



Solvothermal Synthesis, Crystal Structure and Luminescent Property of Metal-Organic Frameworks with New Topology Built from Tetrazole Ligand

CHENGHUA ZENG

School of Resource and Environmental Engineering, Panzhihua University, Panzhihua City 617000, Sichuan Province, P.R. China

Corresponding author: E-mail: zch1963111@163.com

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A novel two-dimensional (2D) Zn(II) metal-organic frameworks $[Zn_2(H_2bdc)(ATZ)_{2.5}(H_2O) \cdot 2(H_2O)]$ (**1**; H_2bdc = 1,4-benzenedicarboxylate; ATZ = 5-aminotetrazole) has been solvothermally prepared and structurally characterized by single-crystal X-ray diffraction, which shows that compound **1** crystallized in the orthorhombic space group $Pbcm$ with $a = 10.2647(3) \text{ \AA}$, $b = 26.1194(12) \text{ \AA}$, $c = 27.3699(13) \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 7338.1(5) \text{ \AA}^3$ and $Z = 4$. Compound **1** exhibits a layered structure with 3,4-connected new topology, and further stacking of layers leads to a 3D supramolecular framework. The thermalgravimetric behaviour and luminescent properties of **1** have been also investigated. The compound exhibits an intense photoluminescence emissions at 450 nm ($\lambda_{exc} = 375 \text{ nm}$).

Keywords: Solvothermal, Crystal structure, Luminescent, Metal-organic frameworks, Tetrazole.

INTRODUCTION

Attention has been focused on the rapidly expanding field of supramolecular chemistry and crystal engineering of the metal-organic frameworks (MOFs) during the past decades because of their intriguing network topologies as well as their potential application as functional materials in many areas such as catalysis, magnetism, gas storage and separation, nonlinear optics, drug delivery, sensing, *etc.*¹⁻¹⁵. The range and variety of the self-assembling structures relies on the presence of suitable metal-ligand interactions and supramolecular contacts, *i.e.*, hydrogen bonding, $\pi \cdots \pi$ stacking interactions and other weak interactions.

Exploring highly symmetrical multitopic ligands and suitable metal salts to construct supramolecular architectures is of great interest. Tetrazoles with various interesting coordination chemistry and a strong networking ability have been extensively used as organic linkers for construction novel MOFs. Remarkably, as aminotetrazoles have highest content of nitrogen among the organic substances and show surprisingly high thermal stabilities, 5-amino-1H-tetrazole (ATZ) also received most attention in the literature and is used as a gas generator and key intermediate in many organic synthesis¹⁶⁻¹⁹.

Although tetrazoles were used to assemble many MOFs with intriguing structures and properties, they were rarely utilized as multifunctional organic linkers mixed with carboxylate group for generating MOFs. The mixed-ligand assembly approach has been widely adopted for the generation of new

networks. Accordingly, our efforts on assembling novel structural MOFs are using tetrazoles and carboxyl mixed-ligands. In this work, ATZ with 1,4-benzenedicarboxylate (H_2bdc) were employed to construct a photoluminescent metal-organic frameworks. The compound, namely $[Zn_2(H_2bdc)(ATZ)_{2.5}(H_2O) \cdot 2(H_2O)]$, characterized by single-crystal X-ray diffraction analysis, powder X-ray diffraction and thermogravimetric analysis. Furthermore, the luminescent property of complex **1** was investigated.

EXPERIMENTAL

All commercially available reagents and solvents purchased were used without further purification. Thermal stability studies were carried out on a NETSCHZ STA-449C simultaneous TG-DSC thermoanalyzer with a heating rate of $15 \text{ }^\circ\text{C min}^{-1}$ in N_2 atmosphere. X-ray powder diffraction (XRD) patterns of **1** were collected on a MiniFlex-II diffractometer.

Preparation of compound: A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.1586 g, 0.54 mmol), 1,4-dimethylpiperazine (0.0350 g 0.31 mmol), 5-amino-1H-tetrazole (ATZ , 0.0531 g, 0.63 mmol), 1,4-benzenedicarboxylate (H_2bdc , 0.0509 g, 0.31 mmol), tetramethylammonium bromide (0.0298 g 0.20 mmol), 3-amino-1-propanol (0.50 g, 5.56 mmol), methanol (3 mL) and N,N -dimethylacetamide (DMA, 3 mL) in a 20 mL Teflon-lined stainless steel vessel was heated at $100 \text{ }^\circ\text{C}$ for 72 h, and then cooled to room temperature. The resulting colourless transparent crystals were obtained, washed using acetone, and dried at room temperature.

X-crystallography: Suitable single crystals of **1** [$\text{Zn}_2(\text{H}_2\text{bdc})(\text{ATZ})_{2.5}(\text{H}_2\text{O}) \cdot 2(\text{H}_2\text{O})$] were carefully selected under an optical microscope and glued to thin glass fibers. Whereafter, single-crystal X-ray diffraction analyses were performed on a computer-controlled XCalibur E CCD diffractometer with graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda_{\text{MoK}\alpha} = 0.71073 \text{ \AA}$) at $T = 293.2 \text{ K}$. Empirical absorption corrections were made using the SADABS program²⁰. The structures were solved using the direct method and refined by full-matrix least-squares methods on F^2 by using the SHELX-97 program package²¹. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms attached to carbon or nitrogen atoms were fixed at their ideal positions.

RESULTS AND DISCUSSION

Single crystal X-ray analysis revealed that compound **1** crystallizes in the space group $Pbcm$. In the structure of **1**, the asymmetric unit consists of two independent Zn centers with the same coordination geometries, two and a half 5-amino-1*H*-tetrazole, one 1,4-benzenedicarboxylate, one coordinated water molecule, and two lattice water molecule. As illustrated in Fig. 1a, two metal Zn centers adopt identical coordination modes. Zn1 center is four-coordinate with tetrahedron geometric configuration by one carboxylate oxygen atom from one H_2bdc ligand, three nitrogen atoms of three ATZ ligands, while Zn2 center is also four-coordinate with tetrahedron geometric configuration: Zn2 is four-coordinated by two oxygen atoms from water molecule and H_2bdc ligand, respectively, two nitrogen atoms of two ATZ ligands. The Zn-N lengths are in the range of 1.988-2.032 \AA , and the Zn-O bond lengths vary from 1.930 to 2.010 \AA .

In compound **1**, each ATZ ligand connects two Zn (Zn1 and Zn2) ions to form a chain, while the adjacent two chains are further linked by ATZ connecting two Zn centers resulting in a 1D neutral polymeric double chain (Fig. 1b). These 1D double chains are bridged by two monodentate carboxylate groups from one H_2bdc ligand, generating a two-dimensional framework. Furthermore, the parallel stacking of the layers results in a three-dimensional framework (Fig. 2a), and there are no obvious interactions between the layers (Fig. 2b). From the viewpoint of topology, each simple framework in **1** can be topologically represented as a 2-nodal (3,4)-connected net by reducing each Zn ion as a 3- and 4-connected node, the ATZ and bdc ligands as linear connectors, which the framework can be abstracted as a 2-nodal 3,4-connected new topological net (Fig. 3).

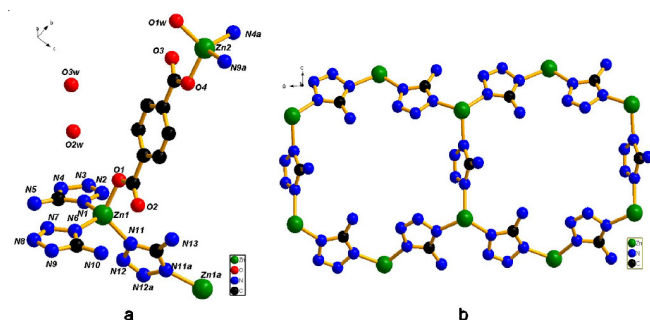


Fig. 1. (a) Coordination environment around the Zn atoms in **1**; (b) the neutral polymeric double chain of **1**. Hydrogen atoms are omitted for clarity

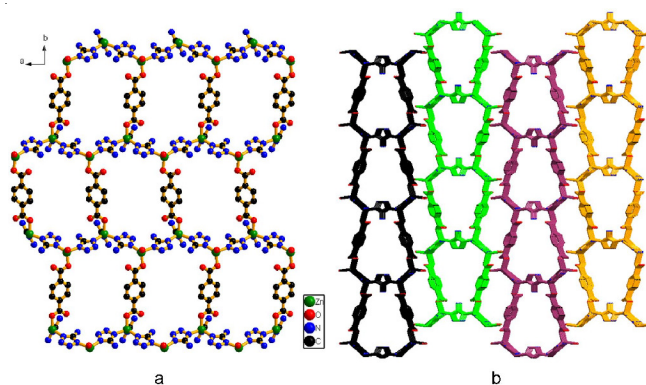


Fig. 2. (a) Perspective view of the two-dimensional sheet of **1**; (b) The three-dimensional framework of **1** formed by the parallel stacking of the 2D layers. Hydrogen atoms are omitted for clarity

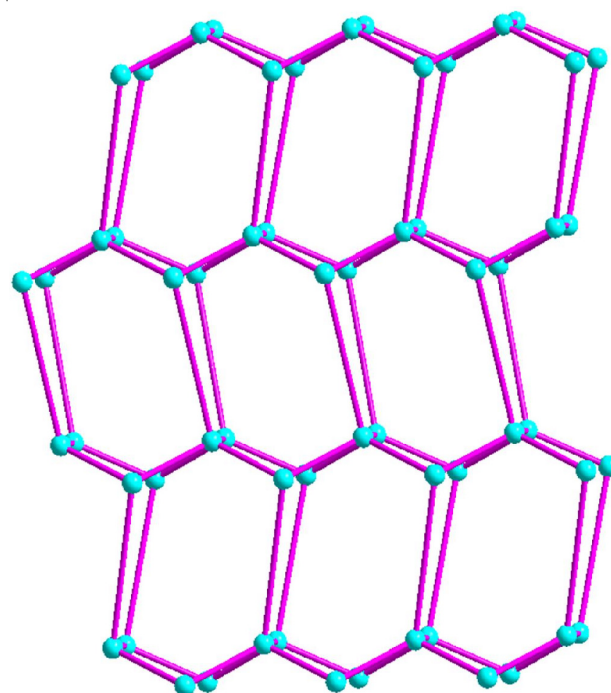


Fig. 3. Topological representation of the 3,4-connected new net in **1**

Thermogravimetric analysis: The phase purity of **1** was confirmed by similarities between its simulated and experimental powder X-ray diffraction (Fig. 4a). The experimental powder X-ray diffraction patterns correspond well with the simulated result from the single crystal data, indicating phase purity of **1**.

The thermal stabilities of **1** was investigated on polycrystalline samples by the thermogravimetric analyses (TGA) under a N_2 atmosphere with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ from 30 to $650 \text{ }^\circ\text{C}$ (Fig. 4b). The thermogravimetric curve of **1** is unchanged up to $100 \text{ }^\circ\text{C}$. Beyond this temperature, the first weight loss of 4.04 % from 100 to $130 \text{ }^\circ\text{C}$ corresponds to the loss of water molecules. The second step of weight loss from 160 to $220 \text{ }^\circ\text{C}$ corresponds to the removal of the dissociative DMA solvents. The observed weight loss of 10.86 % is in agreement with the calculated value of 10.61 %. Above $220 \text{ }^\circ\text{C}$, the weight loss is due to the decomposition of the ATZ and H_2bdc organic ligands, accompanying the collapse of the whole framework.

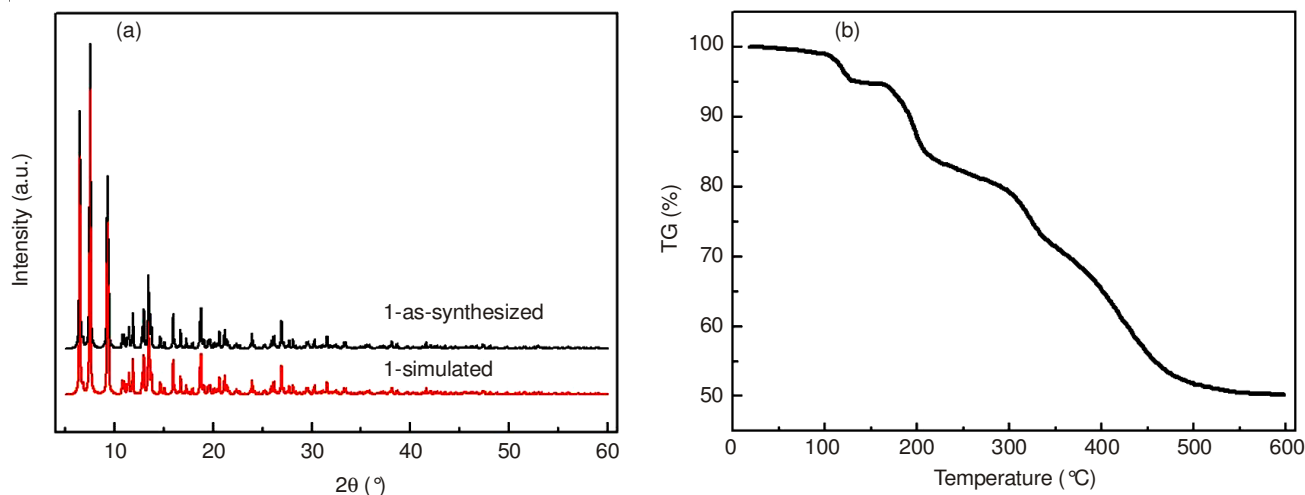


Fig. 4. (a) Characterization of bulk phase of **1** by XRD; (b) the TGA plots of **1**

Luminescent properties: Luminescence compounds are currently of great interest due to their various applications in chemical sensors, photochemistry, and electroluminescence displays²²⁻²⁷. Many studies have shown that MOFs with Zn ions exhibit photoluminescence properties. The luminescent emission spectrum of compound **1** in the solid state at room temperature is shown in Fig. 5. Intense photoluminescence emissions for **1** is observed at 450 nm ($\lambda_{\text{ex}} = 375$ nm), while the ATZ and H₂bdc ligands show luminescence in the range of 480-550 nm and 350-420 nm, respectively.

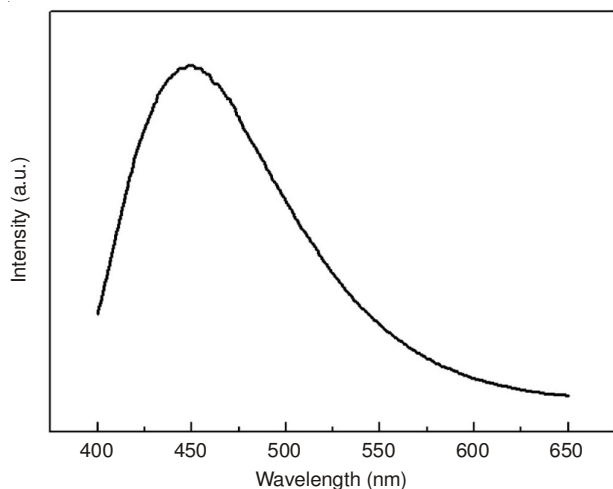


Fig. 5. Luminescent emission spectra of **1** in the solid state at room temperature

Since the fluorescence is basically caused by intra ligand electron transition in complexes containing Zn(II) ion which adopt d^{10} configuration, the fluorescent properties of organic ligands will directly and greatly determine the fluorescence of their corresponding coordination compounds. The emission band of compound **1** is significantly different compared to those of the free organic ligands. Thus, the emission band of compound **1** is attributed to ligand-to-metal-charge-transfer (LMCT). Both ATZ and H₂bdc ligands show contribution to the fluorescence of compound **1** simultaneously. These observations suggest that the compound **1** could be anticipated as potential fluorescent material.

Conclusion

In summary, by employing 5-amino-1H-tetrazole and 1,4-benzenedicarboxylate organic ligands, we have constructed a novel structural MOFs under solvothermal conditions. The title compound possesses good luminescent property and may find potential applications in the fields of lighting, displays or biomedicine.

REFERENCES

- B.F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, **111**, 5962 (1989).
- S. Kitagawa, R. Kitaura and S.I. Noro, *Angew. Chem. Int. Ed.*, **43**, 2334 (2004).
- K. Barthelet, J. Marrot, D. Riou and G. Férey, *Angew. Chem. Int. Ed.*, **41**, 281 (2002).
- X.L. Wang, C. Qin, S.X. Wu, K.Z. Shao, Y.Q. Lan, S. Wang, D.X. Zhu, Z.M. Su and E.B. Wang, *Angew. Chem. Int. Ed.*, **48**, 5291 (2009).
- K. Ove Kongshaug and H. Fjellvåg, *Polyhedron*, **26**, 5113 (2007).
- K.O. Kongshaug and H. Fjellvåg, *Solid State Sci.*, **5**, 303 (2003).
- H.R. Moon, N. Kobayashi and M.P. Suh, *Inorg. Chem.*, **45**, 8672 (2006).
- Y. Liu, G. Li, X. Li and Y. Cui, *Angew. Chem. Int. Ed.*, **46**, 6301 (2007).
- P.K. Chen, S.R. Batten, Y. Qi and J.M. Zheng, *Cryst. Growth Des.*, **9**, 2756 (2009).
- G. Férey, C. Mellot-Draznieks, C. Serre and F. Millange, *Acc. Chem. Res.*, **38**, 217 (2005).
- K. Ove Kongshaug and H. Fjellvåg, *Polyhedron*, **26**, 5113 (2007).
- A.I. Lesnikovich, O.A. Ivashkevich, S.V. Levchik, A.I. Balabanovich, P.N. Gaponik and A.A. Kulak, *Thermochim. Acta*, **388**, 233 (2002).
- X.W. Wang, J.Z. Chen and J.H. Liu, *Cryst. Growth Des.*, **7**, 1227 (2007).
- Z.Z. Lin, F.L. Jiang, D.Q. Yuan, L. Chen, Y.F. Zhou and M.C. Hong, *Eur. J. Inorg. Chem.*, **2005**, 1927 (2005).
- X.M. Lu, P.Z. Li, X.T. Wang, S. Gao, X.J. Wang, S. Wang, Y.H. Deng, Y.J. Zhang and L. Zhou, *Polyhedron*, **27**, 2402 (2008).
- X.W. Wang, J.Z. Chen and J.H. Liu, *Cryst. Growth Des.*, **7**, 1227 (2007).
- J. Neutz, O. Grosshardt, S. Schäufele, H. Schuppler and W. Schweikert, *Pyrotech.*, **28**, 181 (2003).
- Z.P. Demko and K.B. Sharpless, *Org. Lett.*, **4**, 2525 (2002).
- A.R. Katritzky, B.V. Rogovoy and K.V. Kovalenko, *J. Org. Chem.*, **68**, 4941 (2003).
- G.M. Sheldrick, SADABS, Program for Area Detector Adsorption Correction; Institute for Inorganic Chemistry, University of Göttingen; Göttingen, Germany (1996).
- G.M. Sheldrick, SHELXL-97, Program for Solution of Crystal Structures; University of Göttingen; Göttingen, Germany (1997).
- L. Zhao and F. Guo, *Z. Anorg. Allg. Chem.*, **640**, 168 (2014).
- J.Y. Wang and H.P. You, *Z. Anorg. Allg. Chem.*, **637**, 415 (2011).
- K. Jiang, L.F. Ma, X.Y. Sun and L.Y. Wang, *CrystEngComm*, **13**, 330 (2010).
- G.Z. Liu, L.Y. Xin and L.Y. Wang, *CrystEngComm*, **13**, 3013 (2011).
- W.L. Liu, J.H. Yu, J.X. Jiang, L.M. Yuan, B. Xu, Q. Liu, B.T. Qu, G.Q. Zhang and C.G. Yan, *CrystEngComm*, **13**, 2764 (2011).
- K. Liu, W. Shi and P. Cheng, *Dalton Trans.*, **40**, 8475 (2011).