to a possible unresolved twinning problem or a kind of polytype structure (weak reflections) statistics, the final R-values are a bit too large, however, the chemical model of the three-dimensional network structure is unambiguously determined.

Crystal data as well as details of data collection and refinements for the complexes are summarized in Table 1. Selected bond lengths and angles of **1–4** are given in Table 2.

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