

Short communication

Two luminescent Zn(II) metal–organic frameworks for exceptionally selective detection of picric acid

Zhao-Rui Pan^{a,b,*}, Zhen-Zhen Shi^a, Xiang-Jing Gao^a, He-Gen Zheng^{a,**}^a State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210023, PR China^b School of Environmental Science, Nanjing Xiaozhuang University, Nanjing 211171, PR China

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ABSTRACT

Two new luminescent Zn(II) metal–organic frameworks (MOFs) have been solvothermally synthesized from a p-conjugated carbazole-containing pyridine ligand in the presence of auxiliary ligands. Both MOFs were characterized by single crystal X-ray diffraction, infrared spectroscopy, elemental analysis and X-ray powder diffraction. Both MOFs show strong luminescence and their luminescence could be quenched by a series of nitroaromatic explosives. Importantly, they exhibit very highly sensitive and selective detection of picric acid compared to other nitroaromatic explosives.

Synopsis: Two new luminescent Zn(II) metal–organic frameworks (MOFs) have been solvothermally synthesized from a p-conjugated carbazole-containing pyridine ligand in the presence of auxiliary ligands. Both MOFs show strong luminescence and their luminescence could be quenched by a series of nitroaromatic explosives. Importantly, they exhibit very highly sensitive and selective detection of picric acid compared to other nitroaromatic explosives.

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Over the past decades, metal–organic frameworks (MOFs) have undergone rapid development, not only because of their exceptional coordination properties and structural diversity [1–5] but also because of their intriguing potential applications, such as optics, absorption and separation, magnetism, catalysis and sensors [6–10]. Recently, MOF-based luminescent complexes have achieved remarkable development owing to their various applications in chemical sensors, photochemistry, and light-emitting diodes (LEDs) [11–15]. Recently, Yang et al., have reported that coordination polymer [Cu(H₂tac)(phen)]_n shows high selectivity of L-Arginine over other amino acids [16]; and [Cd₂(DTP)₂(bibp)_{1.5}]_n demonstrates highly selective and sensitive bifunctional luminescent sensor towards nitrobenzene and Cu²⁺ ion [17]. Yan et al., have developed new Cd/Zn-based CPs with high-efficiency room temperature phosphorescence [18,19]. Pan et al., have reported the first example of MOC-type NIR fluorescent sensor for PA, and also reported assembly of a Zn-MOF (LIFM-CL1) as a unique water sensor [20,21]. Therefore, it is important to investigate the photophysical properties of coordination polymers in view of potential applications. Up to now, although a large number of luminescent MOFs

have been synthesized and employed for the detection of explosives, the selective detection of one nitro explosive in the presence of others has not been well investigated. Still there is much more important to discover new luminescent coordination polymers for selective detection of one special nitro explosive. One effective strategy to construct MOFs with excellent photoluminescence properties is the use of electron-rich p-conjugated fluorescent ligands. Carbazole-based compounds have been well known for their excellent hole transporting ability, luminescence efficiency, thermal stability, versatile structural derivatization, and unique ability to form amorphous film [22,23]. In this paper, two luminescent Zn(II) MOFs, {[Zn₂(edpc)₂(ga)₂]·2H₂O}_n (**1**) and {[Zn(edpc)(bpdc)]·0.25(H₂O)}_n (**2**) (H₂ga = glutaric acid, edpc = 9-ethyl-2,6-di-pyridin-4-yl-9H-carbazole, H₂bpdc = biphenyl-4,4'-dicarboxylic acid), have been synthesized by using Zn(II) ions and a p-conjugated carbazole-containing pyridine ligand in the presence of auxiliary ligands via solvothermal reaction, and both of which exhibit highly selective responses towards picric acid.

The experimental section has been listed in the ESI†. Crystallographic data for MOFs **1** and **2** are given in Table S1 (ESI†). Selected bond lengths and angles, hydrogen bonding distance and angle data of these complexes are listed in Tables S2 and S3 (ESI†), respectively.

Single-crystal X-ray diffraction analyses reveal that **1** crystallizes in the monoclinic *P*2₁/*c* space group. The asymmetric unit consists of two crystallographically independent Zn(II) cations, two edpc ligands and two distinct ga²⁻ anions. Zn(1) and Zn(2) adopt different coordination

* Correspondence to: Z.-R. Pan, State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210023, PR China.

** Corresponding author.

E-mail addresses: pzr_2006@163.com (Z.-R. Pan), zhenghg@nju.edu.cn (H.-G. Zheng).

geometries in **1** as depicted in Fig. S1 (ESI†). The Zn(1) atoms are five-coordinated by three oxygen atoms from two distinct ga^{2-} and two individual nitrogen atoms from two edpc ligands to form distorted trigonal-bipyramidal $[ZnN_2O_3]$ units. And Zn(2) atoms are envired by four oxygen atoms from two different ga^{2-} and two nitrogen atoms from two distinct edpc ligands to form distorted octahedral $[ZnN_2O_4]$ geometry. The Zn—N and Zn—O bond lengths fall in the normal range of 1.980(2)–2.074(2) Å and 1.902(2)–1.953(3) Å, respectively. The ga^{2-} anions adopt two different coordination modes in **1**. The deprotonated carboxylic groups of H_2ga ligands coordinated with Zn(1) ions adopt the $\mu_1-\eta^1:\eta^1$ modes, and with Zn(2) ions take $\mu_1-\eta^1:\eta^1$ and $\mu_1-\eta^1:\eta^0$ modes. The edpc ligands adopting μ_2 -bridged coordination mode bridge the Zn(II) cations into left-handed helical chains L1 along the *c* axis via two pyridyl arms, and the carboxyl groups coming from ga^{2-} initially bridge the Zn(II) cations into a left-handed helical chains L2 along the *c* axis respectively (Fig. S2a, ESI†). These adjacent single-handed helical chains are further interconnected into a 2D chiral layer by sharing the Zn(II) cations. For better understanding of the structure, topological analysis [24] of **1** is employed. Zn(II) ions are regarded as 4-connected nodes, ga^{2-} and edpc anions as the linkers, **1** can be simplified to a 4-connected **sql** net with the point symbol $\{4^4 \cdot 6^2\}$ (Fig. S2b, ESI†). Lattice water molecules O10 oriented between the layers of (4,4) nets and coordinated carboxylate oxygen atoms O4, O5 form strong hydrogen bonds (Table S3, ESI†), which bridge the Zn(1) cations into right-handed helical chains R along the *c* axis (Fig. 1). Furthermore, the adjacent 2D networks packed parallel in a $\cdots AAAA \cdots$ fashion are further linked into a 2D layered structure by above hydrogen bonds. Besides the aforementioned inter-/intramolecular interactions, O9 are also involved in C—H \cdots O contacting with the carboxylate oxygen O1 and O6 in stabilizing the supramolecular network. Details of all these pertinent H-bonding interactions with symmetry codes are given in Table S3 (ESI†).

Single-crystal X-ray diffraction analyses reveal that **2** crystallizes in the monoclinic $C2/c$ space group. In the asymmetric unit of **2**, there are one Zn(II) ion, one edpc ligand, one deprotonated $bpdc^{2-}$ ligand and one-quarter water molecules. As shown in Fig. S3, Zn(1) is six-coordinated in an octahedral coordination environment, defined by four

oxygen atoms of two chelating bidentate carboxylate groups from two $bpdc^{2-}$ ligands and two nitrogen atoms from two edpc ligands. As shown in Fig. S4, the edpc ligands link Zn(II) cations to form one infinite 1D linear chain with the Zn \cdots Zn distance of 15.2980 Å and Zn—Zn—Zn angle of 180.00°. Then, the other infinite 1D zig-zag chain with the Zn \cdots Zn distance of 15.1678 Å and Zn—Zn—Zn angle of 124.475° is also generated through the coordination between the carboxylate groups of $bpdc^{2-}$ and the Zn(II) cations. Finally, these two kinds of chains are cross-linked by sharing the Zn(II) cations into a highly undulating 2D network. In this network, each 56-membered macrocycle is formed by four Zn(II) cations, two edpc and two $bpdc^{2-}$ ligands with a dimension of 25.2943 Å \times 16.9816 Å (diagonal lengths) (Fig. S4, ESI†). From a topological viewpoint, the Zn(II) cations can be considered as 4-connected nodes, and edpc and $bpdc^{2-}$ ligands are considered as linkers; thus, the 2D network can be simplified to a puckered $4^4 \cdot 6^2$ -**sql** network, which contains a window of 15.298 Å \times 14.805 Å (Fig. 2a). Such large windows of the net and high undulation of the single **sql** sheet allows two nearest neighbouring sheets to penetrate each other in a parallel mode leading to a 2D network (Fig. 2b).

MOFs constructed from d^{10} metal cations and *p*-conjugated ligands are promising to have abundant photoluminescence properties. Therefore, the luminescence properties of the two compounds and free ligand edpc were investigated in the solid state ($\lambda_{ex} = 373$ nm). **1** and **2** show strong emission peaks at 464 nm and 424 nm, respectively (Fig. S6, ESI†). The strong emissions of **1** and **2** in the solid state make it possible to use them in fluorescence detection. So, the photoluminescence of **1** was investigated in different organic solvents to examine the potentials of sensing of small molecules. 1 mg of compound **1** or **2** was finely ground and then immersed in 2 mL different organic solvents. After treatment by ultrasonication for 2 h, the mixtures were aged for 3 days in order to form stable suspensions before the fluorescence measurements. The organic solvents used were DMA, DMF, dichloromethane (CH_2Cl_2), trichloromethane ($CHCl_3$), methanol, ethanol, acetone, tetrahydrofuran (THF), nitrobenzene, and acetonitrile. As shown in Fig. S7 (ESI†), the photoluminescence intensities are strongly dependent on the organic solvents. Both **1** and **2** show the strongest emissions

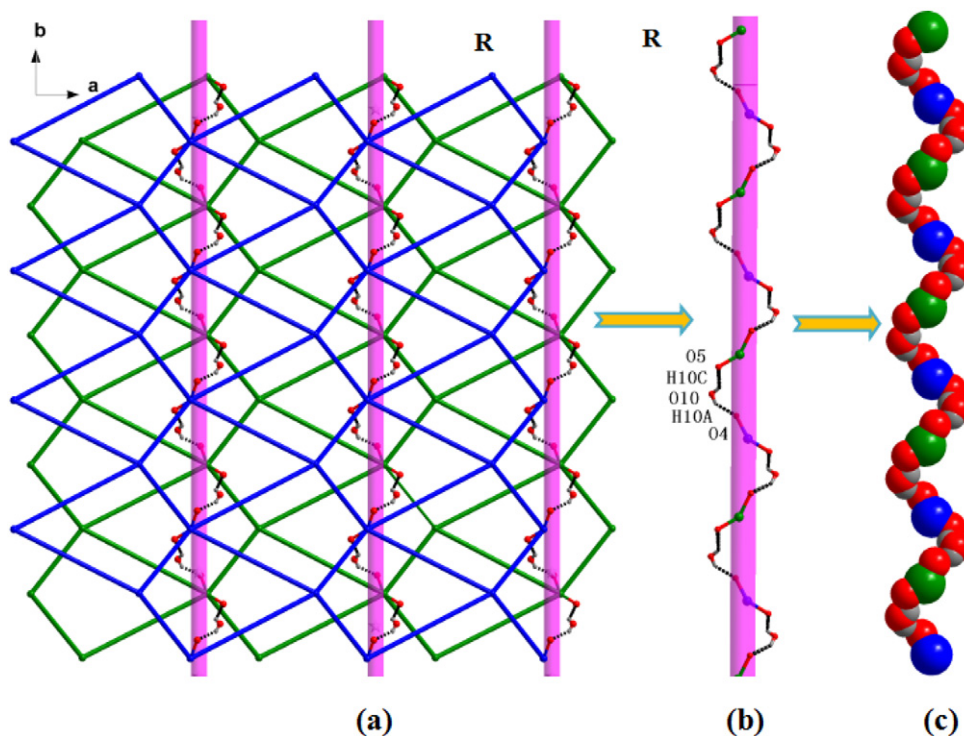


Fig. 1. (a) 2D + 2D \rightarrow 2D layered structure viewed along the *c* axis; (b) a perspective of right-handed helical chains R bridged by the hydrogen bonds along the *c* axis in **1**; (c) spacefilling diagram of the right-handed helical chain in **1**.

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