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 ($AmTAZ^-$) 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 (AmTAZAc). Their structures were determined by single-crystal X-ray diffraction analysis. $[Zn(AmTAZ)(CH_3COO)]$ (1) presents a two-dimensional framework constructed from Zn(II) ions and μ_3-$AmTAZ^-$ ligands. A remarkable feature of $[Zn_4(AmTAZ)_4(SO_4)(OH)(C_2O_4)_{0.5}] \cdot 2H_2O$ (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. $[Cd(AmTAZ)Br]$ (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 $[Cd(AmTAZH)SO_4]$ (4) behave as neutral μ_2-2,4-bridges to connect the two-dimensional $CdSO_4$ 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.

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 poly-pyridines 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 cycload-dition 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, [ZnF(AmTAZ)] · solvents (AmTAZ$^-$ = 3-amino-1,2,4-triazolate). The 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 (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 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 CdSO$_4$ sheets and μ_2-2,4-bridges when the anion was changed into 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 [Zn(AmTAZ)(CH$_3$COO)] (**1**)

A mixture of Zn(CH$_3$COO)$_2$ · 2H$_2$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). C$_4$H$_6$N$_4$O$_2$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) cm^{-1}.

2.2.2. Synthesis of [Zn$_4$(AmTAZ)$_4$(SO$_4$)(OH)(C$_2$O$_4$)$_{0.5}$] · 2H$_2$O (**2**)

A mixture of ZnSO$_4$ · 7H$_2$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). C$_9$H$_{17}$N$_{16}$O$_9$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), 1361(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) cm^{-1}.

2.2.3. Synthesis of [Cd(AmTAZ)Br] (**3**)

Hydrothermal treatment (160 °C, 168 h) of CdBr$_2$ · 4H$_2$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). C$_2$H$_3$N$_4$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) cm^{-1}.

2.2.4. Synthesis of [Cd(AmTAZH)SO$_4$] (**4**)

Hydrothermal treatment (170 °C for 168 h) of CdSO$_4$ · 8H$_2$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). C$_2$H$_4$N$_4$O$_4$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) 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–Kα radiation (λ = 0.71073 Å). 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 *C*222 and *Pnma* and monoclinic space groups *P*2$_1$/*n*, *P*2$_1$/*m*, *P*2/*m*, *P*2$_1$, *Pn*, *P*2, 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 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.

Table 1
Summary of crystallographic data and refinements of compounds **1**–**4**

	1	2	3	4
Formula	$C_4H_6N_4O_2Zn$	$C_9H_{17}N_{16}O_9SZn_4$	$C_2H_3BrN_4Cd$	$C_2H_4N_4O_4SCd$
Formula weight	207.50	786.93	275.39	292.55
T (K)	293(2) K	293(2) K	183(2) K	293(2) K
λ (Å)	0.71073	0.71073	0.71073	0.71073
Cryst syst	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic
Space group	Pccn	C2/m	$P2_12_12_1$	Pba2
a (Å)	15.678(8)	18.5934(12)	6.4715(11)	13.973(4)
b (Å)	9.450(5)	17.9100(11)	7.9554(10)	6.6440(17)
c (Å)	9.782(5)	7.4267(5)	10.4171(18)	6.7133(17)
α (deg)	90	90	90	90
β (deg)	90	96.3020(10)	90	90
γ (deg)	90	90	90	90
V (Å³)	1449.3(13)	2458.2(3)	536.31(15)	623.2(3)
Z	8	4	4	4
D_c (g cm⁻¹)	1.902	2.126	3.411	3.118
μ (mm⁻¹)	3.341	4.018	11.399	3.816
$F(0\,0\,0)$	832	1564	504	560
GOF on F^2	1.211	1.087	1.258	1.089
R_1	0.0761	0.0238	0.0563	0.0204
wR_2	0.1923	0.0663	0.1430	0.0501

Table 2
Selected bond lengths (Å) and angles (deg) for compounds **1**–**4**

1

Zn1–O21	1.93(2)	Zn1–N2A	1.989(9)	N2A–Zn1–N1	106.3(4)	O21–Zn1–N3B	95.9(8)
Zn1–N1	2.010(9)	Zn1–N3B	2.018(9)	N1–Zn1–N3B	107.9(4)	N2A–Zn1–N3B	109.3(4)
				O21–Zn1–N1	103.1(8)	O21–Zn1–N2A	132.5(7)

2

Zn1–N1	2.100(2)	Zn2–N6A	1.970(2)	O4A–Zn1–N5	85.13(8)	O5–Zn3–N3	116.55(11)
Zn1–O4	2.1330(19)	Zn3–N7D	1.991(2)	O4–Zn1–N5	87.76(8)	O5–Zn3–O1	109.69(10)
Zn1–N5	2.167(2)	N1–Zn1–N1A	94.41(13)	N1–Zn1–N5A	96.79(8)	N3–Zn3–O1	100.31(9)
Zn2–N2	2.013(2)	N1–Zn1–O4A	170.80(8)	N5–Zn1–N5A	170.81(13)	O5–Zn3–N7D	106.69(12)
Zn3–O5	1.9101(16)	N1–Zn1–O4	93.62(8)	N6B–Zn2–N6A	131.40(13)	N3–Zn3–N7D	118.28(10)
Zn3–N3	1.977(2)	O4A–Zn1–O4	78.75(10)	N6B–Zn2–N2	101.54(9)	O1–Zn3–N7D	104.22(9)
Zn3–O1	1.978(2)	N1–Zn1–N5	89.46(9)	N6A–Zn2–N2	108.11(9)	N2C–Zn2–N2	103.23(13)

3

Cd1–N1A	2.253(14)	N1A–Cd1–N3B	170.9(5)	N1A–Cd1–Br1C	97.2(4)	N3B–Cd1–Br1	88.8(4)
Cd1–N3B	2.293(13)	N1A–Cd1–N2	101.6(5)	N3B–Cd1–Br1C	88.9(4)	N2–Cd1–Br1	94.8(4)
Cd1–N2	2.319(13)	N3B–Cd1–N2	85.5(5)	N2–Cd1–Br1C	86.0(4)	N4C–Cd1–Br1	78.4(3)
Cd1–N4C	2.581(13)	N1A–Cd1–N4C	90.0(5)	N4C–Cd1–Br1C	100.3(3)	Br1C–Cd1–Br1	177.46(6)
Cd1–Br1C	2.7624(17)	N3B–Cd1–N4C	82.3(5)	N1A–Cd1–Br1	85.0(4)	Cd1D–Br1–Cd1	91.23(4)
Cd1–Br1	2.8057(17)	N2–Cd1–N4C	166.1(5)				

4

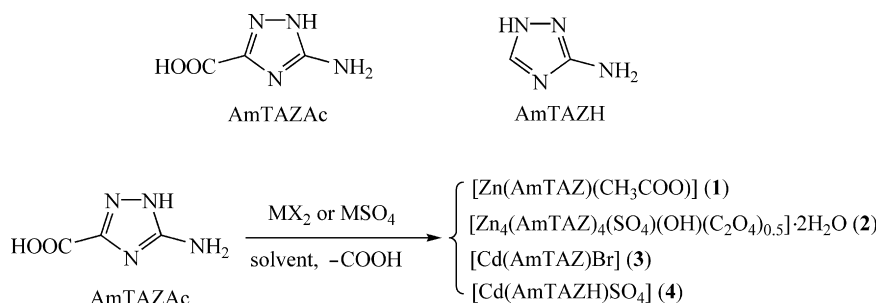|							
Cd–N1	2.267(7)	N1–Cd–N3A	157.01(11)	N1–Cd–O4D	80.5(3)	N3A–Cd–O1	75.2(3)
Cd–N3A	2.283(8)	N1–Cd–O4B	93.0(3)	N3A–Cd–O4D	85.3(3)	O4B–Cd–O1	89.73(19)
Cd–O4B	2.322(2)	N3A–Cd–O4B	99.7(3)	O4B–Cd–O4D	71.65(9)	O2C–Cd–O1	77.58(18)
Cd–O2C	2.396(2)	N1–Cd–O2C	86.7(3)	O2C–Cd–O4D	123.67(8)	O4D–Cd–O1	150.4(3)
Cd–O4D	2.493(2)	N3A–Cd–O2C	86.2(3)	N1–Cd–O1	124.3(3)	CdB–O4–CdF	108.07(9)
Cd–O1	2.531(10)	O4B–Cd–O2C	164.25(11)				

3. Results and discussion

3.1. Synthesis

As shown in Scheme 1, different metal ions (Zn(II) and Cd(II)) and different counterions (Br⁻, CH₃COO⁻, SO₄²⁻) were chosen in this study to manipulate the formation of MOFs. The originally used ligand of 5-amino-1,2,4-triazole-3-carboxylic acid (AmTAZAc) in all solvothermal reactions (Scheme 1) described in the context underwent decarboxylation producing AmTAZ⁻ to interact with the metal ions. This was similar to the analogous ligand of 3-amino-1,2,4-triazole-5-carboxylic acid, which easily undergo decarboxylation liberating AmTAZ⁻ ion in the solvothermal reactions [69]. The thus formed 3-amino-1,2,4-triazolate ion (AmTAZ⁻), having four binding sites (one amino group and three imino-nitrogen atoms), is a nice candidate for the construction of some interesting MOF with special properties. In addition to compounds **1**–**4**, we separated in this study also compounds [Zn(AmTAZ)Cl] and [Zn₅(AmTAZ)₆(OH)₂](NO₃)₂·6H₂O reported by Park et al. [73] lately, and [Cd(AmTAZ)Cl] prepared by Li et al. [74] in the solvothermal reaction of CdCl₂ directly with AmTAZH in an ethanol–water system .

Scheme 1

The counterions in all of these compounds coordinate to the metal ions leading to the formation of neutral complex unit. In **2**, an in situ-generated oxalate ion was also identified, which is similar to the reported cases with the formation of oxalate ions derived from the decomposition of the corresponding carboxylate containing compounds [75–78].

Elemental analysis results of the four compounds are in agreement with the composition derived from the single-crystal X-ray diffraction analysis. Infrared spectra of all synthesized products display essentially similar absorption profiles for the AmTAZ$^-$ ligand. Several vibration bands of sulfate ions observed in the range of 950–1250 cm^{-1} (v_1 and v_3) indicate the lower symmetry of sulfate ions in **2** and **4** [79–83], as the crystal structures revealed. Compounds **2** and **4** possess different vibration bands of sulfate ion due to the distinct coordination modes of sulfate ion presenting in different types of structures [84].

3.2. Molecular structures of complexes **1**–**4**

Every Zn(II) ion of **1** is four coordinated in a distorted tetrahedral geometry (Fig. 1a) by one carboxylato oxygen atom from a disordered CH$_3$COO$^-$ anion and three nitrogen atoms from three 3-amino-1,2,4-triazolate ions. The Zn–N bond lengths lie in the normal range of 1.989(9)–2.018(9) Å and the N–Zn–N bond angles range from 106.3(4)° to 109.3(4)° (Table 2). The AmTAZ$^-$ ligand is located on a twofold axis, causing a twofold disorder of this ligand and thus two possible orientations of the amino group as shown in Fig. 1a. Each 3-amino-1,2,4-triazolate ion connects three Zn(II) ions through its three nitrogen atoms in the ring, while the amino groups is free from coordination. Two Zn(II) ions are connected by two 3-amino-1,2,4-triazolate ions using 1,2-nitrogen atoms to form a centrosymmetric dinuclear block with a Zn⋯Zn distance of 3.6828(12) Å. Each dinuclear building block interacts with another four dinuclear blocks via the coordination of the 4-nitrogen atom in 3-amino-1,2,4-triazolate ion, forming a two-dimensional framework parallel to the *bc* plane (Fig. 1b). It presents 16-membered quadrangular ring windows with a dimension of 3.74 × 3.79 Å considering the van der Waals

radii of Zn atoms. The structure of **1** is similar to that of [ZnCl(AmTAZ)] and [Zn(HCO$_2$)(AmTAZ)] [73], but much different from that of the reported three-dimensional MOF, [ZnF(AmTAZ)], which displays open-ended, hollow nanotubular channels that are formed by hexanuclear metallamacrocyclic Zn$_6$F$_6$(AmTAZ)$_6$ rings [69]. This difference may be attributed to the much smaller size and harder base properties of F$^-$ than Cl$^-$, HCO$_2^-$ and CH$_3$COO$^-$.

X-ray analysis of single crystal revealed three crystallographically unique Zn(II) centers in **2** as shown in Fig. 2a. Zn1(II) ion possesses a distorted octahedral geometry by the coordination of four ring nitrogen atoms from four 3-amino-1,2,4-triazolate ions and two oxygen atoms from one oxalate anion. Zn2(II) ion is coordinated by four ring nitrogen atoms from four 3-amino-1,2,4-triazolate ions and Zn3(II) is coordinated to one hydroxyl group, two ring nitrogen atoms from two 3-amino-1,2,4-triazolate ions and one oxygen atom from one sulfate ion. Both Zn2(II) and Zn3(II) have distorted tetrahedral coordination geometries. Each 3-amino-1,2,4-triazole molecule connects three crystallographically unique Zn(II) ions to establish a two-dimensional sheet parallel to the *ac* plane (Fig. 2b,c). The Zn1(II) ions from the neighboring two-dimensional sheets are bridged by oxalate anion, which behaves as a μ_2-bridge using its four oxygen atoms to chelate to two Zn(II) ions [85–88]. Every pair of Zn3(II) ions from the neighboring two-dimensional sheets are bridged by one μ_2-hydroxyl group and one μ_2-sulfate ion, which afford two oxygen atoms to bridge two Zn(II) ions with the other two oxygen atoms free from coordination. This leads to the construction of a porous three-dimensional network from the stack of the two-dimensional sheets along the *b* axis (Fig. 2d).

It is easy to see from Fig. 2d that the framework of **2** has the building units of octagonal cylinder. Every octagonal cylinder, for example, the one in the center, is surrounded by another five ones by sharing one face and further overlapped with another three ones, resulting in its division into four parts: one hexagonal prismatic channel (type I), three quadrangular prismatic channels (two type II channels and one type III channel). The hexagonal prismatic channel consists of 20-membered hexanuclear metallamacrocycles made up of six Zn(II) centers, four AmTAZ$^-$ ions, two hydroxide ions and two sulfate ions with a size of ca. 11.5 × 8.0 Å. Two of the quadrangular prismatic channels (type II) show the
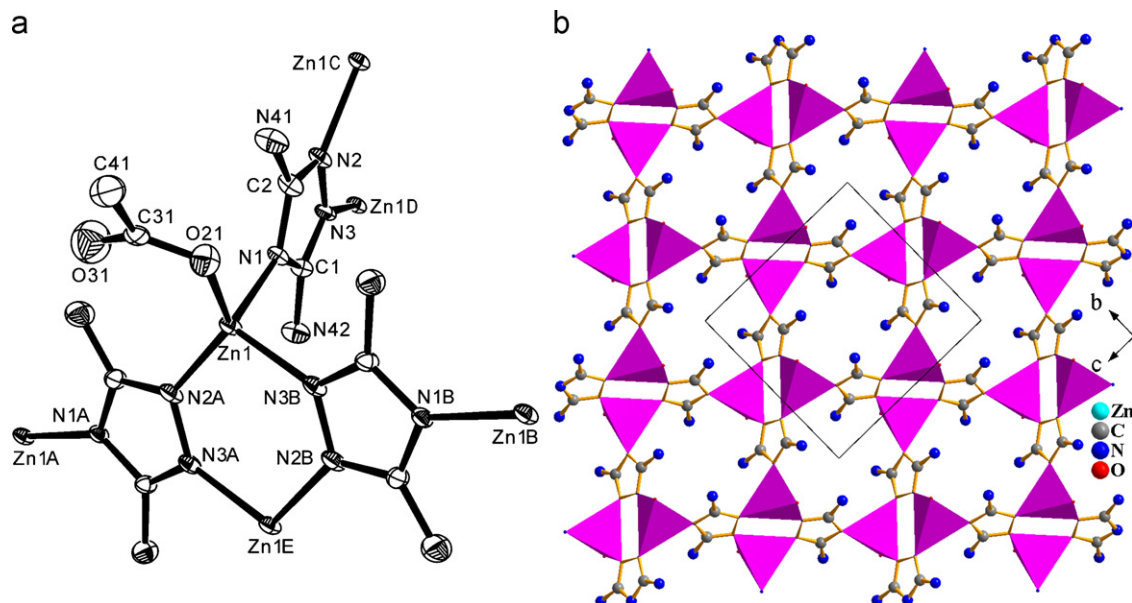
Fig. 1. (a) ORTEP view of the structure of **1**, showing the atom-labeling scheme and 30% thermal ellipsoids. Hydrogen atoms and the disorder of CH$_3$COO$^-$ are omitted for clarity. (b) View of the structure of **1** in the *bc* plane with hydrogen atoms and CH$_3$COO$^-$ ligands omitted for clarity. Symmetry transformations used to generate equivalent atoms: (A) *x*, −*y*+0.5, *z*+0.5; (B) −*x*, *y* − 0.5, −*z*+0.5; (C) *x*, −*y*+0.5, *z* − 0.5; (D) −*x*, *y*+0.5, −*z*+0.5; and (E) −*x*, − *y*, 1 −*z*.
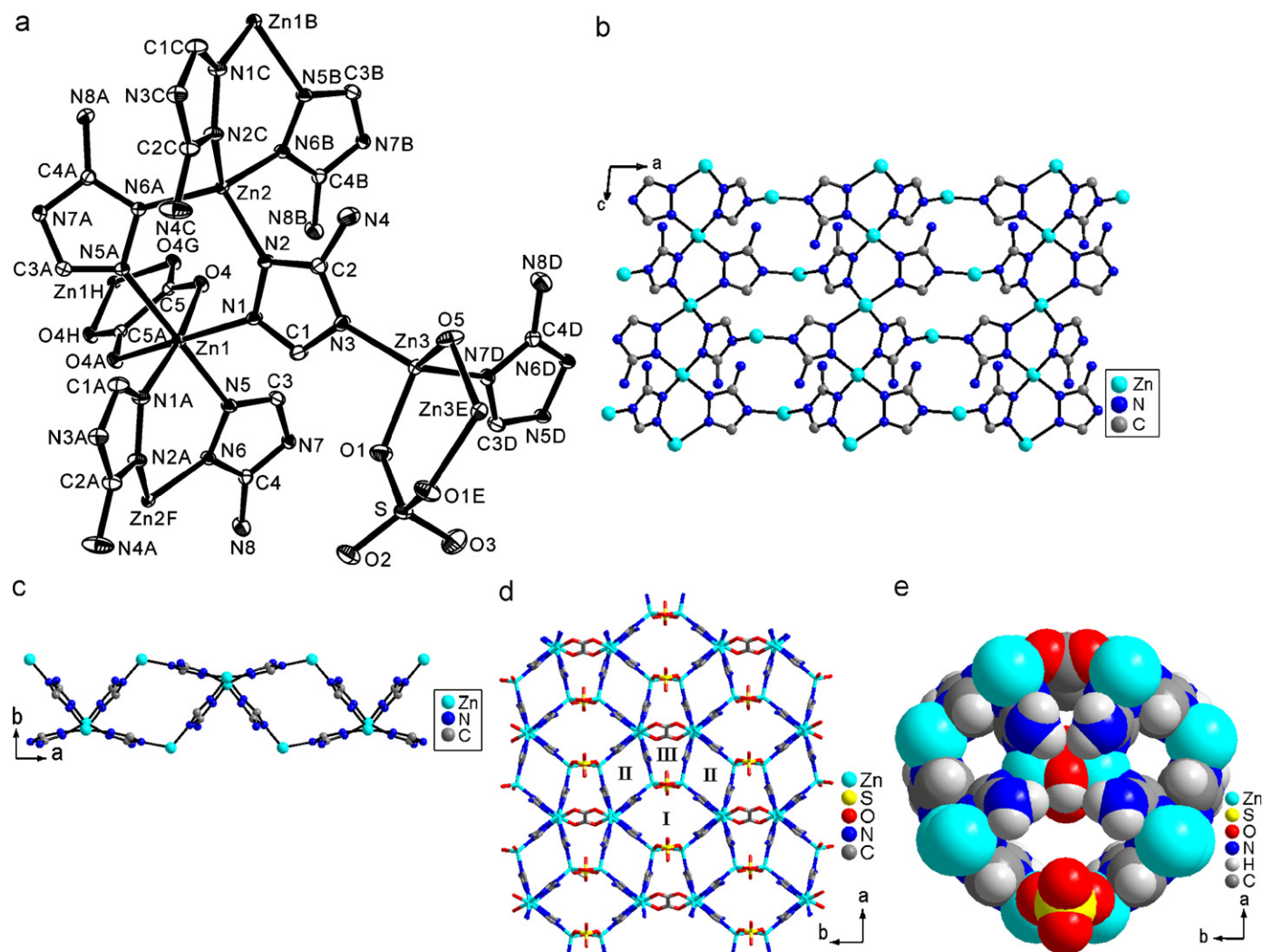
Fig. 2. (a) ORTEP view of the structure of **2** showing the atom-labeling scheme and 30% thermal ellipsoids with hydrogen atoms and solvated water molecules omitted for clarity. (b) View of the two-dimensional sheet of **2** in the *ac* plane from the *b*-axis with sulfate, hydroxyl and oxalate ligands, solvated water molecules and hydrogen atoms omitted. (c) View of the two-dimensional sheet of **2** in the *ac* plane from the *c* axis. (d) Three-dimensional structure of **2** seen from the *c* axis with the solvated water molecules and hydrogen atoms omitted for clarity. (e) A view of the three kinds of one-dimensional channels in **2**. Symmetry transformations used to generate equivalent atoms: (A) −x+1, y, −z+3; (B) x, y, z−1; (C) −x+1, y, −z+2; (D) −x+0.5, −y+0.5, −z+3; (E) x, −y, z; (F) x, y, z+1; (G) x, −y+1, z; and (H) −x+1, −y+1, −z+3.

same shape and size (6.9 × 9.6 Å). They consist of 16-membered tetranuclear metallamacrocycles made up of four Zn(II) centers and four AmTAZ⁻ units. The third quadrangular prismatic channel (type III) consists 14-membered tetranuclear metallamacrocycles made up of four Zn(II) metal centers, two AmTAZ⁻ ions, one hydroxide, one sulfate and one oxalate ion with a dimension of 7.1 × 7.1 Å. In both type I and III channels, one pair of Zn(II) ions are bridged by one μ_2-hydroxyl group and one sulfate ion. The sizes of these channels are calculated based on the distance of the corresponding opposite edges of the channels. Thus, it results in the formation of an open three-dimensional framework with three kinds of one-dimensional channels running along the *c* axis (Fig. 2e), which is unprecedented. In the framework, some amino groups of AmTAZ⁻ ligands point slightly into the hexagonal channels with a dihedral angle of 11° between the molecular plane of AmTAZ⁻ ligand and the corresponding wall plane of the hexagonal channel. However, the amino groups of other AmTAZ⁻ ligands points slightly into the type III channel with a dihedral angle of 8° between the molecular plane of AmTAZ⁻ ligand and the corresponding wall plane of the quadrangular channel. This leads to the hydrophilic properties of these channels. No amino groups points into the type II channels. In the open-ended

framework structure, every hexagonal channel is separated from four type II channels by "single layer" wall formed by AmTAZ⁻ and also from two type III channels by the wall constructed from sulfate and hydroxide ions. Another four type III channels are also around it just by sharing one edge. Each type II channel is separated from two type I and two type III channels around it by "single layer" wall formed from AmTAZ⁻, and also from another two type II and two type III channels by sharing one edge. Two neighboring type III channels share a wall built from oxalate ions connected by Zn(II) ions. The free water molecules are clathrated in the hexagonal channels by forming hydrogen bonds with the oxygen atoms of sulfate ion (O6···O1: 3.338(12) Å; O6···O2: 2.886(9) Å) and the ring nitrogen atom of AmTAZ⁻ ligand (O6···N3: 3.088(9) Å). The neighboring water molecules also interact with each other by forming hydrogen bond (O6···O6: 3.08(3) Å).

Of all, **3** crystallizes in a chiral space group $P2_12_12_1$ and has a similar structure to [CdCl(AmTAZ)], which was synthesized from a solvothermal reaction of $CdCl_2$ with AmTAZH in ethanol–water system.[74] It is shown in Fig. 3a that the Cd(II) ion of **3** is six-coordinated in a distorted octahedral geometry by four nitrogen atoms from four 3-amino-1,2,4-triazolate ions and two bromide
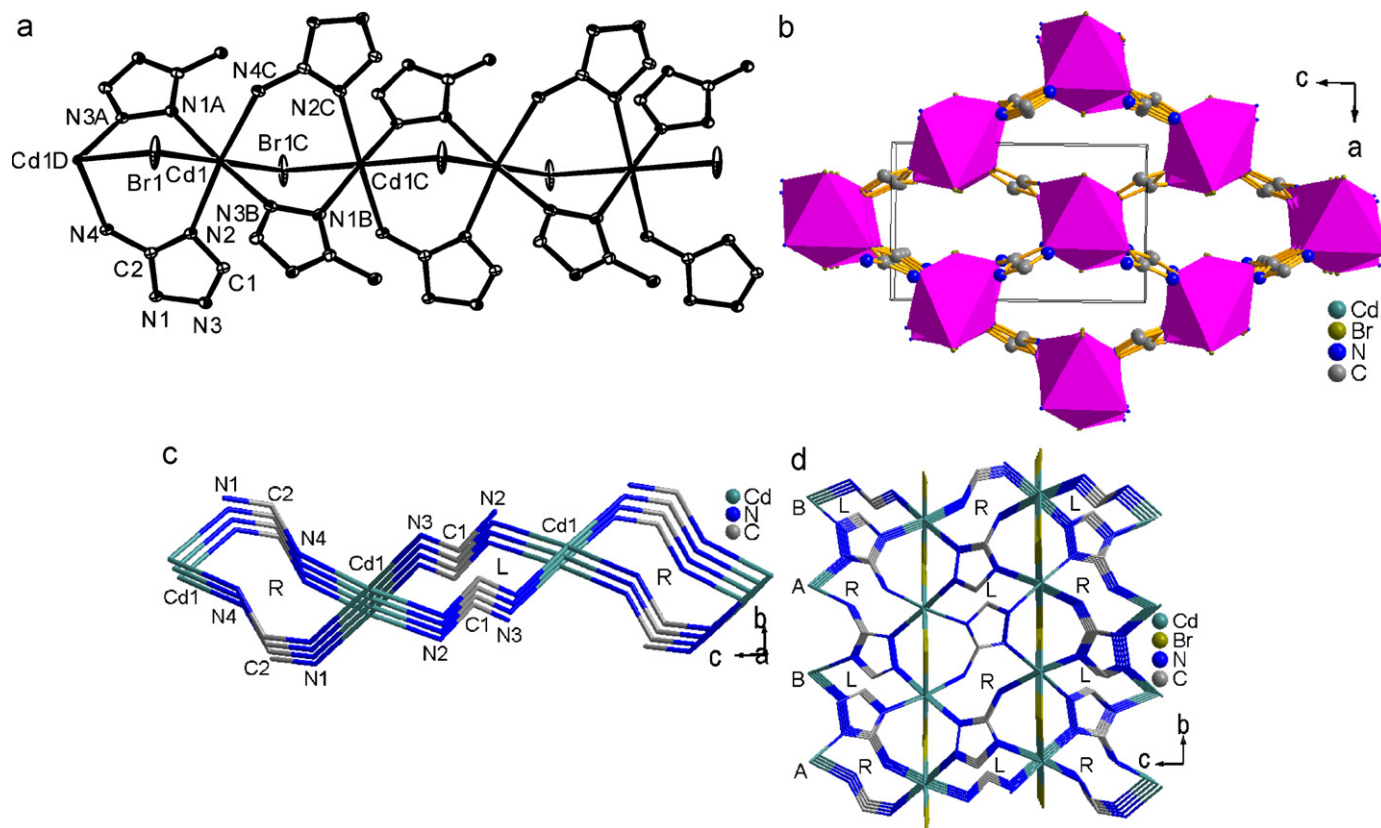
Fig. 3. (a) One-dimensional chain of **3** along the *b*-axis, showing the selected atom-labeling scheme and 30% thermal ellipsoids. (b) View of the 3D structure of **3** from the *b*-axis. (c) View of the alternatively arranged left- and right-handed helical channels. (d) The Stacking of the two-dimensional framework parallel to the *ac* plane into a three-dimensional MOF in a fashion of –ABAB– along the *b*-axis. Hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms: (A) $-x$ -0.5, $-y+1$, $z+0.5$; (B) $x+0.5$, $-y+1.5$, $-z+1$; (C) $-x$, $y+0.5$, $-z+1.5$; and (D) $-x$, y -0.5, $-z+1.5$.

ions. Every two neighboring Cd(II) ions along the *b* axis are connected by one bromide ion and two 3-amino-1,2,4-triazolate ions forming infinite chains (Fig. 3a). The two 3-amino-1,2,4-triazolate ions show different bridging mode in forming the chain. One of them use its two neighboring ring nitrogen atoms to bridge two Cd(II) ions in the chain and the other one use one ring nitrogen atom and one amino group. Every chain interacts with another four adjacent chains by the coordination of the remaining nitrogen atoms in 3-amino-1,2,4-triazolate ions to the Cd(II) ions in the neighboring chains, producing a three-dimensional network of **3** (Fig. 3b). It is noteworthy that the 3-amino-1,2,4-triazolate ion in this compound acts as an unusual μ_4-bridge, different from that in Zn(II) compounds discussed in the context and also those in the reported papers [69,89]. The AmTAZ$^-$ ions in **1** have a twofold disorder with the amino groups free from coordination. This disorder destroys the original asymmetry of AmTAZ$^-$ ions in **1**. However, the coordination of the amino group of AmTAZ$^-$ ion in **3** makes it possible to retain its original asymmetry and gives a chance to construct a homochiral 3D framework.

The most interesting feature of **3** is that it presents two kinds of helical channels with opposite chirality (left- and right-handed) along the crystallographic *a*-axis (Fig. 3c). Both types of helical channels are made from unclosed 8-membered rings with a pitch of 6.4715(11) Å. The left-handed helical channel is formed by a repeated -N3-C1-N2-Cd1-N3-C1-N2-Cd1-sequence and the right-handed helical channel heads with a repeated -N4-C2-N1-Cd1-N4-C2-N1-Cd1- sequence. They show obviously different shape and size. The left-handed helical channels, being like compressed right-handed ones, are thus much smaller than the right-handed ones. The left- and right-handed helical channels are arranged

alternatively parallel to the *ac* plane by sharing the Cd(II) ions to form a two-dimensional network with two kinds of one-dimensional helical channels. The two-dimensional network are further connected in a fashion of –ABAB– along the *b*-axis by triazole rings and bromide ions to construct a homochiral three-dimensional framework (Fig. 3d).

The Cd(II) ion in **4** is coordinated in a trigonal antiprism by two nitrogen atoms from two 3-amino-1,2,4-triazole molecules and four oxygen atoms from four sulfate ions (Fig. 4a). The Cd–O and Cd–N bond lengths are in the range of 2.322(2)–2.542(10) and 2.259(8)–2.294(7) Å (Table 2), respectively. All sulfate anions adopt an unusual μ_4-η^3-tetradentate bridging mode (Scheme 2D) using three oxygen atoms to coordinate to four Cd(II) ions. This means one oxygen atom of sulfate anion behaves as a μ_2-bridge. To the best of our knowledge, this bridging mode of the sulfate anion is unprecedented. Eleven possible coordination modes of the sulfate ion in metal complexes have ever been summarized by the groups of Cheng and Cini [82,90]. Here, we present another four coordination modes of the sulfate anion μ_3-η^4-pentadentate [81,91]; B, μ_4-η^4-pentadentate [92]; C, μ_4-η^3-pentadentate [80]; D, μ_4-η^3-tetradentate) including the new one discussed in the context, as shown in Scheme 2. The connection of Cd(II) ions by the unusual μ_4-η^3-tetradentate bridging sulfate ions results in the construction of two-dimensional CdSO$_4$ sheets parallel to the *ab* plane (Fig. 4b), which is different from the reported μ_3-bridging 2D CdSO$_4$ layer [93,94] and μ_4-η^4-tetradentate bridging 2D CdSO$_4$ structure [83]. In the two-dimensional sheet, some couples of Cd(II) ions are connected by double mono oxygen atoms from two sulfate anions with a distance of 3.8981(7) (CdB···CdF). The other couples are bridged by two sulfate anions acting as μ_2-η^2 bridgings, giving much longer Cd···Cd distances of 5.4096(10)
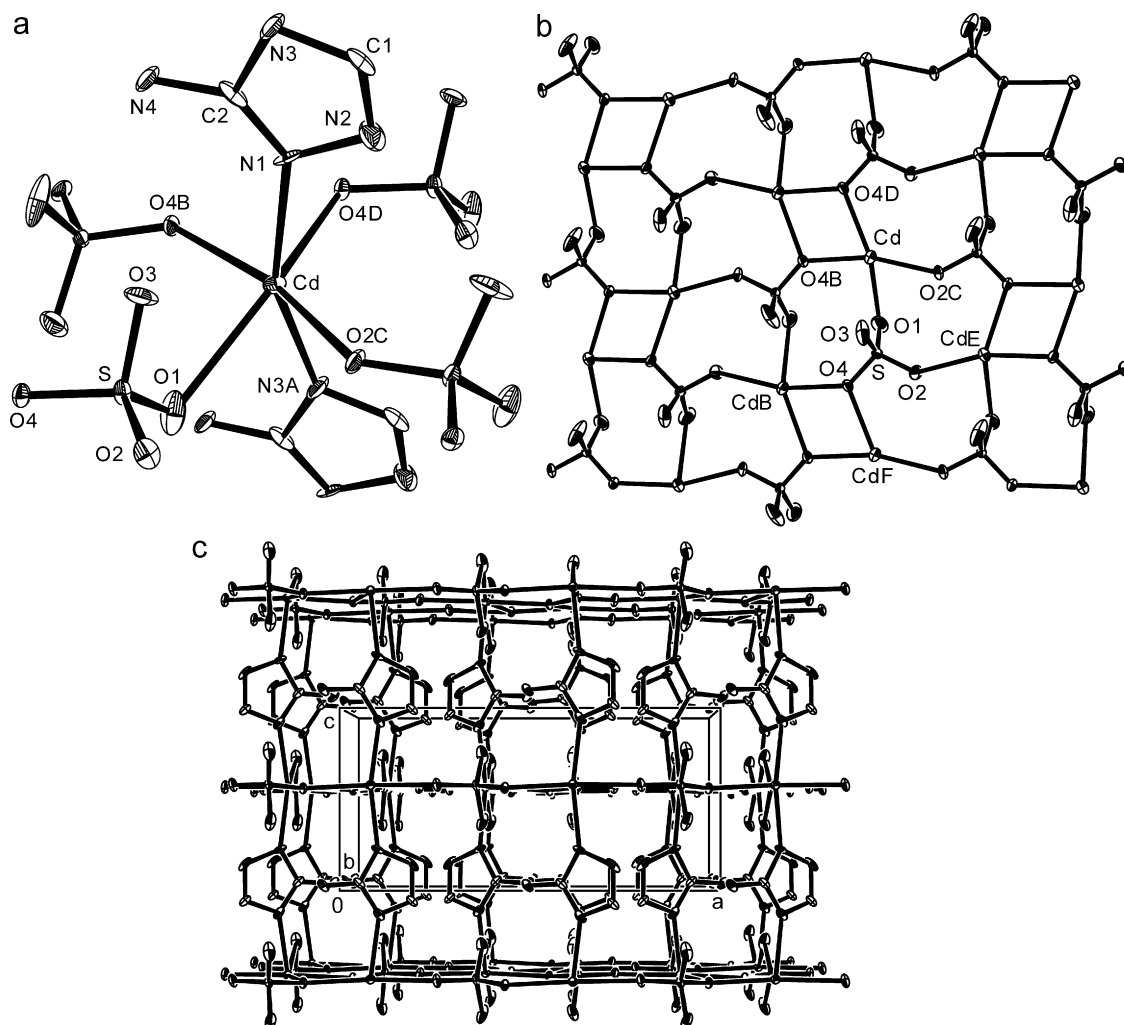
Fig. 4. (a) ORTEP view of the structure of **4**, showing the atom-labeling scheme and 30% thermal ellipsoids. (b) View of the two-dimensional CdSO$_4$ structure of **4** in the *ab* plane. (c) The three-dimensional structure of **4**. Hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms: (A) *x*, *y*, *z*+1; (B) −*x*+1, −*y*+1, *z*; (C) −*x*+1.5, *y* − 0.5, *z*; (D) *x*, *y* −1, *z*; (E) −*x*+1.5, *y*+0.5, *z*; and (F) *x*, *y*+1, *z*.
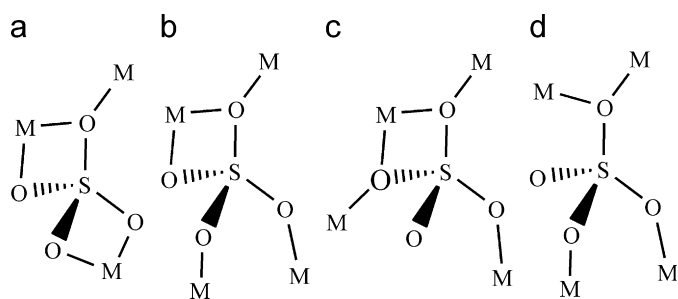
Scheme 2. Some possible coordination modes of the sulfate anion

(Cd···CdB) and 5.0568(9) Å (Cd···CdE and CdE···CdF). The co-ordination of 3-amino-1,2,4-triazole molecules to Cd(II) ions from the neighboring sheets produces a three-dimensional network (Fig. 4c). Thus, the 3-amino-1,2,4-triazole molecule in this compound acts as a neutral μ_2-2,4-bridge, different from those in the other compounds discussed in the context which act as μ_3-bridge or μ_4-bridge in an anionic form.

In this study, the metal ions of Zn(II) and Cd(II) and anions of Br$^-$, CH$_3$COO$^-$, and SO$_4^{2-}$ were applied to manipulate the formation of MOFs under solvothermal conditions. In Zn(II) series the usage of CH$_3$COO$^-$ as anions gave just an open two-dimensional framework with the anions coordinated to the metal

ions restricting the growth of dimensionality. However, an open three-dimensional structure with three kinds of channels was constructed with SO$_4^{2-}$ as anion. These results seem to suggest that the anion has the ability of tuning the formation of different kinds of MOF in the self-assembly process under solvothermal conditions. This was further confirmed by the Cd(II) series. The anions of Br$^-$ help to construct a homochiral three-dimensional Cd(II) framework with two types of helical channels. And the anion of SO$_4^{2-}$ helps to the formation of two-dimensional CdSO$_4$ sheets which are further connected by 3-amino-1,2,4-triazolate ion to form a three-dimensional framework. Comparing the structures of Zn(II) series, the Cd(II) series, one can easily find that the coordination modes of the metal ions could also play an important role in the construction of MOFs.

3.3. Luminescent properties

The emission spectra of the AmTAZH ligand and complexes **2** and **3** in the solid state at room temperature are shown in Fig. 5. Compound **2** features blue fluorescence with a broad emission at 420 nm excited at 300 nm. Excitation of the solid sample **3** with UV ray at 302 nm produces blue fluorescence at 438 nm. The free AmTAZH molecule displays fluorescence at 356 nm in the solid state at room temperature with excitation at 276 nm. The
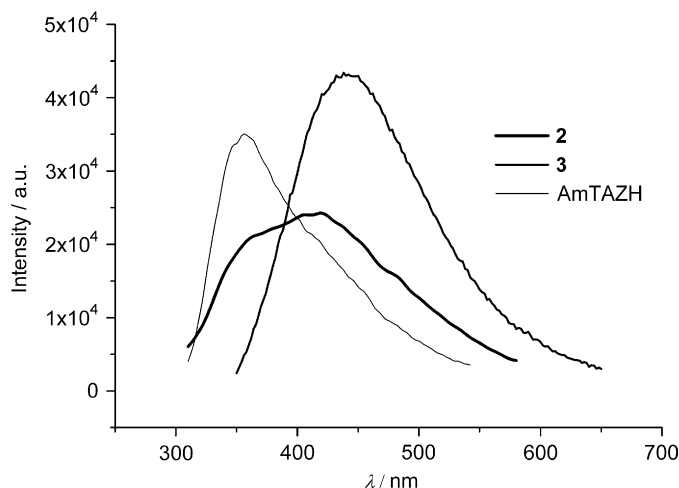
Fig. 5. Emission spectra of **2**, **3** and free 3-amino-1,2,4-triazole (AmTAZH) in the solid state at room temperature.

emission intensity of **2** is a little weaker than that of the free AmTAZH upon the coordination of the deprotonated AmTAZH to Zn^{2+} in the presence of SO_4^{2-}. Compared to the emission at 356 nm ($\lambda_{ex} = 276$ nm) for free ligand the broad emission at 420 and 438 nm for **2** and **3**, respectively, are possibly due to the ligand-to-metal charge-transfer (LMCT) mixed with some intraligand $\pi-\pi^*$ transition of 3-amino-1,2,4-triazolate ion. This assignments are consistent with the cases for 1,2,4-triazole and its derivatives [59,95–97]. The different red shift, shape and intensities of these emission bands in comparison to the ligand are probably due to the differences of the metal ions, the coordination environment around them and even the different structure topologies because the photoluminescence behavior is closely associated with the metal ions and the ligands coordinated around them [93,98–100].

4. Conclusion

The solvothermal reactions of Cd(II) and Zn(II) salts bearing different anions with AmTAZAc produced four Cd(II) and Zn(II) MOFs with the in situ-generated $AmTAZ^-$ ion as ligand. Anion-dependent structural diversity in the isolated polymers was observed. The use of Zn(II) and acetate ions gave two-dimensional open frameworks. The choice of SO_4^{2-} as anion in the Zn(II) system led to the construction of an open three-dimensional MOF based on the building units of octagonal cylinders with three kinds of one-dimensional channels. The $AmTAZ^-$ ligand in the Zn(II) compounds described in this study behaves as μ_3-bridge with the amino group free from coordination. The unusual μ_4-bridging $AmTAZ^-$ in [Cd(AmTAZ)Br] gave a homochiral three-dimensional framework with two types of helical channels (left- and right-handed). The $AmTAZ^-$ ions in [Cd(AmTAZH)SO$_4$] behave as μ_2-2,4-bridges to connect the two-dimensional CdSO$_4$ sheets into a three-dimensional framework. The fluorescent properties of **2** and **3** were tested and it was shown that they exhibit different fluorescent emissions probably due to the differences of the metal ions, the coordination environment around them and even the structure topologies.

5. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 665260, 665261,

665264 and 665265 for complexes **1**–**4**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

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