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Short communication

Interconvertible structural transformations between two Zn(II) interpenetrating coordination polymers

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ABSTRACT

Two distinct Zn(II) coordination polymers (CPs) have been prepared based on $Zn(NO_3)_2$ and 4-(2-ethyl-1*H*-imidazol-1-yl)benzoic acid (2-Heiba) via different synthetic approaches, solvothermal synthesis and layer diffusion, respectively. Upon solvothermal condition, a 2D undulated CP $[Zn_2(2\text{-eiba})_3(OH)]_n$ (**1**) can be obtained, which incorporates the polythreading structural motifs and then results in the 3-fold **pcu** topological network with the aid of interlayer O—H···N hydrogen bonds. Employment of layer diffusion method affords another 3D CP $\{[Zn(2\text{-eiba})_2](H_2O)_3\}_n$ (**2**), featuring a **dia** topological network in 2 + 2 → 4-fold interpenetrating pattern. Interestingly, interconvertible structural transformations between **1** and **2** can be achieved by immersing in CH_3OH-H_2O solution under stirring or solvothermal conditions, respectively. In addition, thermal stability and fluorescence properties of these complexes have also been studied.

Long-standing interest in the area of coordination polymers (CPs) or metal-organic frameworks (MOFs) stems from their tectonic aesthetics of crystalline architectures and potential functions in fields of optical, magnetic, electronic, catalysis, chiral, and microporous crystalline materials [1–12]. At this stage, design of the target materials is based upon the sophisticated selection and utilization of specific organic and inorganic building tectons [13–16]. Furthermore, some accessorial reaction parameters, such as pH [17], solvent [18], anion [19], and additive [20], are also critical for the fabrication of well-defined CPs. In comparison, studies on the regulation effect of CPs and their reversible structural transformations, via tuning distinct synthetic approaches, have been rarely reported [21,22]. As a continuation of our research [23–25], we will present herein two distinct Zn(II) CPs of $[Zn_2(2\text{-eiba})_3(OH)]_n$ (**1**) and $\{[Zn(2\text{-eiba})_2](H_2O)_3\}_n$ (**2**) via solvothermal synthesis and layer diffusion method, respectively.[1] Single-crystal X-ray structural analyses reveal that they display different entangled architectures, 3-fold and 2 + 2 → 4-fold types, respectively. More interestingly, interconvertible structrual transformations between **1** and **2** can be achieved with intensive rearrangement of the overall crystalline lattice. Thermal stability and fluorescence properties of these complexes have also been studied.

Single crystal X-ray diffraction (SC-XRD) study shows that the structure of **1**[2] is a 2D undulated polymeric layer, which crystallizes in the monoclinic crystal system with *Cm* space group. The asymmetric coordination unit comprises one Zn(II), one and a half independent 2-eiba ligands, and a half-occupied hydroxide ions. As shown in Fig. 1a, each Zn(II) is coordinated by four O atoms from two 2-eiba ligands and one hydroxide ion, and one N atom from another 2-eiba ligand. The coordination geometry of the Zn center ($\tau = 0.48$) can be portrayed as a distorted polyhedron between trigonal bipyramid and square pyramid, where the τ values of the ideal trigonal bipyramid and square pyramid

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[1] Synthesis of $[Zn_2(2\text{-eiba})_3(OH)]_n$ **(1)**. Mixture of $Zn(NO_3)_2\cdot 6H_2O$ (29.7 mg, 0.1 mmol) and 2-Heiba (21.6 mg, 0.1 mmol) in CH_3OH (5 mL) and H_2O (5 mL) was sealed in a Teflon-lined autoclave and heated at 100 °C for 3 days. Colorless block single crystals of **1** were collected by cooling to room temperature at a rate of 15 °C/h (yield: 15.6 mg). Anal. Calcd for $C_{36}H_{34}O_7N_6Zn_2$: C,54.49; H,4.32; N,10.59%. Found: C, 54.68; H, 4.29; N, 10.39%. IR (cm^{-1}): 3401m, 3146m, 3058m, 1617vs, 1561m, 1513m, 1466m, 1379vs, 1307w, 1254w, 1176m, 1149w, 1107w, 1053s, 1009w, 960w, 879w, 849m, 788s, 743w, 722m, 644w, 617w, 584w, 547m, 524w, 504w, 458w, 411w. Synthesis of $\{[Zn(2\text{-eiba})_2](H_2O)_3\}_n$ **(2)**. A methanol solution (3 mL) of 2-Heiba (21.6 mg, 0.1 mmol) was carefully layered onto a water solution (3 mL) of $Zn(NO_3)_2\cdot 6H_2O$ (29.7 mg, 0.1 mmol) in a glass tube. Colorless block crystals of **2** were obtained by slow evaporation of the solvent at room temperature after three days (yield: 18.6 mg). Anal. Calcd for $C_{24}H_{28}N_4O_7Zn$: C, 52.42; H, 5.13; N, 10.19%. Found: C, 52.46; H, 5.18; N, 10.11%. IR (cm^{-1}): 3405b, 1632vs, 1575w, 1510m, 1462m, 1361vs, 1308m, 1251w, 1172m, 1147w, 1110w, 1053s, 1012m, 874w, 843m, 787m, 704m, 574m, 546m, 513m, 442w.

[2] Single crystal X-ray diffraction data for complexes **1** and **2** were collected on a Bruker APEX II CCD diffractometer equipped with a graphite monochromated Mo Kα radiation. The structures were solved by direct methods and refined anisotropically on F^2 for all non-H atoms by full-matrix least-squares methods using SHELXTL. H atoms of the ligands were located geometrically with assigned isotropic thermal parameters. The water molecules in **2** were treated as the diffuse contribution to the overall scattering without specific atom sites by SQUEEZE/PLATON. Crystallographic data for **1**: $C_{36}H_{34}Zn_2N_6O_7$, $M = 793.43$, $0.18 \times 0.17 \times 0.15$ mm^3, monoclinic, *Cm*, $a = 12.179(4)$, $b = 19.368(6)$, $c = 7.751(3)$ Å, $\beta = 97.382(8)^\circ$, $V = 1813.2(11)$ Å^3, $Z = 2$, $D_c = 1.453$ g/cm^3, $F(000) = 816$, GOF = 1.006, $\mu = 1.379$ mm^{-1}, $R_{int} = 0.0246$, final R indices $[I > 2\sigma(I)]$ $R_1 = 0.0244$ and $wR_2 = 0.0526$. Crystallographic data for **2**: $C_{24}H_{22}ZnN_4O_4$, $M = 495.83$, $0.22 \times 0.21 \times 0.17$ mm^3, tetragonal, *P4nc*, $a = 14.106(3)$, $b = 14.106(3)$, $c = 13.972(3)$ Å, $V = 2780.1(10)$ Å^3, $Z = 4$, $D_c = 1.185$ g/cm^3, $F(000) = 1024$, GOF = 1.074, $\mu = 0.915$ mm^{-1}, $R_{int} = 0.0311$, final R indices $[I > 2\sigma(I)]$ $R_1 = 0.0348$ and $wR_2 = 0.0886$.

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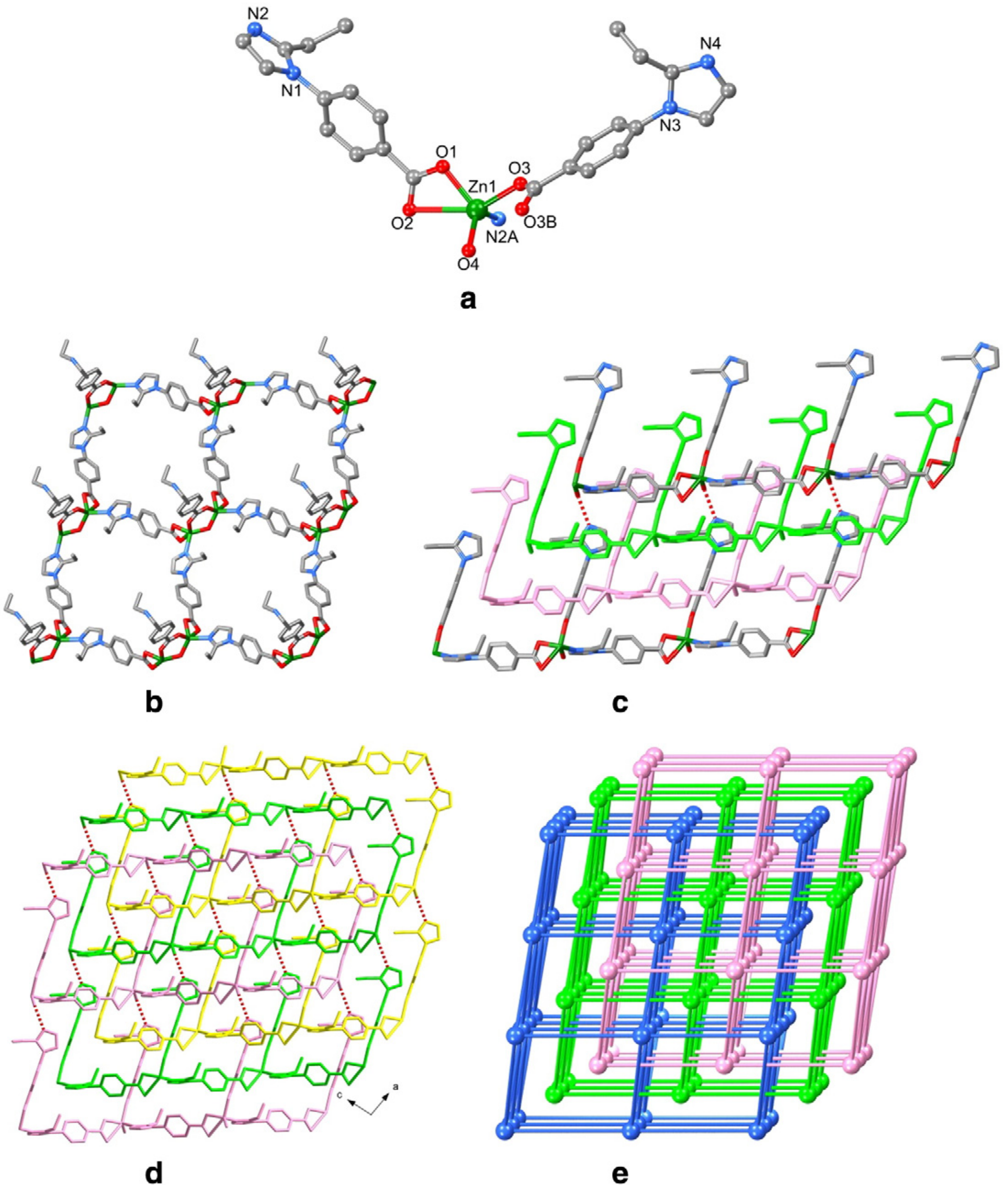

Fig. 1. Views of **1**. (a) Coordination environment of Zn^{II} center (symmetry codes for A: $x + 1/2, -y + 1/2, z - 1$; B: $x, -y, z$). (b) 2D undulated coordination layer with protrudent 2-eiba ligands. (c) One 2D layer penetrate into the grids of the adjacent two layers to give a polythreading architecture, which then forms the O—H···N hydrogen bonds with the third layer. (d) 3-Fold interpenetrating 3D networks directed by interlayer hydrogen bonding interactions. (e) Topological view of the 3-fold interpenetrating pattern of **pcu** nets.

are defined as 1 and 0, respectively [26]. A pair of Zn^{II} centers are interconnected by the μ_2-hydroxyl and μ_2-COO^- bridges to form a $[Zn_2(COO)(OH)]$ secondary building unit (SBU), with the Zn···Zn separation of 3.292(2) Å. As for the 2-eiba ligands, they show the bridging and terminal linking role to connect the binuclear Zn(II) SBU, respectively. In this way, a grid-like layered coordination net (14.25×14.25 Å^2), being extended through 2-eiba ligands, is formed (Fig. 1b). This 2D pattern is considerably undulated and of further importance, decorated with the unidentate 2-eiba pendants as side arms at single side. Interestingly, these long prominent arms, with a length of ca.7.824 Å between the pyridyl N atom and carboxylate C atom, penetrate into the grids of two adjacent layers to build a 3D polythreading supramolecular architecture with finite components [27]. In fact, each lateral 2-eiba arm goes through two parallel grids and forms a O—H···N hydrogen bond with the third one (O···N = 2.759 Å, H···N = 1.91 Å, ∠O—H···N = 172°) (Fig. 1c). Thus, if these H-bonding interactions are also taken into account, $[Zn_2(COO)(OH)]$ SBUs behave as 6-connected nodes and 2-eiba ligands act as bridges. Then three uniform 3D networks are generated, which are 3-fold interpenetrating (Fig. 1d and e). In view of topological simplification, a single net is isolated and classified as a **pcu** net [28].

When employing layer diffusion condition, another 3D coordination polymer **2**[2] is achieved, which crystallizes in the tetragonal crystal system with *P*4*nc* space group. In the asymmetric coordination unit, it consists of half crystallographic independent Zn^{II} atoms and one independent 2-eiba ligand. As shown in Fig. 2a, each Zn(II) is coordinated by two O atoms from two 2-eiba ligands, and two N atoms from two 2-eiba ligands, displaying a distorted tetrahedral geometry. In this way, each tetrahedral Zn(II) center is extended by four 2-eiba bridges to form a 3D architecture. This network possesses a channel with dimension of ca. 12.17×12.17 Å^2 along the *c* axis, showing a **dia** topological pattern (Fig. 2b). Two adjacent nets are entangled with each other in a parallel fashion, to form a 2-fold interpenetrating framework (Fig. 2c). Further study reveals that two sets of such normal 2-fold interpenetrating nets