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Temperature-controlled assembly of two fluorescent Zn^{II} polymers from 3D pillared-layer framework to 2D (4, 4) layer

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ABSTRACT

Two ternary coordination polymers with the same ingredients but different structures, $[Zn_2(datrz)_2(nip)]_n$ (**1**) and $\{[Zn(Hdatrz)(nip)]\cdot H_2O\}_n$ (**2**) (Hdatrz = 3,5-diamino-1,2,4-triazole; nip^{2-} = 5-nitroisophthalate), were respectively obtained by temperature-controlled hydrothermal reactions and fully structural characterized. Interestingly, tetrahedral Zn^{II} ions in **1** are linked into wavy layers by anionic μ_3-N1,N2,N4-datrz ligands, which are further supported by deprotonated bis-monodentate nip^{2-} to generate a 3D pillared-layer framework. In contrast, the tetrahedral Zn^{II} ions in **2** are aggregated into a (4, 4) covalent layer through alternate μ_2-N1,N4-Hdatrz and bis-monodentate nip^{2-} bridges. Thus, the competitive binding of the two polydentate ligands to the metal ion plays essential roles on the connectivity and dimensionality of the two complexes. Thermal stability and the fluorescent emissions of the two complexes were also investigated and compared.

Controllable self-assembly of metal-organic frameworks (MOFs) with the same ingredients but different structures has recently attracted wide-spread interest due to their potential applications in magnetism, adsorption, separation, transportation of gases and liquids as well as catalysis [1–3]. Structurally, these interesting complexes and their ir-/reversible inter-conversions among different structures can be carefully manipulated by tuning of some external factors, such as the ratio of reactants [2,4], solvent [5–8], temperature and pressure [9,10], pH value [11,12], uncoordinated counter anions [13–16], and template/guest molecules [17–19]. Undoubtedly, all these structural control strategies significantly depend on the nature of the ligands (steric hindrance, cation binding sites, and modes) and variable coordination polyhedrons of the metal ions. In this regard, both triazole and polycarboxylate ligands have multideprotonated forms [20–22], flexible metallic bonding sites [20,21,23] as well as abundant binding modes [20,21,24] and their combination as ligands can potentially produce some unpredictable interesting structures. On the other hand, some inorganic metal ions, such as Cd^{2+}, Zn^{2+}, Cu^{2+} and so on, can potentially exhibit various coordinated polyhedrons (tetrahedron, trigonal bipyramid, and octahedron), and easily meet the binding requirement of the polydentate ligands. Herein, as a continuation of the structural construction and property investigations on the functional MOFs [22,25], controllable hydrothermal reactions of 3,5-diamino-1,2,4-triazole (Hdatrz), 5-nitroisophthalic acid (H_2nip) and Zn^{II} ion were performed. As a result, two novel polymers with same components and different structural motifs, three-dimensional (3D) pillared-layer framework for **1** and 2D (4, 4) covalent layer for **2**, were generated by varying the temperature of hydrothermal reactions. Structural determinations suggest that the competitive binding of the mixed ligands towards the tetrahedral Zn^{II} ion changed the spatial arrangement of the mixed ligands and tuned the overall dimensionality of the resulting complexes.

The two target complexes were obtained in a molar ration of 2:1:2 (Hdatrz:H_2nip:Zn^{II}) by decreasing the hydrothermal temperature [26]. Elemental analysis, FT-IR spectroscopy, thermal gravimetric analysis (TGA), and X-ray crystallography confirmed the formula of as-synthesized complexes. In the IR spectra, strong and broad absorption at 3631 cm^{-1} in **2** suggests the presence of water molecules. Two weak bands between 3450 and 3350 cm^{-1} should be assigned to the stretch vibrations of the amino group appended on triazole ring. Compared with the free H_2nip, the disappearance of a band at 1716 cm^{-1} in the both complexes is indicative of the fully deprotonation of aromatic coligand. Correspondingly, the asymmetric (ν_{as}) and symmetric stretch (ν_s) vibrations for the carboxylate are observed at 1633, 1584 and 1376, 1342 cm^{-1} for **1** and at 1622 and 1359 cm^{-1} for **2**, respectively. Their differences ($\Delta\nu = \nu_{as} - \nu_s = 208$ and 263 cm^{-1}) suggest the unidentate carboxylate group of nip^{2-} anion [27].

X-ray single-crystal diffraction analysis [28] shows that complex **1** is a 3D pillared-layer framework with the cationic Zn^{II}-datrz layers supported by anionic nip^{2-} ligands. As shown in Fig. 1a, the sole crystallographically independent Zn^{II} ion is four coordinated to one carboxylate O atom from a nip^{2-} anion and three N donors from three symmetry-related datrz ligands, exhibiting distorted tetrahedral coordination geometry. The Zn—O and Zn—N distances are fall in the normal range of 1.9479(14)—2.0125(16) Å (Table S1), and are

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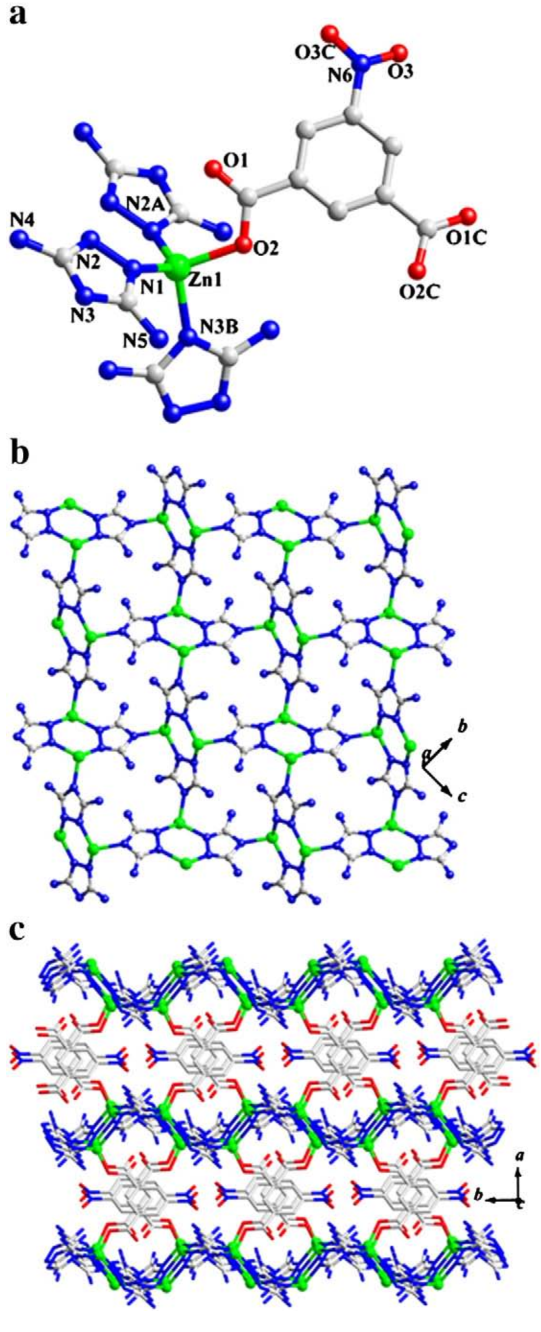

Fig. 1. (a) Local coordination environment of the Zn^{II} ion in **1** (Hydrogen atoms were omitted for clarity, symmetric codes: A = 0.5 − *x*, 0.5 − *y*, −*z*; B = *x*, −*y*, *z* − 0.5; C = 1 − *x*, *y*, −0.5 − *z*). (b) 2D Zn^{II}-datrz layer of **1**. (c) 3D pillared-layer framework of **1**.

comparable to those reported values [29]. The unique Hdatrz ligand in **1** is in a mono-deprotonated anionic form, and presents its three triazole N donors to coordinate with the Zn^{II} ion in a tridentate μ_3-N1, N2, N4-bridging mode, generating a cationic Zn^{II}-datrz 2D covalent layer in a crystallographic *bc* plane (Fig. 1b). Obviously, due to the specific spatial arrangement of the datrz ligands towards the Zn^{II} atom (Table S1), the 2D layer is wavy, and consists of 16-membered macrocycles enclosed by four Zn^{II} ions and four datrz ligands (Fig. 1b). Furthermore, the aromatic nip^{2-} coligand, lying at a 2-fold rotation axis, affords its two symmetry-related carboxylate O atoms to support the wavy Zn^{II}-datrz layer through a bis-monodentate fashion. Thus, a 3D pillared-layer MOF is generated (Fig. 1c).

Much different from the higher-dimensional framework of **1**, complex **2** generated from the relatively low hydrothermal temperature crystallizes in a chiral space group $P4_12_12$, exhibits a 2D (4, 4) covalent sheet alternately extended by neutral Hdatrz and anionic nip^{2-} ligands. Rather than being in a N_3O donor set, the tetrahedral Zn^{II} ion in **2** is surrounded by two carboxylate O and two triazole N donors from pairs of symmetry-related Hdatrz and nip^{2-} ligands (Fig. 2a). Moreover, the Hdatrz ligand in **2** is in a neutral molecule, and only presents its two N donors to coordinate with the Zn^{II} ion in a bidentate μ_2-N1,N4-bridging mode. Thus, each Zn^{II} ion in **2** is connected together by pairs of bidentate nip^{2-} and datrz bridges to generate a grid-based (4, 4) layer with a closet Zn···Zn distance of being 7.8645(2) and 6.1235(1) Å, respectively (Fig. 2b). Furthermore, the separate layers are stacked together into a 3D supramolecular network through O–H···O hydrogen-bonding interactions between the lattice water and the nitro/carboxylate group of nip^{2-} ligand (see Fig. S1 and Table S2). Thus, the structural determinations indicate that the different reaction temperature essentially influenced the cooperative coordination of the two ligands to the tetrahedron Zn^{II} ion, which further induced the specific coordination frameworks with distinct dimensionality and connectivity.

Complexes **1** and **2** with different dimensionality exhibited considerably different thermal stability (Fig. S2). For the 3D framework of **1** without any lattice molecules, only one weight-loss stage with an obvious exothermic effect was observed between 414 °C and 561 °C, which is corresponding to the collapse of the pillared-layer framework (obsd. 70.7%; calcd. 69.6%). In contrast, low-dimensional **2** displayed two separate thermal weight-loss processes due to the presence of the lattice water molecules. The first weight-loss stage with an endothermic effect began at 293 °C and ended at 333 °C, which is due to the removal of the lattice water molecule

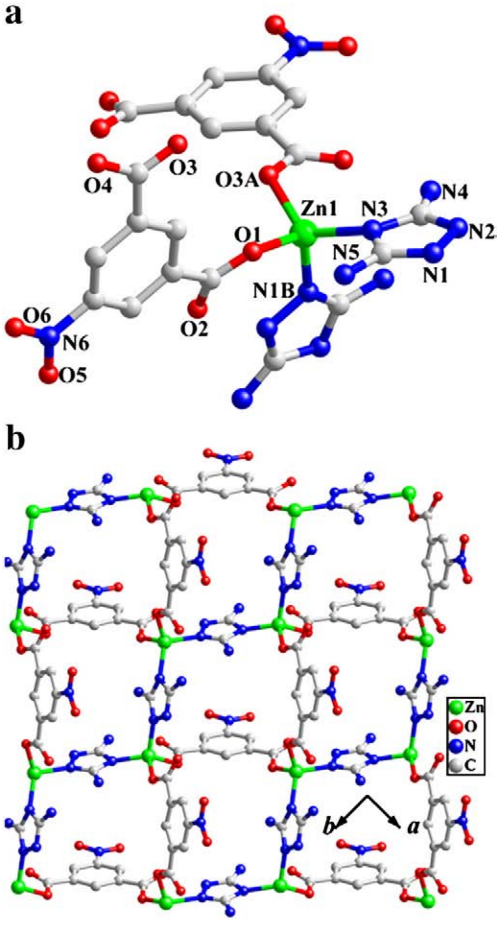

Fig. 2. (a) Local coordination environment of the Zn^{II} ion in **2** (Hydrogen atoms were omitted for clarity, symmetric codes: A = 1.5 − *x*, *y* − 0.5, 0.25 − *z*; B = 2.5 − *x*, *y* − 0.5, 0.25 − *z*). (b) 2D grid-based (4, 4) covalent layer of **2**.

(obsd. 5.7%; calcd. 4.6%). The second stage corresponding to the decomposition of the mixed ligands was observed between 310 °C and 564 °C with two consecutive exothermic processes. The final products of the two complexes are all calculated to be ZnO (obsd. 29.3%; calcd. 30.4% for **1**; obsd. 19.5%; calcd. 20.8% for **2**). Luminescence complexes are of great current interest because of their various applications in chemical sensors, photochemistry and structure electroluminescence (EL) displays and light-emitting diodes (LEDs) [30]. Thus, the solid UV–vis absorption and luminescent spectra of the two interesting Zn^{II} complexes were measured (Fig. S3 and Fig. S4). Upon excitation at 357 nm for **1** and at 355 nm for **2**, both complexes with the same components exhibit intense emissions at 394 nm with different intensity. Similar emission can also be observed for free Hdatrz ligand when excited at 355 nm originated from π–π^* transitions. Thus, the emissions of the two complexes should be assigned to intra-ligand charge transfer and their slight difference in the intensity is due to the change of the coordination environments and the fixation of the ligand in a coordination network [30].

In summary, two different fluorescent polymers with the same components, 3D pillared-layer framework for **1** and 2D (4, 4) grid-layer for **2**, were obtained by changing the temperature of the hydrothermal reactions. Interestingly, their structural diversity is significantly resulted from the competitive coordination of the mixed ligands toward the same metal ion, which encourage us the revenant investigations on the controllable constructions of the metal complexes with polydentate mixed ligands.

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Appendix A. Supplementary material

X-ray crystallographic file in CIF format (CCDC 789249 and 789250 for **1** and **2**, respectively), additional Tables, Figures, TG-DTA curves and solid state UV–vis and fluorescent spectra for **1**−**2**. Supplementary data to this article can be found online at doi:10.1016/j.inoche.2010.11.015.

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