DE GRUYTER Open Chemistry 2024; 22: 20230211

Research Article

Jing Li, Hongjiang Ren, Jiangtao Li, Liuchang Wang*

Two triazole-based coordination polymers: Synthesis and crystal structure characterization

https://doi.org/10.1515/chem-2023-0211
received December 12, 2023; accepted February 12, 2024

Abstract: Here we reported two new triazole-based coordination polymers (CPs), i.e., $[Zn(Hdatrz)(\mu_2\text{-}O)]_n$ (**1**) together with $[Mn(Hdatrz)(C_2O_4)]_n \cdot n(H_2O)$ (**2**) (Hdatrz = 3,5-diamino-1,2,4-triazole), which were generated under solvothermal conditions. The influence of different metal ions on the structure and properties of CPs was investigated. The CPs' whole structures have been completely characterized by the powder X-ray diffraction, Fourier transform infrared spectroscopy, and thermogravimetric analysis. It is noteworthy that, upon excitation at 390 nm, ligands of compounds 1 and 2, as well as the metal complexes, all exhibit luminescence at 432 nm.

Keywords: coordination polymer, triazole-based, luminescence

1 Introduction

As a novel type of hybrid functional materials, coordination polymers (CPs) have been extensively investigated not only due to their diversified structural components but also due to their extensive applications in magnetism, luminescence, catalysis, gas adsorption/separation, biomedicine, and so forth [1–4]. Although a great achievement in the construction of CPs has been gained during the past few decades, a truly controlled generation of CPs with required structures and performances at the molecular level remains an unattainable goal at present [5,6]. To manipulate the CPs' network structures, it is a requirement for us to reasonably select organic ligands as the "building blocks." Because polycarboxylate ligands have strong chemical stabilities and a large number of coordination modes, they have been applied extensively to combine with metal ions for the creation of CPs to date [7–11]. In addition to polycarboxylate ligands, 1,2,4-triazole ligand and their derivatives, owing to their simple five-membered heterocycle structure, have also been extensively exploited to construct functionalized CPs with charming structures and interesting properties [12–15]. More importantly, the triazole ligands can bridge metal ions in neutral or anionic form during the self-assembly process. The Hdatrz ligand, possessing four potential coordination sites on one plane, has been deemed as a suitable organic ligand for the construction of CPs [16–18]. For example, Yao and his co-workers used the Hdatrz as a bridging ligand to construct a series of luminescent Cd(II) compounds by tuning the auxiliary anions [19].

Although the Hdatrz ligand possesses a variety of coordination patterns, its exploration in the development of novel crystal materials is still largely untapped. Given this current situation, in the present study, the Hdatrz ligand has been selected as an organic building block assembled with transition metal ions to construct new crystal materials. The aim is to enrich the existing crystal database and provide theoretical guidance for the development of novel materials. When choosing zinc (Zn) and manganese (Mn) as metal ions for constructing metal-organic frameworks (MOFs), the aim is to delve into their differences in crystal structure, properties, and potential applications. This selection not only introduces diversity in physical properties but also provides broader possibilities for the multifunctional performance of MOFs, particularly in areas such as catalysis and adsorption. Furthermore, considering the distinct electron structures and coordination chemistry of Zn and Mn, this choice also facilitates in-depth theoretical research to comprehensively understand their interactions in MOFs and their impact on material properties. Overall, the choice of Zn and Mn as metal ions for constructing MOFs is intended to offer a more profound understanding for material design, thereby expanding the potential applications of MOFs across various fields. Successfully,

---

* **Corresponding author: Liuchang Wang**, The Key Laboratory for Surface Engineering and Remanufacturing in Shaanxi Province, Key Laboratory of Chemistry of New Material of Functional Inorganic Composites, School of Chemical Engineering, Xi'an University, Xi'an, Shaanxi, China, e-mail: wlg_112@163.com

Jing Li, **Hongjiang Ren**, **Jiangtao Li:** The Key Laboratory for Surface Engineering and Remanufacturing in Shaanxi Province, Key Laboratory of Chemistry of New Material of Functional Inorganic Composites, School of Chemical Engineering, Xi'an University, Xi'an, Shaanxi, China

two novel CPs were synthesized through the solvothermal reaction of the Hdatrz with $C_2O_4^{2-}$ anion and Mn(II) or Zn(II) salts. XRD analyses displayed that CP **1** possesses a two-dimensional layered structure, and CP **2** exhibits a three-dimensional framework presenting a 4-linked dia-type topological network. In both CPs, the Hdatrz ligand presents two diverse coordination fashions: μ_2-N1, N2 mode for **1** and μ_2-N1, N3 mode for **2**. Further characterization of the crystal properties of **1** and **2** was conducted through fluorescence testing.

2 Experimental

2.1 Materials and instrumentation

In this work, the reagents together with the chemicals utilized were acquired from commercial sources and are of remanufactured-grade quality and ready for immediate use. Through Vario III Elemental Analyzer, the elemental analyzer of N, H, and C was implemented. With PANalytical X'Pert Pro powder diffractometer, powder X-ray diffraction (PXRD) data were recorded at 1.54056 Å Cu/Kα radiation with 0.05° step size. Thermal gravimetric analyzer was implemented on a NETSCHZ STA-449C thermoanalyzer under N_2 atmosphere with a 10°C/min heating rate from 30 to 800°C. The Edinburg FLS920 TCSPC fluorescence spectrophotometer was exploited for luminescent spectra in the solid state.

2.2 Synthesis of $[Zn(Hdatrz)(\mu_2\text{-}O)]_n$ (1) and $[Mn(Hdatrz)(C_2O_4)]_n{\cdot}n(H_2O)$ (2)

References to the preparation of compounds 1 and 2 are provided below, with typical procedures as follows [20,21]. A mixture formed by 0.1 mmol Hdatrz, 0.1 mmol $Zn(NO_3)_2{\cdot}6H_2O$, 4 mL H_2O, and 2 mL N,N-dimethylformamide (DMF) was heated in a small glass vial (20 mL) at 110°C for 5 days. **1**'s colorless block crystals were gathered after cooling to room temperature (RT) at a 2°C/min rate in a yield of 36% in accordance with $Zn(NO_3)_2{\cdot}6H_2O$. IR (KBr, cm^{-1}): 465 m, 523 m, 716 s, 785 s, 844 w, 1,056 m, 1,128 m, 1,236 vs, 1,409 s, 1,467 s, 1,648 vs, 1,694 s, 1,711 s, 1,763 s, 1,911 w, 2,689 w, 2,849 m, 2,970 m, 3,075 m, 3,309 m. Anal. Calcd. (%) for $C_2H_5ZnN_5O$ (180.50): N, 38.78; H, 2.77; C, 13.30. Found (%): N, 38.82; H, 2.79; C, 13.28.

A mixture formed by 0.1 mmol Hdatrz, 0.1 mmol Mn $(OAc)_2{\cdot}4H_2O$, 0.1 mmol $Na_2C_2O_4$, 2 mL DMF, and 4 mL H_2O was heated in a small glass vial (23 mL) at 110°C for 72 h. **2**'s colorless block crystals were acquired after cooling to RT at a 2°C/min rate in a yield of 46% in accordance with Mn $(OAc)_2{\cdot}4H_2O$. IR (KBr, cm^{-1}): 469 m, 499 m, 736 s, 785 s, 846 w, 1,059 m, 1,178 m, 1,256 vs, 1,419 s, 1,437 s, 1,623 vs, 1,689 s, 1,701 s, 1,759 s, 1,901 w, 2,579 w, 2,849 m, 2,970 m, 3,075 m, 3,309 m, 3,430 m. Anal. calcd. (%) for $C_4H_7MnN_5O_5$ (260.09): N, 26.91; H, 2.69; C, 18.46. Found (%): N, 26.87; H, 2.72; C, 18.47.

2.3 X-ray crystallography

A computer-controlled Rigaku Mercury CCD diffractometer was equipped with 0.71073 Å graphite-monochromated MoKα radiation, and employed to gather the CPs' single crystal data at 293 K. The solution and refinement of CPs' structures were implemented with the direct method through *SHELXT* as well as the full-matrix least square technique on the basis of F^2 via *SHELXL*-2014 [22]. CPs' crystallographic data along with their structural refinements are given in Table 1.

3 Results and discussion

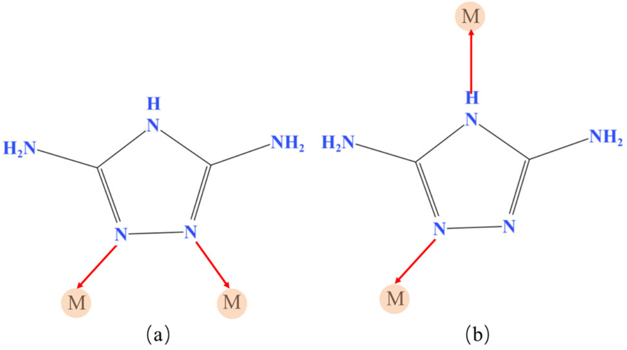
3.1 Crystal structure of compound 1

Compound **1** is crystallized in an orthorhombic system with a space group *of Cmce*. And **1**'s fundamental building

Table 1: CPs' crystal data and their structure refinements

Sample	1	2
Formula	$C_2H_5ZnN_5O$	$C_4H_7MnN_5O_5$
Fw	180.50	260.09
Crystal system	Orthorhombic	Monoclinic
Space group	*C*mce	*P*2$_1$/c
a (Å)	19.342(3)	9.553(3)
b (Å)	5.4335(9)	14.1640(17)
c (Å)	10.0860(13)	9.286(2)
α°	90	90
β°	90	118.495(7)
γ°	90	90
Volume ($Å^3$)	1060.0(3)	1104.3(4)
Z	8	4
Density (calculated)	2.262	1.564
Abs. coeff. (mm^{-1})	4.541	1.207
Total reflections	3,735	8,125
Unique reflections	624	2,493
Goodness of fit on F^2	1.159	1.077
Final *R* indices [$I > 2$ sigma(I^2)]	$R = 0.0314$, $wR_2 = 0.0695$	$R = 0.0564$, $wR_2 = 0.1668$
R (all data)	$R = 0.0349$, $wR_2 = 0.0714$	$R = 0.0636$, $wR_2 = 0.1776$

unit consisted of a half μ_2-O anion, a half Hdatrz ligand as well as a half Zn(II) ion. The Zn1 ion coordination polyhedron, as presented in Figure 1a, may be represented as a tetrahedron, completed via two μ_2-O anions and two N atoms derived from two diverse Hdatrz ligands. When in contrast to previously documented Zn(II)-based CPs, the lengths between Zn–O and Zn–N are within the normal range. The Hdatrz ligands in μ_2-N1, N2 mode (Scheme 1a), and the μ_2-O anions synergistically bridge all Zn(II) ions together, creating a two-dimensional layer along the crystallographic plane *bc* (Figure 1b). By calculation using the PLATON program, no intermolecular or intramolecular hydrogen bonds were found. Thus, these 2D layers in a parallel mode are stacked together *through* weak van der Waals interactions (Figure 1c).



(a) (b)

Scheme 1: Coordination fashions of Hdatrz ligand: (a) μ_2-N1, N2 mode for **1** and (b) μ_2-N1, N3 mode for **2.**

3.2 Crystal structure of compound 2

Compound **2** is crystallized in the monoclinic space group of $P2_1/c$, and its asymmetric unit is composed of two halves $C_2O_4^{2-}$ anions, a Hdatrz ligand, a Mn(II) ion, along with a lattice molecule of water. Figure 2a displays that the Mn1 ion coordination environment consists of four O atoms derived from two $C_2O_4^{2-}$ anions together with two N atoms coming from two ligands of the Hdatrz, creating slightly twisted octahedrons with the distances of Mn–N and Mn–O in the range of 2.202(3)–2.215(3) Å and 2.160(3)–2.223(2) Å, separately. In **2**, the Hdatrz ligand shows another μ_2-N1, N3 coordination mode (Scheme 1b). Such a bridging mode enables Hatraz ligands to connect Mn(II) ions into a 1D infinite chain with neighboring Mn…Mn 6.38 Å away from each other (Figure 2b). Finally, these adjacent 1D infinite chains are bridged by the $C_2O_4^{2-}$ anions, affording the three-dimensional framework of CP **2** (Figure 2c). Mn(II) ions were viewed as 4-linked nodes, $C_2O_4^{2-}$ anions and the Hdatrz ligands were regarded as linear linkers, the **2**'s 3D frameworks can be topologically reduced into a 4-linked dia-type network with $\{6^6\}$ point symbol.

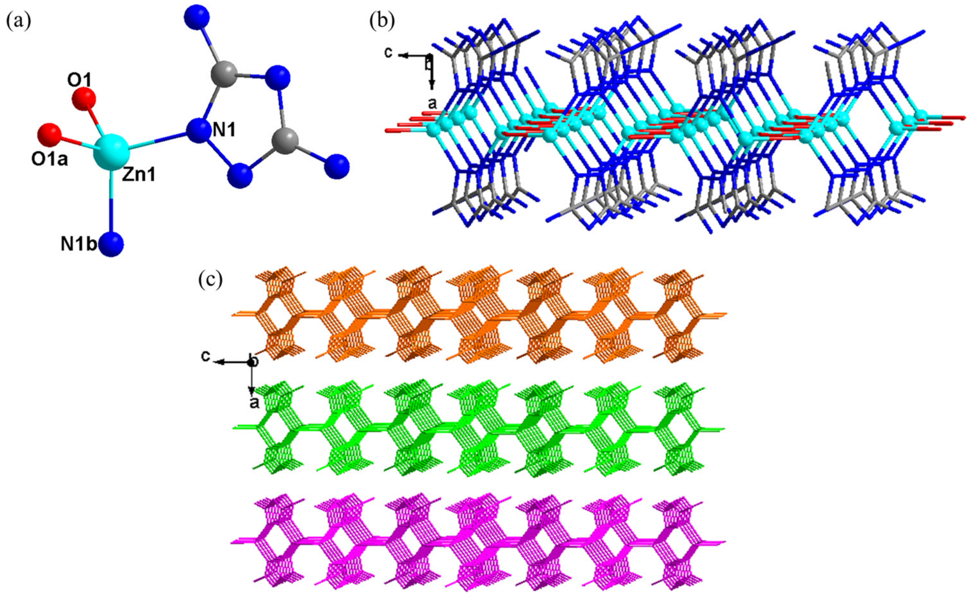


Figure 1: (a) Perspective view of coordination setting of Zn(II) ion in CP **1**. (b) **1**'s two-dimensional layered structure. (c) Weak Van der Waals-induced interlayer stacking of three-dimensional supramolecular frameworks for CP **1**.

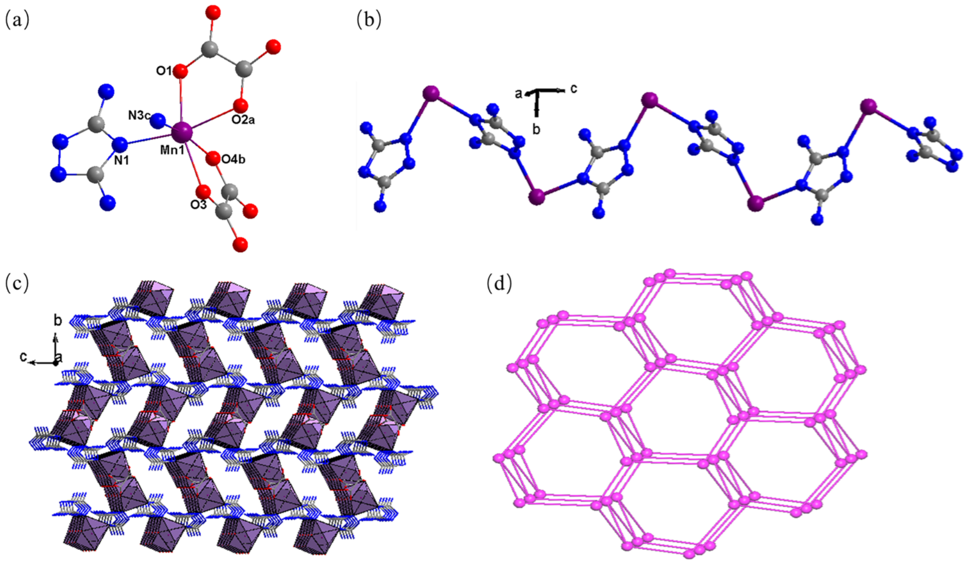


Figure 2: (a) Perspective view of coordination setting of Mn(II) ion in CP **2**. (b) The one-dimensional infinite chain constructed via Mn(II) ions and the Hdatrz ligand. (c) **2**'s three-dimensional framework. (d) Schematic diagram of the 4-linked dia topological network for CP **2**.

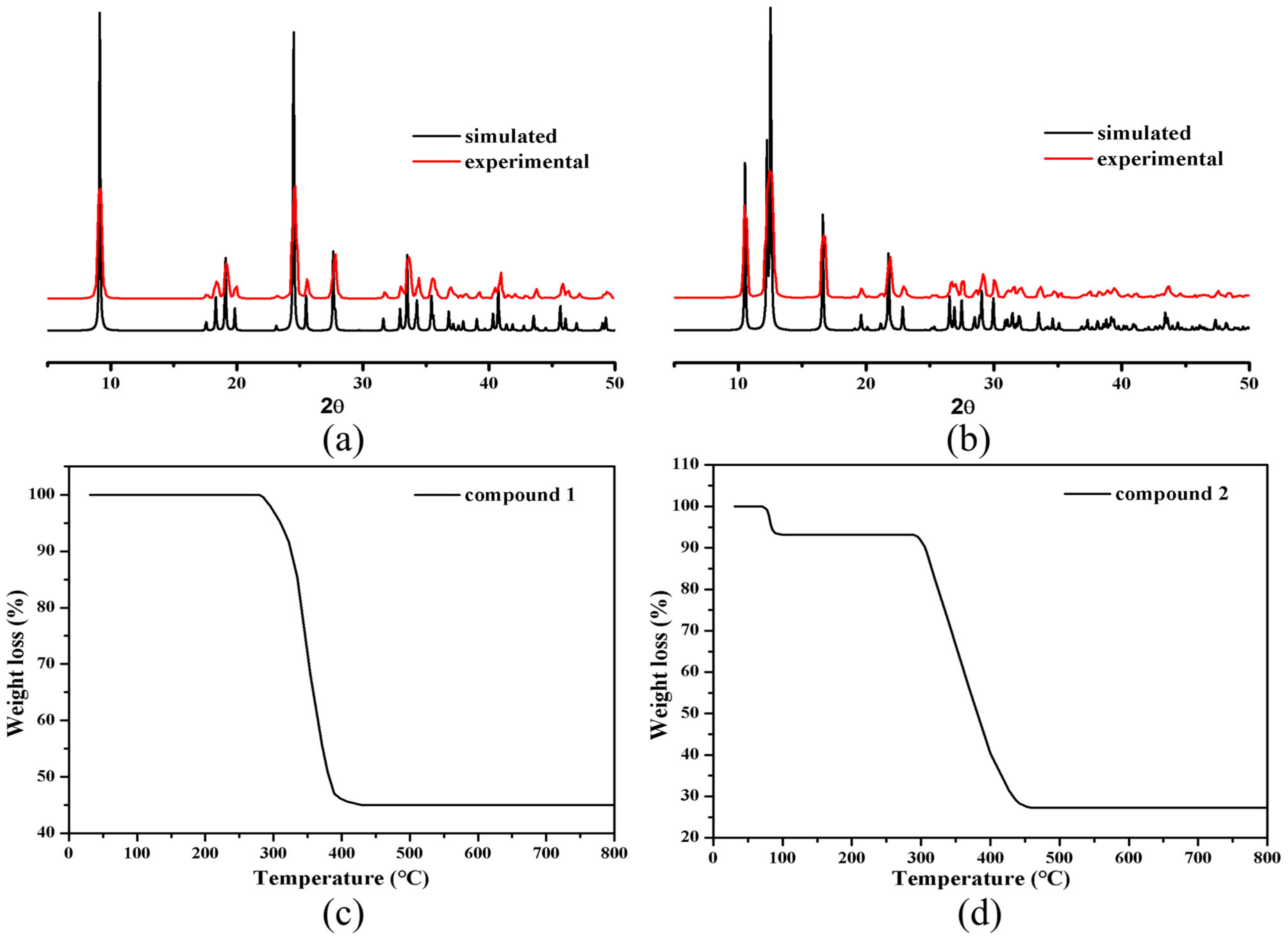


Figure 3: (a) and (b) represent the comparison between simulated and experimental PXRD data for compounds **1** and **2**, respectively. (c) and (d) depict the thermal stability test results for compounds **1** and **2**, respectively.

3.3 PXRD patterns and thermogravimetric analyses (TGA)

PXRD was conducted to confirm the CPs' phase purity. As displayed in Figure 3a and b, the locations and shapes of the diffraction peaks of calculated patterns on the basis of single crystal diffraction data and the experimental patterns agree well, indicating the produced bulk solids' high phase purity for **1–2**. These results are consistent with the description in relevant literature to further indicate that it is the target product [23,24].

Their structural thermostabilities were also assessed by applying the TGA analysis under an N_2 atmosphere. The analysis results are plotted in Figure 3c and d. For **1**, its structure shows good stability at 280°C, from which rapid weight reduction started since the organic ligand decomposition. For CP **2**, its structure reveals a two-stage process of weight loss: the first step happened between 70 and 100°C and was attributed to the loss of the free molecules of water (obsd: 6.87%, calcd: 6.92%) and the second step happened between 288 and 460°C and was related to the burning of the organic ligand. Based on the above research results, it is evident that CPs constructed with different metal ions have a significant impact on their structure and thermal stability.

3.4 Fluorescence tests of compounds 1 and 2

Transition metal-organic CPs have been extensively studied due to their intriguing luminescent properties [25,26]. In this study, the solid-state luminescence emission spectra of CPs **1–2**, along with the corresponding free ligand, were determined at RT (Figure 4). The emission spectrum of the Hdatrz ligands exhibits a maximum peak at approximately 432 nm under 390 nm excitation, primarily attributed to $\pi^* \rightarrow \pi/n$ charge transitions. Upon stimulation at 390 nm, **1** shows an emission band at about 438 nm, while 2 exhibits an emission band around 436 nm. The emission spectra of the CPs are slightly red-shifted (6 nm for **1** and 4 nm for **2**) compared to that of the free Hdatrz ligand. Due to the distinct d^{10} electronic structure and stable half-filled d^5 electronic configuration of Mn(II) and Zn(II) ions, they are challenging to either oxidize or reduce. Consequently, the luminescent behaviors of compounds **1** and **2** can be explained as metal ions perturbing intraligand $\pi^* \rightarrow \pi/n$ charge transfer transitions [27]. It is noteworthy that the luminescence intensities of **1** and **2** surpass that of the Hdatrz ligand, primarily attributed to the coordination of the Hdatrz ligand with metal centers, leading to increased ligand rigidity.

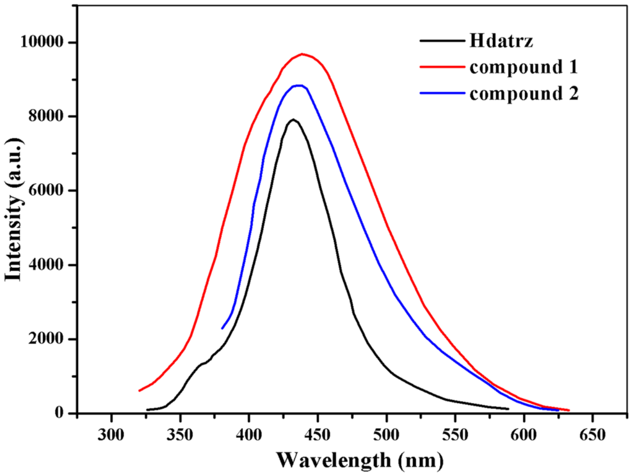


Figure 4: At room temperature, emission spectra were recorded for compounds **1** and **2**, as well as free Hdatrz, in the solid state.

4 Conclusions

In conclusion, two novel triazole-based transition metal CPs with the formulae $[Zn(Hdatrz)(\mu_2\text{-}O)]_n$ (**1**) and $[Mn(Hdatrz)(C_2O_4)]_n \cdot n(H_2O)$ (**2**) were successfully synthesized through a one-pot self-assembly reaction involving Hatrz ligand, Mn(II) or Zn(II) ions, and Hatrz and $C_2O_4^{2-}$ anions under solvothermal conditions. A detailed study was conducted on the structure and properties of CPs constructed from two different metal ions. For **1**, the Hdatrz ligands and μ_2-O anions bridge all Zn(II) ions into a 2D layer. For **2**, the $C_2O_4^{2-}$ anions and Hdatrz ligands link all Mn(II) ions into a 3D framework showing a dia-type topological network. Moreover, compounds **1** and **2** are luminescent at room temperature. However, due to limitations in the experimental conditions, further exploration was not conducted. In future work, we plan to delve deeper into its applications.

Funding information: The research was supported by Research on the Application of Inorganic Nanofunctional Composite Materials (XAWLKYTD202312), Natural Science Basic Research Plan in Shaanxi Province of China (2022JM-075), and three-year action plan project of Xi'an University (21XJZZ0001-11).

Author contributions: Jing Li and Liuchang Wang synthesized and characterized the compounds; Hongjiang Ren and Jiangtao Li performed other experiments.

Conflict of interest: Authors state no conflict of interest.

Ethical approval: The conducted research is not related to either human or animals use.

Data availability statement: The data used to support the findings of this study are included within the article.

References

[1] Thoonen S, Hua C. Chiral detection with coordination polymers. Chem-Asian J. 2021;16:890–901.

[2] Lei N, Wang H, Fan L, Chen X. Highly luminescent soft aggregates and films assembled by amphiphilic polyoxometalate complex in a polymerizable aprotic ionic liquid. J Photochem Photobiol A. 2014;448:115290.

[3] Tay HM, Kyratzis N, Thoonen S, Boer SA, Turner DR, Hua C. Synthetic strategies towards chiral coordination polymers. Coord Chem Rev. 2021;435:213763.

[4] Wan YM, Hong QL, Zhang HX, Zhang J. Synthesis of supramolecular boron imidazolate frameworks for CO_2 photoreduction. Inorg Chem. 2020;59:17851–5.

[5] Zhang S, Lu L, Wang J, Tan X, An B, Singh A, et al. Photocatalytic and magnetic properties two new Co(ii) cluster-based metal-organic frameworks. Inorg Chem Commun. 2020;111:107563.

[6] Zhang S. Anion-directed two cadmium(ii) metal-organic frameworks based on bis(imidazol-1-yl)methane with diverse supramolecular structures and luminescence properties. J Mol Struct. 2021;1230:129871.

[7] Feng YQ, Zhong ZG, Chen SY, Liu KC, Meng ZH. Improved catalytic performance toward selective oxidation of benzyl alcohols originated from new open-framework copper molybdovanadate with a unique V/Mo ratio. Chem Eur J. 2023;29:e202302051.

[8] Bai H, Zhang D, Zhang R, Wang J, Zeng S, Fan Y, et al. A novel metal-organic framework using heterometallic tetranuclear cluster as secondary building block and isophthalic acid as ligand. Chem Res Chin U. 2016;32:709–12.

[9] Kong CY. Syntheses, crystal structure and luminescent properties of a novel Mn(ii) coordination polymer based on 1,3,5benzenetricarboxylic acid. Chin J Struct Chem. 2018;37:988–94.

[10] Wang XF, Guo XY, Liu T. Two two Co(ii) based coordination polymers constructed from π-electron rich polycarboxylate aryl ether ligand: structural insights and photocatalytic dye degradation. Chin J Struct Chem. 2021;40:722–8.

[11] Yang JX, Qin YY, Zhang X, Yao YG. Construction of three new metal-organic frameworks with distinct SBUs: trinuclear $\{Cd_3(COO)_6\}$ clusters, inorganic -Cd-O-Cd- chains, and heterometallic trinuclear $\{Cd_2Ba(COO)_4\}$ clusters. J Coord Chem. 2016;69:1568–76.

[12] Wu MZ, Ma ZL, Shi JY, Shi XJ, Tian L. Cationic Cd(ii) metal-organic framework based on tetrakis(1,2,4-triazol-1-yl)methane. J Coord Chem. 2019;72:3495–501.

[13] Lei N, Li W, Zhao D, Li W, Liu X, Liu L, et al. A bifunctional luminescence sensor for biomarkers detection in serum and urine based on chemorobust nickel(ii) metal-organic framework. Spectrochim Acta A. 2024;306:123585.

[14] Smirnova KS, Lider EV, Sukhikh TS, Berezin AS, Potapov AS. Cadmium coordination compounds with flexible ligand 1,3-bis (1,2,4-triazol-1-yl)propane: synthesis, structure and luminescent properties. Polyhedron. 2020;177:114286.

[15] Ge H, Liu K, Yang Y, Li B, Zhang Y. Synthesis, structures and luminescence properties of three manganese coordination polymers with bis(1,2,4-triazol-1-ylmethyl)benzene. Inorg Chem Commun. 2008;11:260–4.

[16] Li W, Li W, Liu X, Zhao D, Liu L, Yin J, et al. Two chemorobust cobalt (ii) organic frameworks as high sensitivity and selectivity sensors for efficient detection of 3-nitrotyrosine biomarker in serum. Cryst Growth Des. 2023;23:7716–24.

[17] Wei ZW, Mu X. Organic carboxylate ligands tuned structural variations of three new Cd(ii) coordination polymers with guanazole as co-ligand. J Inorg Organomet Poly. 2015;25:1425–33.

[18] Zhao HX, Dong YL, Liu HP. Two new luminescent Zn(ii) compounds constructed from guanazole and aromatic polycarboxylate ligands. J Mol Struct. 2016;1105:112–7.

[19] Zhang RB, Li ZJ, Qin YY, Cheng JK, Zhang J, Yao YG. Synthesis, structure, and physical properties of a new anions-controlled Cd(ii)-guanazole (3,5-diamino-1,2,4-triazole) hybrid family. Inorg Chem. 2008;47:4861–76.

[20] Mihaela D, Scutaru ALC, Roman G. Detection of nitroaromatics by a Zn(ii)-containing coordination polymer derived from a 1,2,3-triazole-based tricarboxylate ligand. J Mol Liq. 2023;386:122457.

[21] Ma QC, Yue TC, Cao QW, Xie ZB, Dong QW, Wang DZ, et al. Study on magnetic and dye adsorption properties of five coordination polymers based on triazole carboxylic acid ligands. J Mol Struct. 2023;1284:135379.

[22] Sheldrick GM. Crystal structure refinement with SHELXL. Acta Crystallogr Sect C: Struct Chem. 2015;71:3–8.

[23] Nikolia L, Giannopoulou E, Charitos A, Parthenios J, Malina O, Tangoulis V. Observation of two-step spin transition in iron(ii) 4-amino-1,2,4-triazole based spin crossover nanoparticles. Dalton Trans. 2023;52:2937–41.

[24] Robb MG, Brooker S. Incorporation of switchable inorganic building blocks into heterometallic coordination polymers. Cyst Growth Des. 2023;23:1848–59.

[25] Chen SC, Yu RM, Zhao ZG, Chen SM, Zhang QS, Wu XY, et al. A series of polynuclear complexes of d^{10} metals with interesting luminescent properties. Cryst Growth Des. 2010;10:1155–60.

[26] Ma LF, Wang LY, Hu JL, Wang YY, Yang GP. Syntheses, structures, and photoluminescence of a series of d^{10} coordination polymers with R-isophthalate ($R = -OH, -CH_3$, and $-C(CH_3)_3$). Cryst Growth Des. 2009;9:5334–42.

[27] Bera M, Jana SK, Rana A, Chowdhuri DS, Debdoot H, Liu CM, et al. Two new coordination polymers of manganese(ii) with O/O- and N/O-donor ligands: synthesis, structure, luminescence study and thermal behavior. J Inorg Organomet Polym. 2013;23:736–42.