Supplementary Information

Two enantiomorphic 3D Zn(II)/carboxylate MOFs with double helical structures serving as a chiral source induced by hydrogen bonding

Huabin Zhang,[a,b] Shuting Wu,[c] Chongbin Tian,[a,b] Zujin Lin,[a,b] Zhihua Li,[a] Ping Lin,[a] and Shaowu Du[a*]

[a] *State Key Laboratory of Structure Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China. E-mail: swdu@fjirsm.ac.cn.*

Fax: 86-591-83709470

[b] *Graduate School of the Chinese Academy of Sciences, Beijing, 100049, China*

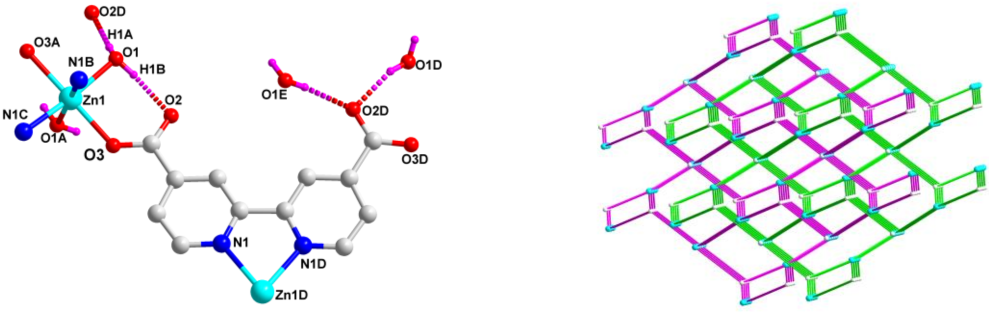
[c] *College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou, Fujian, 350002, P. R. China.*

Materials and Instruments. All the chemicals were purchased commercially and used as received. Thermogravimetric experiments were performed using a TGA/NETZSCH STA449C instrument heated from 30–800 ºC (heating rate of 10 ºC /min, nitrogen stream). The powder X-ray diffraction (XRD) patterns were recorded on crushed single crystals in the 2θ range 5–55º using Cu-Kα radiation. The XRD were measured on a PAN alytical X'pert PRO X-Ray Diffractometer. IR spectra using the KBr pellet technique were recorded on a Spectrum-One FT-IR spectrophotometer. Elemental analyses (C, H, and N) were measured with an Elemental Vairo EL III Analyzer. Fluorescence spectra for the solid samples were performed on an Edinburgh Analytical instrument FLS920. The solid-state CD spectrua was carried out with a MOS-450 spectropolarimeter using a mixture of about title compounds and dried KCl powder, which was well grounded and then pressed into a disk for use in the CD measurement.

Synthesis

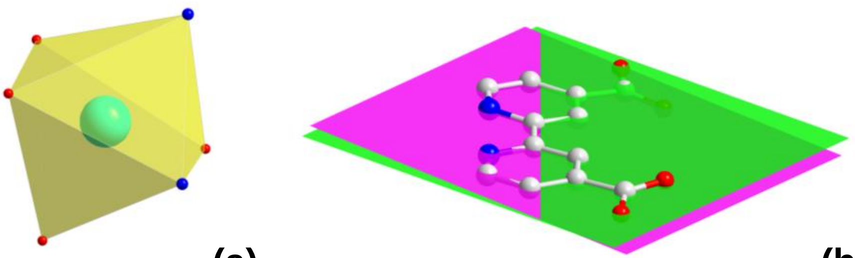
[Zn(bpydc)·(H$_2$O)$_2$] (1M or **1P):** In a typical reaction, a mixture of Zn(NO$_3$)$_2$·6H$_2$O (0.1487 g, 0.5 mmol) and H$_2$bpydc (0.0806 g, 0.33 mmol) were placed in a 20 mL of Teflon-lined stainless steel vessel with 6 mL of mixed-solvent of CH$_3$CN (acetonitrile) and H$_2$O (V/V = 1:1). The mixture was heated to 120 ºC in 4 h and kept to this temperature for 3 days. The reaction system was cooled slowly to room temperature during another 2 days. Colorless needle crystals of compound 1 were collected in 35% yield based on the $Zn(NO_3)_3 \cdot 6H_2O$. Elemental Anal. Calcd for $C_{12}H_{10}N_2O_6Zn$ (343.59): C, 41.95; H, 2.93; N, 8.15%. Anal. Found: C, 42.82; H, 2.96; N, 8.21%.

X-ray Crystallography Single-crystal X-ray diffraction data were collected on a Rigaku diffractometer with a Mercury CCD area detector (Mo Kα; λ=0.71073Å) at room temperature. Empirical absorption corrections were applied to the data using the Crystal Clear program. The structures were solved by the direct method and refined by the full-matrix least-squares on F^2 using the SHELXTL-97 program. Metal atoms in each compound were located from the *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were positioned geometrically, while those of the water molecules were located using the difference Fourier method and refined freely. Crystallographic data and other pertinent information are summarized in Table S1.



(a) (b)

Fig. **S1 (a)** The coordination environment of Zn in compound **1M.** H atoms were omitted for clarity. Symmetry codes: (A) 3 - x, 0.5 + y, 3.5 - z; (B) 1 + x, y, z; (C) 2 + x, 1+ y, z; (D) x, 0.5 + y, 3.5 + z. (E) y, x, 1-z. **(b)** Schematic description of the (3, 12)–connected 3D net (blue balls represent the Zn atoms; white balls represent the centers of the bpydc^{2-} ligands).



(a) (b)

Fig. **S2** (a) The nearly ideal octahedral configuration with geometrical parameter τ values of 0.03. (b) The dihedral angle between the two pyridyl rings is 3.7°.

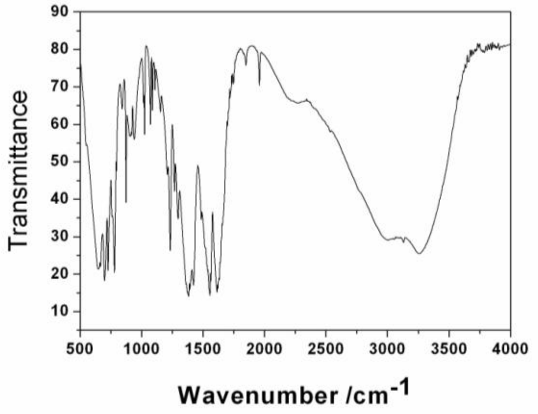


Fig. S3 IR spectrum of compounds **1**.

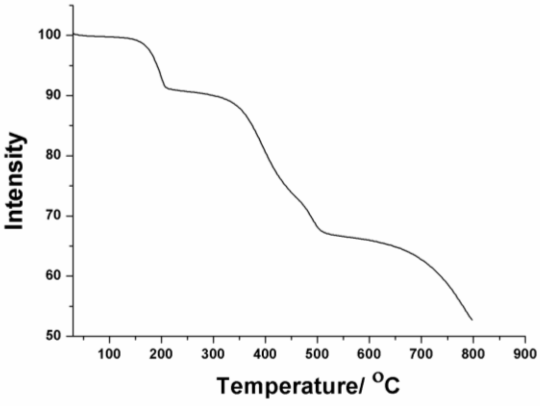


Fig. **S4**. The TGA diagram of **1**.

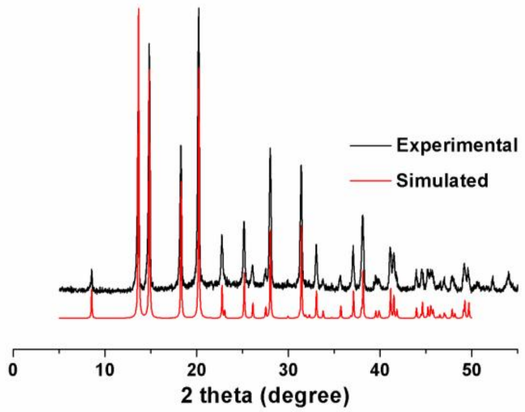


Fig. S5. Simulated and experimental XRD powder patterns for compound **1**.

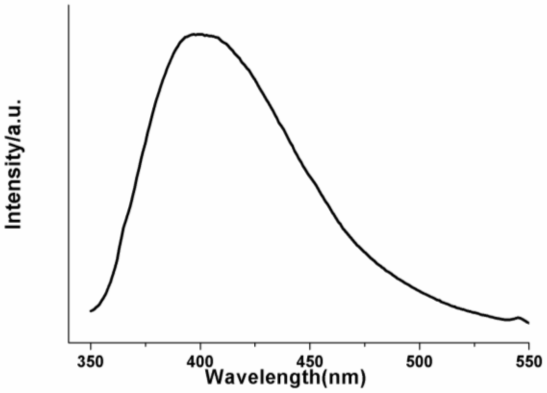


Fig. S6. The luminescence spectrum of ligand (H_2bpydc) at room temperature.

Table S1. Crystallographic data and structure refinement details for ten random selected crystals.

Comp	**1P-1**	**1P-2**	**1P-3**	**1P-4**	**1P-5**
formula	$C_{12}H_{10}N_2O_6Zn$	$C_{12}H_{10}N_2O_6Zn$	$C_{12}H_{10}N_2O_6Zn$	$C_{12}H_{10}N_2O_6Zn$	$C_{12}H_{10}N_2O_6Zn$
formula mass	343.59	343.59	343.59	343.59	343.59
space group	$P3_12_1$	$P3_12_1$	$P3_12_1$	$P3_12_1$	$P3_12_1$
a (Å)	11.9088(4)	11.8429(1)	11.9109(6)	11.9194(6)	11.9329(1)
c (Å)	8.3166(6)	8.2715(1)	8.3215(9)	8.3261(1)	8.3384(2)
V (Å^3)	1021.4(4)	1004.7(2)	1022.4(0)	1024.4 (3)	1028.3(3)
Z	3	3	3	3	3
D_c(g cm^{-3})	1.676	1.704	1.674	1.671	1.665
μ (mm^{-1})	1.83	1.86	1.83	1.83	1.82
F(000)	522	522	522	522	522
Flack	0.0201(8)	-0.01(3)	0.02	0.025	-0.0021(9)
GOF	0.90	1.01	1.09	1.05	1.09
$R_1{}^a$	0.032	0.040	0.025	0.031	0.031
$wR_2{}^a$	0.210	0.101	0.060	0.074	0.153

Comp	**1P-6**	**1M-1**	**1M-2**	**1M-3**	**1M-4**
formula	$C_{12}H_{10}N_2O_6Zn$	$C_{12}H_{10}N_2O_6Zn$	$C_{12}H_{10}N_2O_6Zn$	$C_{12}H_{10}N_2O_6Zn$	$C_{12}H_{10}N_2O_6Zn$
formula mass	343.59	343.59	343.59	343.59	343.59
space group	$P3_12_1$	$P3_22_1$	$P3_22_1$	$P3_22_1$	$P3_22_1$
a (Å)	11.9072(5)	11.9058 (7)	11.9175 (6)	11.9166 (4)	11.9118 (4)
c (Å)	8.3161(6)	8.3177 (1)	8.3253 (1)	8.3263 (4)	8.3260 (5)
V (Å^3)	1021.1(1)	1021.0(1)	1024.0 (2)	1023.9(8)	1023.1(2)
Z	3	3	3	3	3
D_c(g cm^{-3})	1.676	1.676	1.672	1.672	1.673
μ (mm^{-1})	1.83	1.83	1.83	1.83	1.83
F(000)	522	522	522	522	522
Flack	0.0001(9)	0.01 (2)	−0.0041(4)	0.0101(5)	0.0261(4)
GOF	1.09	1.31	1.05	1.05	1.01
$R_1{}^a$	0.025	0.027	0.023	0.024	0.024
$wR_2{}^a$	0.065	0.065	0.058	0.060	0.052

^{a} $R = \sum (||F_o| - |F_c||)/\sum |F_o|$, $wR = \{ \sum w[(F_o^2 - F_c^2)^2]/ \sum w[(F_o^2)^2]\}^{1/2}$

Table S2. Hydrogen bonding distances (Å) and angle (°) data for **1M**

Compound **1M**	D–H (Å)	H...A(Å)	D...A(Å)	D–H...A(°)
O1—H1a...O2	0.860(1)	1.988(3)	2.753 (2)	117.02(2)
O1—H1a...O2A	0.780(6)	1.871(8)	2.620(6)	117.02(2)

Symmetry codes: (A) x, 0.5 + y, 3.5 + z.