

Synthesis, Structure, and Characterization of a Novel Coordination Polymer with Polythreading Feature^①

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ABSTRACT A novel coordination polymer **1** with formula of $\text{Zn}_2(\text{BDC})_2(\text{TPPA})$ was built from 1,4-dicarboxybenzene (H_2BDC), tris(4-(pyridin-3-yl)phenyl)amine (TPPA), and $\text{Zn}(\text{II})$ ion. It was characterized by single-crystal and powder X-ray diffraction, Fourier-transform infrared spectra (FT-IR), thermal gravimetric analysis (TGA), and UV-vis. **1** crystallizes in triclinic space group $P\bar{1}$ with $a = 14.589$, $b = 14.606$, $c = 16.108$ Å, $\alpha = 115.635^\circ$, $\beta = 90.328^\circ$, $\gamma = 114.662^\circ$, $V = 2738.6$ Å³, $Z = 2$, $M_r = 935.52$ g/mol, $D_c = 1.134$ g/cm³, $F(000) = 956$, $\text{GOOF} = 1.062$, the final $R = 0.0685$ and $wR = 0.1817$ for 7701 observed reflections with ($I > 2\sigma(I)$), and $R = 0.0717$ and $wR = 0.1843$ for all data. In **1**, $\text{Zn}(\text{II})$ is coordinated with H_2BDC to form a 2D square grid, and TPPA ligands were arranged above and beneath the 2D layer. Two neighbor layers are interpenetrated each other by π - π interactions to generate a polythreading framework structure. Moreover, the photoluminescence of **1** was also studied.

Keywords: coordination polymer, polythreading, single crystal, photoluminescence;

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1 INTRODUCTION

Coordination polymers (CPs), comprising of metal ions and organic ligands, appeal the great interest of chemists due to their fascinating architectures and topologies, as well as their potential applications in gas storage and separation, heterogeneous catalysis, luminescence and magnetism^[1-15]. The intense interest in CPs has led to the discovery of more types of topological entanglements such as polycatenation, polythreading, and polyknotting that resemble molecular catenanes, rotaxanes, and knots^[16-20], of which, the particular attention has been recently paid to polythreaded coordination networks, which can be considered as periodic analogues of the molecule rotaxanes or pseudorotaxanes^[21]. Undoubtedly, the exploration of entangled structures can be helpful not only for both the design and analysis of crystal structures but also for understanding the relationships between the structure and function of these coordination polymers^[22]. To rationally design polythreading framework, herein we utilize the mix-ligand strategy to combine the dicarboxylate and

tripyrindyl ligands to construct polythreading structures. The 2D sheet with windows is formed by the coordination of BDC^{2-} and Zn ion, and the TPPA^[23, 24] ligands acting as threads penetrate into the windows of neighboring layers. The triphenyl core has been demonstrated to exhibit excellent luminescent properties, thus endowing the whole framework functionality.

2 EXPERIMENTAL

2.1 Materials and methods

Reagents and solvents employed were commercially available. FT-IR absorption spectra of the compounds were recorded in the range of 400~4000 cm⁻¹ on a Nicolet (Impact 410) spectrometer with KBr pellets. C and H analyses were carried out with a Perkin-Elmer 240C elemental analyzer. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 VENTURE CMOS photon 100 diffractometer with Helios MX multilayer monochromatic $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54178$ Å)

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in which the X-ray tube was operated at 40 kV and 40 mA. Luminescent spectra were recorded on a Perkin-Elmer LS55 fluorescence spectrophotometer at room temperature.

2.2 Synthesis of **1**

A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (29.7 mg, 0.1 mmol), TPPA (47.6 mg, 0.1 mmol), and H_2BDC (16.6 mg, 0.1 mmol) was dissolved in 15 mL of DMF/MeCN (2/1, V/V). The final mixture was placed in a 50 mL sealed vial and heated at 100 °C for 3d. Block yellow crystals of **1** [$\text{Zn}_2(\text{BDC})_2(\text{TPPA}) \cdot \text{CH}_3\text{CN}$] were collected in 80% yield (based on TPPA ligand). Calcd. for $\text{Zn}_2\text{C}_{51}\text{N}_5\text{O}_8\text{H}_{36}$: C, 62.66; H, 3.71%. Found: C, 62.44; H, 3.45%. FT-IR (KBr, cm^{-1}): 537 (w), 563 (s), 705 (s), 749 (s), 807 (s), 825 (m), 1187 (s), 1214 (w), 1272 (m), 1292 (s), 1436 (m), 1473 (m), 1513 (m), 1600 (s), 1924 (w), 2203 (m), 2554 (w), 2929 (w), 3037 (s), 3403 (s).

2.3 X-ray structure determination

Single-crystal X-ray crystallographic data of **1** were collected on a Bruker D8 VENTURE CMOS photon 100

diffractometer with Helios MX multilayer monochromatic Cu- $K\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) at 298 K. The structure was solved by direct methods with SHELXS-2014 and refined with SHELXL-2014^[25] using Olex2^[26]. All the non-hydrogen atoms were refined by full-matrix least-squares techniques with anisotropic displacement parameters, and the hydrogen atoms were geometrically fixed at the calculated positions attached to their parent atoms, and treated as riding atoms. Contributions to scattering due to these highly disordered solvent molecules were removed using the solvent mask program of Olex2; structures were then refined again using the data generated. **1** crystallizes in triclinic space group $P\bar{1}$ with $a = 14.589$, $b = 14.606$, $c = 16.108 \text{ \AA}$, $\alpha = 115.635^\circ$, $\beta = 90.328^\circ$, $\gamma = 114.662^\circ$, $V = 2738.6 \text{ \AA}^3$, $Z = 2$, $M_r = 935.52 \text{ g/mol}$, $D_c = 1.134 \text{ g/cm}^3$, $F(000) = 956$, $GOOF = 1.062$, the final $R = 0.0685$ and $wR = 0.1817$ for 7701 observed reflections with ($I > 2\sigma(I)$), and $R = 0.0717$ and $wR = 0.1843$ for all data. The selected bond lengths and bond angles are given in Table 1.

Table 1. Selected Bond Lengths (Å) and Bond Angles (°)

Bond	Dist.	Bond	Dist.	Bond	Dist.
Zn(1)–Zn(1)#1	2.9581(13)	Zn(1)–O(5)	2.045(3)	Zn(2)–O(1)#3	2.041(3)
Zn(1)–O(6)#1	2.053(3)	Zn(1)–N(1)	2.028(2)	Zn(2)–O(2)#4	2.038(3)
Zn(1)–O(4)#1	2.036(3)	Zn(2)–Zn(2)#2	2.9729(13)	Zn(2)–O(8)	2.029(4)
Zn(1)–O(3)	2.045(3)	Zn(2)–O(7)#2	2.061(3)	Zn(2)–N(2)#3	2.033(2)
Angle	(°)	Angle	(°)	Angle	(°)
O(6)#1–Zn(1)–Zn(1)#1	71.81(10)	N(1)–Zn(1)–O(5)	105.75(16)	N(2)#3–Zn(2)–O(1)#3	101.12(13)
O(4)#1–Zn(1)–Zn(1)#1	78.53(10)	O(7)#2–Zn(2)–Zn(2)#2	75.54(10)	N(2)#3–Zn(2)–O(2)#4	99.78(13)
O(4)#1–Zn(1)–O(6)#1	87.38(16)	O(1)#3–Zn(2)–Zn(2)#2	84.31(11)	C(15)–O(7)–Zn(2)#2	132.0(3)
O(4)#1–Zn(1)–O(3)	159.01(15)	O(1)#3–Zn(2)–O(7)#2	86.54(15)	C(16)–O(6)–Zn(1)#1	136.8(3)
O(4)#1–Zn(1)–O(5)	87.87(16)	O(2)#4–Zn(2)–Zn(2)#2	74.72(11)	C(7)–O(4)–Zn(1)#1	128.8(3)
O(3)–Zn(1)–Zn(1)#1	80.78(10)	O(2)#4–Zn(2)–O(7)#2	89.16(15)	C(8)–O(1)–Zn(2)#3	121.3(3)
O(3)–Zn(1)–O(6)#1	89.54(15)	O(2)#4–Zn(2)–O(1)#3	159.00(15)	C(7)–O(3)–Zn(1)	125.7(3)
O(3)–Zn(1)–O(5)	88.46(16)	O(8)–Zn(2)–Zn(2)#2	83.06(13)	C(8)–O(2)–Zn(2)#5	134.1(3)
O(5)–Zn(1)–Zn(1)#1	89.59(12)	O(8)–Zn(2)–O(7)#2	158.49(17)	C(16)–O(5)–Zn(1)	113.2(3)
O(5)–Zn(1)–O(6)#1	161.37(16)	O(8)–Zn(2)–O(1)#3	89.25(17)	C(15)–O(8)–Zn(2)	122.8(4)
N(1)–Zn(1)–Zn(1)#1	164.66(11)	O(8)–Zn(2)–O(2)#4	87.25(17)	C(26)–N(1)–Zn(1)	120.52(16)
N(1)–Zn(1)–O(6)#1	92.86(15)	O(8)–Zn(2)–N(2)#3	104.94(17)	C(27)–N(1)–Zn(1)	119.13(16)
N(1)–Zn(1)–O(4)#1	101.63(13)	N(2)#3–Zn(2)–Zn(2)#2	170.26(10)	C(35)–N(2)–Zn(2)#3	117.99(15)
N(1)–Zn(1)–O(3)	99.26(13)	N(2)#3–Zn(2)–O(7)#2	96.57(14)	C(36)–N(2)–Zn(2)#3	121.90(15)

Symmetry transformations used to generate the equivalent atoms for **1**: #1: $-x+1, -y, -z$;

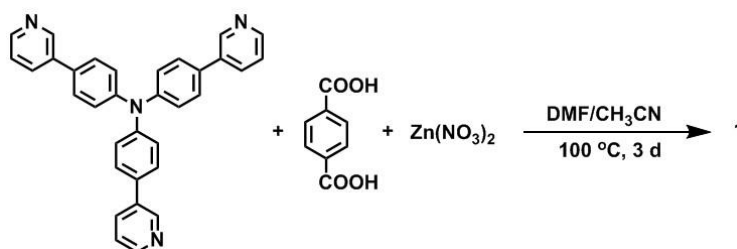
#2: $-x+2, -y, -z+1$; #3: $-x+1, -y, -z+1$; #4: $x+1, y, z$; #5: $x-1, y, z$

3 RESULTS AND DISCUSSION

3.1 Synthesis and characterization

As shown in Scheme 1, **1** was synthesized through solvent thermal reactions between $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, TPPA, and H_2BDC . The phase purity was established by the general agreement between the experimental and simulated X-ray powder diffraction patterns (Fig. 1a). The major peaks of the PXRD pattern between the simulated **1** and synthesized **1** can be matched very well. The missing of some peaks and

minor shift of the peaks can be explained by the crystal orientation distribution and the flexible framework. **1** shows a strong band at 1600 cm^{-1} , characteristic of carboxylic acid $\nu(\text{C}=\text{O})$ (Fig. 1b). The thermogravimetric analysis of **1** was investigated under a N_2 atmosphere from 40 to $800\text{ }^\circ\text{C}$, and the result indicates that the solvent molecules are released below $200\text{ }^\circ\text{C}$, with 4.1% weight loss. The framework of **1** starts to collapse when heating upon to $330\text{ }^\circ\text{C}$ (Fig. 1c). The ultraviolet visible light absorption of **1** was mostly due to the transition of $n-\pi^*$ and $\pi-\pi^*$ of the ligand^[27] (Fig. 1d).



Scheme 1. Synthesis of 1

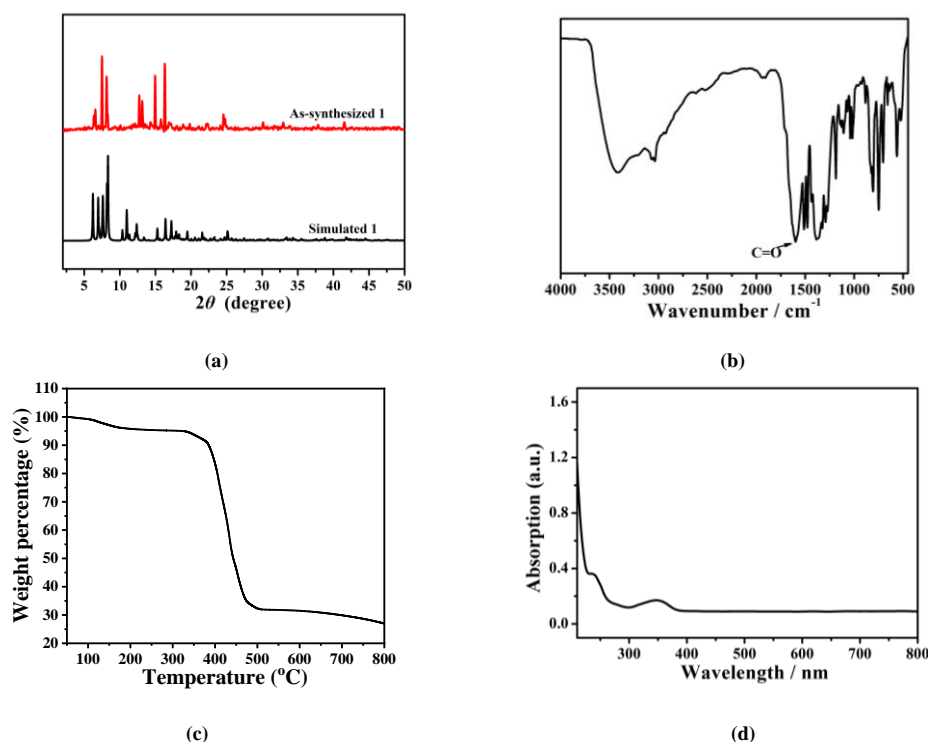


Fig. 1. (a) PXRD patterns, (b) FT-IR spectra, (c) TGA curves, and (d) UV-vis spectra of 1

3.2 X-ray crystal structure

Single-crystal X-ray diffraction reveals that compound **1** crystallizes in the triclinic $P\bar{1}$ space group. The asymmetric unit consists of two Zn(II) ions, one TPPA ligand, and two BDC²⁻ molecules. As shown in Fig. 2a, the two pyridine groups of TPPA were coordinated with Zn ions, while the third one remains uncoordinated. The zinc ion adopts a

distorted square-pyramidal geometry by coordinating to four O atoms of four separate BDC²⁻ ligands, while the apical positions are occupied by two N atoms from two distinct TPPA ligands (Fig. 2b). The bond lengths of Zn–N are 2.028(2), 2.033(2) Å and those of Zn–O are 2.029(4) to 2.061(3) Å, which are similar to the typical Zn–N and Zn–O bond lengths of other reported MOFs^[28, 29].

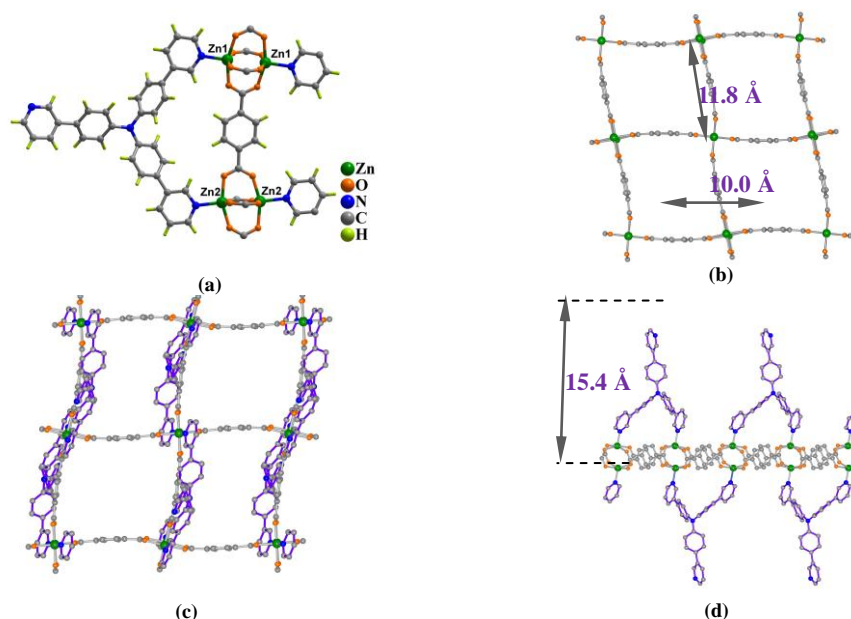


Fig. 2. (a) Coordination mode of ligand TPPA, (b) structure of Zn-based paddlewheel cluster, (c) 2D grid formed by Zn^{2+} and BDC^{2-} , (d) TPPA ligands arranged above and beneath the 2D layer with one pyridine uncoordinated

The paddlewheel clusters are further bridged by BDC^{2-} to form a 2D rectangular sheet. There are large distorted rhombic windows with approximate dimensions of about $9.9 \times 11.7 \text{ \AA}^2$ built by four clusters and four bent BDC^{2-} molecules (Fig. 2b). Moreover, each metal in the dimeric unit bears a terminally bound pyridyl group of TPPA ligand along the *b* direction (Fig. 2c). Two pyridine groups of each TPPA ligand bridge two zinc clusters, and the third pyridine

group is uncoordinated. Therefore, the TPPA ligands are arranged above and beneath the 2D layer, exhibiting an overall multi-arm sheet. Each dangling arm has a length of about 15.4 \AA (Fig. 2d). Each window is threaded by two arms above and below through π - π interactions between the neighbor phenyl rings (Fig. 3a), thus resulting in the formation of a rare polythreading coordination framework (Figs. 3b and 3c).

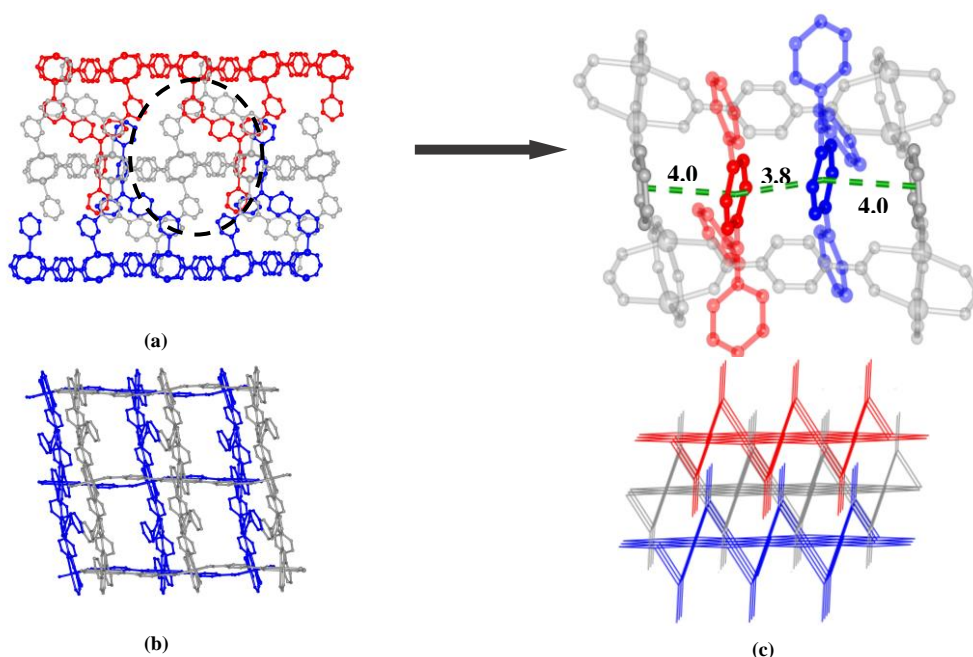


Fig. 3. (a) Packing diagram of 1 showing the π - π interactions between the neighbor phenyl rings, (b) 3D packing structure of 1, (c) schematic illustration of the polythreading structure of 1

3.3 Photoluminescence

Upon excitation at 350 nm, as shown in Fig. 4, the free ligand TPPA displayed fluorescent emission at 435 nm, while the emission of **1** at 488 nm exhibits 53 nm red-shift.

The observed shift in the emission for **1** originated from the coordination of nitrogen atom to the Zn(II) ions, which effectively increases the rigidity of the ligand and reduces the loss of energy.

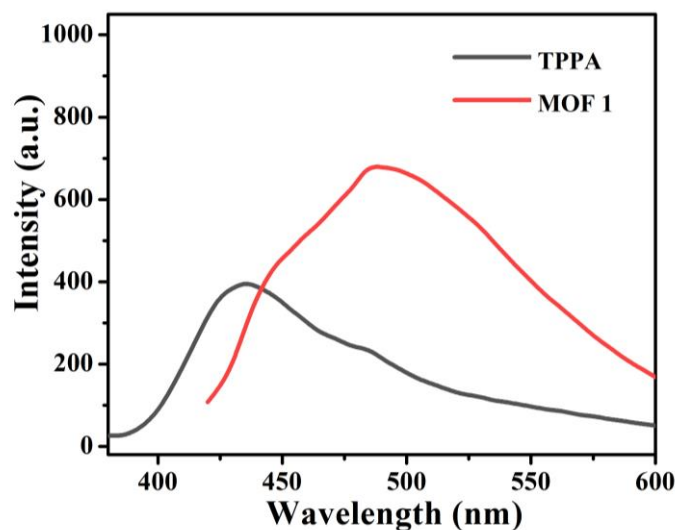


Fig. 4. Fluorescent emission spectra of **1**

4 CONCLUSION

In summary, a novel coordination polymer **1** with polythreading structure was synthesized by a pot solvo-

thermal reaction of Zn(II) ion, H₂BDC, and TPPA. It was characterized by single-crystal and powder X-ray diffraction, TGA, FT-IR, and UV-vis. In addition, the photoluminescence of **1** and free ligand was also investigated.

REFERENCES

- (1) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. Reticular synthesis and the design of new materials. *Nature* **2003**, 423, 705–714.
- (2) Xuan, W.; Zhu, C.; Liu, Y.; Cui, Y. Mesoporous metal-organic framework materials. *Chem. Soc. Rev.* **2012**, 41, 1677–1695.
- (3) Li, J. R.; Kuppler, R.; Zhou, H. C. Selective gas adsorption and separation in metal-organic frameworks. *Chem. Soc. Rev.* **2009**, 38, 1477–1504.
- (4) Lysova, A. A.; Samsonenko, D. G.; Dorovatovskii, P. V.; Lazarenko, V. A.; Khrustalev, V. N.; Kovalenko, K. A.; Dybtsev, D. N.; Fedin, V. P. Tuning the molecular and cationic affinity in a series of multifunctional metal-organic frameworks based on dodecanuclear Zn(II) carboxylate wheels. *J. Am. Chem. Soc.* **2019**, 141, 17260–17269.
- (5) Jiang, H.; Zhang, W.; Kang, X.; Cao, Z.; Chen, X.; Liu, Y.; Cui, Y. Topology-based functionalization of robust chiral Zr-based metal-organic frameworks for catalytic enantioselective hydrogenation. *J. Am. Chem. Soc.* **2020**, 142, 9642–9652.
- (6) Gong, W.; Chen, X.; Jiang, H.; Chu, D.; Cui, Y.; Liu, Y. Highly stable Zr(IV)-based metal-organic frameworks with chiral phosphoric acids for catalytic asymmetric tandem reactions. *J. Am. Chem. Soc.* **2019**, 141, 7498–7508.
- (7) Allendorf, M. D.; Bauer, C. A.; Bhakta, R. K.; Houk, R. J. T. Luminescent metal-organic frameworks. *Chem. Soc. Rev.* **2009**, 38, 1330–1352.
- (8) Sussardi, A.; Hobday, C. L.; Marshall, R. J.; Forgan, R. S.; Jones, A. C.; Moggach, S. A. Correlating pressure-induced emission modulation with linker rotation in a photoluminescent MOF. *Angew. Chem. Int. Ed.* **2020**, 132, 8195–8199.
- (9) Zeng, M. H.; Yin, Z.; Tan, Y. X.; Zhang, W. X.; He, Y. P.; Kurmoo, M. Nanoporous cobalt(II) MOF exhibiting four magnetic ground states and changes in gas sorption upon post-synthetic modification. *J. Am. Chem. Soc.* **2014**, 136, 4680–4688.
- (10) Terzopoulou, A.; Hoop, M.; Chen, X. Z.; Hirt, A. M.; Charilaou, M.; Shen, Y.; Mushtaq, F.; del Pino, A. P.; Logofatu, C.; Simonelli, L.; de Mello, A. J.; Doonan, C. J.; Sort, J.; Nelson, B. J.; Pané S.; Puigmartí Luis, J. Mineralization-inspired synthesis of magnetic zeolitic imidazole framework composites. *Angew. Chem. Int. Ed.* **2019**, 58, 13550–13555.
- (11) Fu, H. R.; Xu, Z. X.; Zhang, J. Water-stable metal-organic frameworks for fast and high dichromate trapping via single-crystal-to-single-crystal ion

- exchange. *Chem. Mater.* **2015**, 27, 205–210.
- (12) Zhuo, C.; Wang, F.; Zhang, J. Mixed short and long ligands toward the construction of metal-organic frameworks with large pore openings. *Cryst. Growth Des.* **2019**, 19, 3120–3123.
- (13) An, Z.; Zhou, T. Mixed-ligands self-assembly strategy affording a new 4-fold interpenetrated 3D Co(II)-based coordination polymer: synthesis, crystal structure and magnetic property. *Chin. J. Struct. Chem.* **2019**, 38, 777–782.
- (14) Liu, Z. Y.; Fu, M.; Wang, X. G.; Wang, L. L.; Yang, E. C.; Zhao, X. J. Two preparation methods-dominated Cd^{II}-based coordination polymers with mixed adenine nucleobase and 5-nitroisophthalate ligands: synthesis, structure and fluorescence. *Chin. J. Struct. Chem.* **2019**, 38, 613–620.
- (15) Liu, N.; Xing, G. E.; Huang, X. X.; Guo, J. A new Zn(II) coordination polymer constructed from 4-(1H-pyrazol-3-yl)pyridine as fluorescent sensor for Fe³⁺. *Chin. J. Struct. Chem.* **2019**, 38, 660–666.
- (16) Kitagawa, S.; Kitaura, R.; Noro, S. I. Functional porous coordination polymers. *Angew. Chem. Int. Ed.* **2004**, 43, 2334–2375.
- (17) Liu, G.; Li, Y.; Lu, Z.; Li, X.; Wang, X. L.; Wang, X.; Chen, X. Versatile carboxylate-directed structures of ten 1D → 3D Ni(II) coordination polymers: fluorescence behaviors and electrochemical activities. *CrystEngComm*. **2019**, 21, 5344–5355.
- (18) Qian, L. L.; Han, S. S.; Zheng, L. Y.; Yang, Z.; Li, K.; Li, B. L.; Wu, B. Syntheses, structures and properties of structural diversity of 3D coordination polymers based on bis(imidazole) and dicarboxylate. *Polyhedron* **2019**, 162, 303–310.
- (19) Zhang, L.; Ma, J.; Yang, J.; Pang, Y.; Ma, J. Series of 2D and 3D coordination polymers based on 1,2,3,4-benzenetetracarboxylate and N-donor ligands: synthesis, topological structures, and photoluminescent properties. *Inorg. Chem.* **2010**, 49, 1535–1550.
- (20) Gu, Z.; Xu, X.; Zhou, W.; Pang, C.; Bao, F.; Li, Z. A new type of entangled coordination network: coexistence of polythreading and polyknotting involved molecular braids. *Chem. Commun.* **2012**, 48, 3212–3214.
- (21) Carlucci, L.; Ciani, G.; Proserpio, D. M. Polycatenation, polythreading and polyknotting in coordination network chemistry. *Coord. Chem. Rev.* **2003**, 246, 247–289.
- (22) Yao, Q.; Ju, Z.; Jin, X.; Zhang, J. Novel polythreaded coordination polymer: from an armed-polyrotaxane sheet to a 3D polypseudorotaxane array, photo- and thermochromic behaviors. *Inorg. Chem.* **2009**, 48, 1266–1268.
- (23) Hu, B.; Chen, X.; Wang, Y.; Lu, P.; Wang, Y. Structure-property investigations of substituted triaryl amines and their applications as fluorescent pH sensors. *Chem. Asian J.* **2013**, 8, 1144–1151.
- (24) Wang, T.; Liu, L.; Xu, K.; Xie, H.; Shen, H.; Zhao, W. X. Synthesis and characterization of trinuclear N-heterocyclic carbene-palladium(II) complexes and their applications in the Suzuki-Miyaura cross-coupling reaction. *RSC Adv.* **2016**, 6, 100690–100695.
- (25) Sheldrick, G. M. *SHELXS-97, Program for X-ray Crystal Structure Solution*. University of Göttingen, Germany **1997**.
- (26) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, 42, 339–341.
- (27) Mohamed, G.; El-Gamel, N. Synthesis, investigation and spectroscopic characterization of piroxicam ternary complexes of Fe(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) with glycine and dl-phenylalanine. *Spectrochim. Acta Part A* **2004**, 60, 3141–3154.
- (28) Farha, O. K.; Malliakas, C. D.; Kanatzidis, M. G.; Hupp, J. T. Control over catenation in metal-organic frameworks via rational design of the organic building block. *J. Am. Chem. Soc.* **2010**, 132, 950–952.
- (29) Yang, H.; Peng, F.; Dang, C.; Wang, Y.; Hu, D.; Zhao, X.; Feng, P.; Bu, X. Ligand charge separation to build highly stable quasi-isomer of MOF-74-Zn. *J. Am. Chem. Soc.* **2019**, 141, 9808–9812.