Supporting Information

A pair of 3D enantiotopic zinc(II) complexes based on two asymmetric achiral ligands

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Experimental section

Materials and Measurements.

Reagents and solvents employed were commercially available. MIDPPA ligand was synthesized according to our previous report.[S1] All of the crystal samples are stored in mother solutions until the study of properties. 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 (5 mg of sample in 500 mg of KBr). C, H and N analysis was carried out with a Perkin-Elmer 240C elemental analyzer. Using a Philip X' Pert Pro system, variable temperature PXRD (VT-PXRD) measurements were recorded after the sample had stayed at the respective temperature for 30 min in N_2 atmosphere. The as-synthesized sample was characterized by thermogravimetric analysis (TGA) on a Perkin Elmer thermogravimetric analyzer Pyris 1 TGA up to 1023 K using a heating rate of 10 K min^{-1} under the N_2 atmosphere. Measurement of solid CD spectra: A mixture of about 3 mg sample and 40 mg dried KBr powder was well ground and then pressed into a disk for use in the CD measurements using a J-810 spectropolarimeter. Second-order NLO properties are studied using a pulsed Q-switched Nd:YAG laser at a wavelength of 1064 nm as SHG signals. The electric hysteresis loops were recorded on a Ferroelectric Tester PrecisionPremier II made by Radiant Technologies, Inc.

X-ray crystallographic data of **1L** and **1R** were collected at room temperature by way of sealing the better single crystals in a quartz tube with mother liquor. X-ray crystallographic data of these compounds were collected on a Bruker Smart ApexII

CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å).[45] Structure solutions were solved by direct methods and the non-hydrogen atoms were located from the trial structures and then refined anisotropically with *SHELXTL* using full-matrix least-squares procedures based on F^2 values.[S2] The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. The topological analysis and some diagrams were produced using the TOPOS program.[S3]

Synthesis of complex 1

A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (14.9 mg, 0.05 mmol), 1,2,4-Benzenetricarboxylic acid(10.5 mg, 0.05 mmol) and MIDPPA (23.3 mg, 0.05 mmol) was dissolved in 12 mL of DMF/H_2O(1:2, v/v). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (20 mL) under autogenous pressure and heated at 130 ℃ for 3 d. Large quantity of yellow crystals were obtained, which were washed with mother liquid, and dried under ambient conditions (yield: 74%, based on MIDPPA). Calcd for $Zn_6C_{120}H_{98}N_{18}O_{34}$: C, 52.82%; H, 3.62%; N, 9.24%. Found: C, 52.76%; H, 3.68%; N, 9.28%. IR(KBr, cm^{-1}): 3145 (m), 1617 (s), 1586 (s), 1493 (m), 1417 (m), 1368 (s), 1310 (m), 1290 (w), 1230 (w), 1133 (w), 1075 (m), 1041 (w), 1019 (w), 966 (w), 858 (w), 834 (w), 812 (m), 782 (m), 758 (m), 758 (w), 669 (w), 649 (w), 594 (w), 498 (w), 441 (w). Crystallographic data for **1L**: $C_{120}H_{98}N_{18}O_{34}Zn_6$, M_r = 2728.38, Trigonal, space group *R*3, a = 33.3463(16) Å, b = 33.3463(16) Å, c = 9.5459(10) Å, α = 90°, β = 90 °, γ = 120°, V = 9192.7(13) $Å^3$, Z = 3, D_c = 1.479 g cm^{-3}, μ(Mo-Ka) = 1.242 mm^{-1}, T = 296(2) K, 7549 reflections measured, 6319 independent reflections (R_{int} =

0.0626), final R_1 [$I > 2\sigma(I)$] = 0.0547, w$R(F^2)$ = 0.1280, GOF = 0.995. Crystallographic data for **1R**: $C_{40}H_{32}N_6O_{11}Zn_2$, M_r = 903.45, Trigonal, space group $R3$, a = 33.3064(10) Å, b = 33.3064(10) Å, c = 9.5764(6) Å, α = 90°, β = 90 °, γ = 120°, V = 9200.0(8) Å^3, Z = 9, D_c = 1.468 g cm^{-3}, μ(Mo-Ka) = 1.240 mm^{-1}, T = 296(2) K, 17285 reflections measured, 7211 independent reflections (R_{int} = 0.0632), final R_1 [$I > 2\sigma(I)$] = 0.0572, w$R(F^2)$ = 0.1650, GOF = 1.031. The selected bond lengths and angles of **1L** and **1R** are given in Tables S1 and S2.

Table S1. Hydrogen-Bonding Geometry (Å, °) for complexes **1L** and **1R**.

D-H···A	d(H···A)	d(D···A)	∠D-H···A
Complex **1L**[a]			
O1-H1B···O10^{i}	1.89	2.69	139
O1-H1A···O10	1.98	2.74	134
O11-H11A···O6	2.32	3.09	151
O11-H11B···O12^{ii}	2.44	2.90	115
O12-H12B···O7^{iii}	2.22	2.92	140
Complex **1R**[b]			
O2W-H2WA···O4	2.19	3.02	166
O2W-H2WB···O3W^{iv}	2.42	3.12	139
O3W-H3WA···O3	2.21	3.06	178

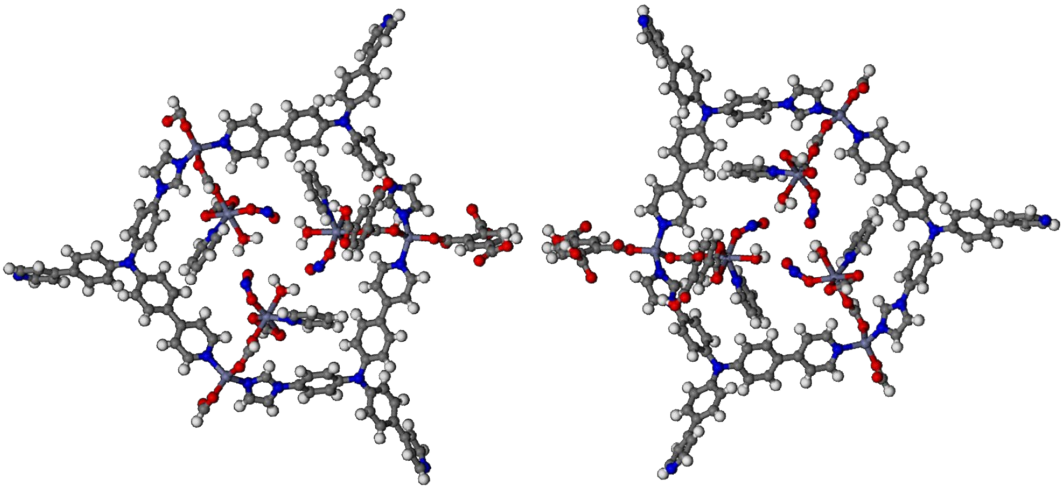
[a]Symmetry codes: (i) 1 - y, x - y, z; (ii) x, y, -1 + z; (iii) 1 – x + y, 1 – x 1 + z. [b]Symmetry codes: (iv) 1 – y, 1 + x - y, z.

Table S2. Selected Bond Lengths (Å) and Angles (deg) for Compound **1L**.

N(1)-Zn(2)	2.053(7)	N(2)-Zn(1)	2.022(7)
N(3)-Zn(1)	1.971(7)	O(2)-Zn(1)	1.949(6)
O(4)-Zn(1)	1.988(5)	O(5)-Zn(2)	2.099(6)
O(6)-Zn(2)	2.072(7)	O(1)-Zn(2)	2.260(10)
O(9)-Zn(2)	1.965(8)		
O(2)-Zn(1)-N(3)	118.4 (3)	O(2)-Zn(1)-O(4)	95.4(2)
N(3)-Zn(1)-O(4)	102.7 (2)	O(2)-Zn(1)-N(2)	108.6(3)
N(3)-Zn(1)-N(2)	121.7(3)	O(4)-Zn(1)-N(2)	105.2(3)
O(9)-Zn(2)-N(1)	102.8(4)	O(9)-Zn(2)-O(6)	108.3(3)
N(1)-Zn(2)-O(6)	146.7(3)	O(9)-Zn(2)-O(5)	92.5(3)
N(1)-Zn(2)-O(5)	99.4 (3)	O(6)-Zn(2)-O(5)	91.0(2)
O(9)-Zn(2)-O(1)	91.6(4)	N(1)-Zn(2)-O(1)	86.5(3)
O(6)-Zn(2)-O(1)	81.1(3)	O(5)-Zn(2)-O(1)	171.9(3)

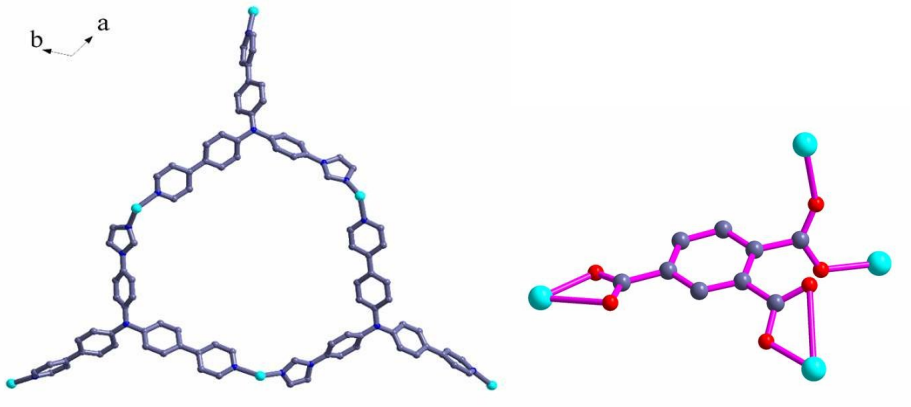
Table S3. Selected Bond Lengths (Å) and Angles (deg) for Compound **1R**.

Zn(1)-O(5)	1.929(6)	Zn(1)-N(3)	1.968(7)
Zn(1)-O(2)	1.989(6)	Zn(1)-N(2)	2.013(7)
Zn(2)-O(3)	2.033(8)	Zn(2)-N(1)	2.041(8)
Zn(2)-O(7)	2.087(13)	Zn(2)-O(1)	2.082(7)
Zn(2)-O(1W)	2.247(12)	Zn(2)-O(4)	2.453(8)
O(5)-Zn(1)-N(3)	117.7(3)	O(5)-Zn(1)-O(2)	97.6(3)
N(3)-Zn(1)-O(2)	101.8(3)	O(5)-Zn(1)-N(2)	108.9(3)
N(3)-Zn(1)-N(2)	121.5(3)	O(2)-Zn(1)-N(2)	105.2(3)
O(3)-Zn(2)-N(1)	147.3(4)	O(3)-Zn(2)-O(7)	105.1(6)
N(1)-Zn(2)-O(7)	104.0(6)	O(3)-Zn(2)-O(1)	91.6(3)
N(1)-Zn(2)-O(1)	100.5(3)	O(7)-Zn(2)-O(1)	94.8(5)
O(3)-Zn(2)-O(1W)	80.7(5)	N(1)-Zn(2)-O(1W)	85.0(5)
O(7)-Zn(2)-O(1W)	89.3(6)	O(1)-Zn(2)-O(1W)	172.0(5)
O(3)-Zn(2)-O(4)	57.7(3)	N(1)-Zn(2)-O(4)	91.5(3)
O(7)-Zn(2)-O(4)	161.9(6)	O(1)-Zn(2)-O(4)	91.4(3)
O(1W)-Zn(2)-O(4)	82.7(5)		



(a) **(b)**

Fig. S1. Asymmetric units of (a) **1L** and (b) **1R**.



(a) **(b)**

Fig. S2. (a) 51-membered ring formed by three nearby MIDPPA moleculars coordinating to metal atoms in **1L** or **1R**. (b) Coordination mode of deprotonated 1,2,4-Benzenetricarboxylic acid in **1L** or **1R**.

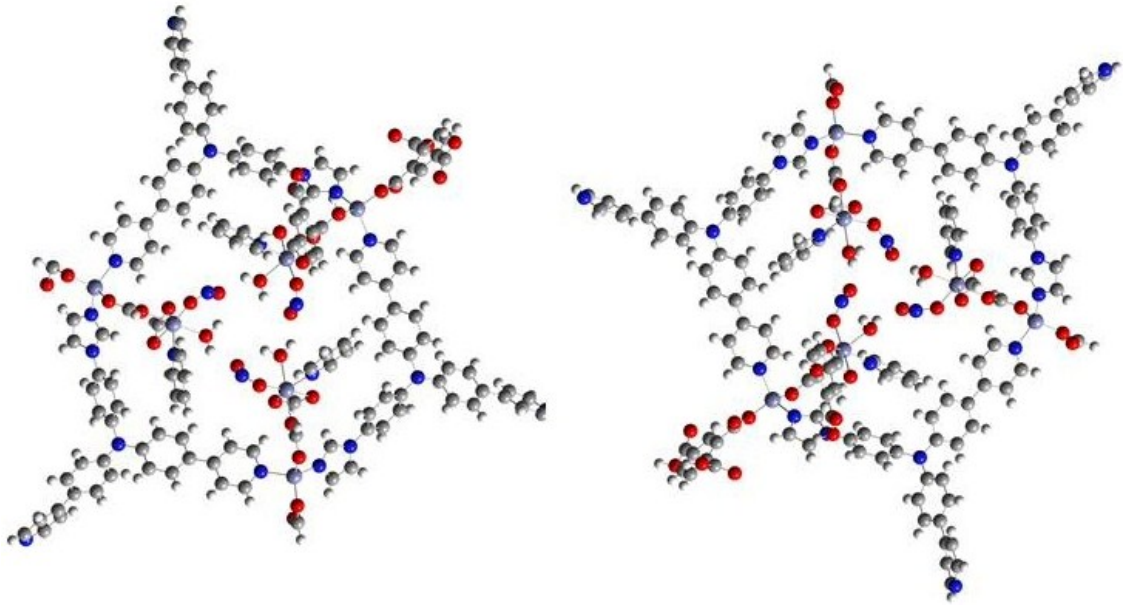
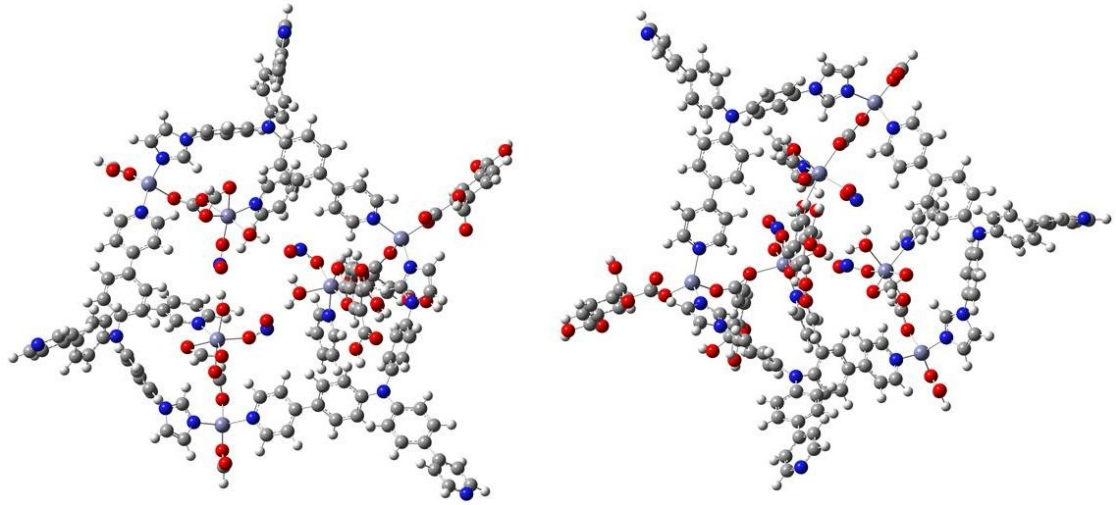


Fig. S3. The models of **1L** (a) and **1R** (b) before optimization by DFT.



(a) **(b)**

Fig. S4. The models of **1L** (a) and **1R** (b) after optimization by DFT.

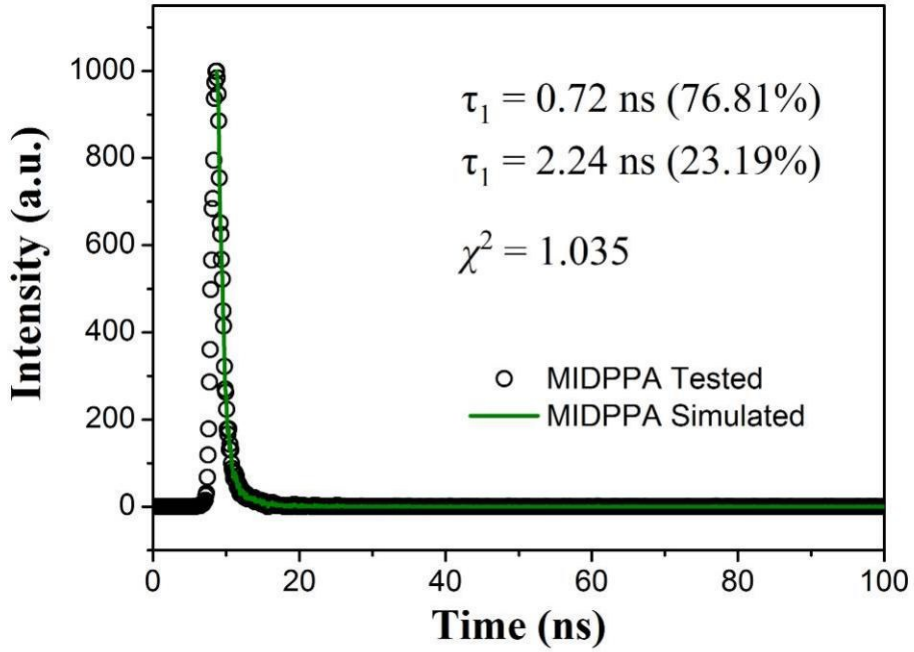


Fig. S5. The fitted decay curve monitored at 455 nm for free MIDPPA ligand in the solid state at room temperature. The sample was excited at 405 nm. Blank circles: experimental data; Solid line: fitted by Fit = $A + B_1 \times \exp(-t / \tau_1) + B_2 \times \exp(-t / \tau_2)$.

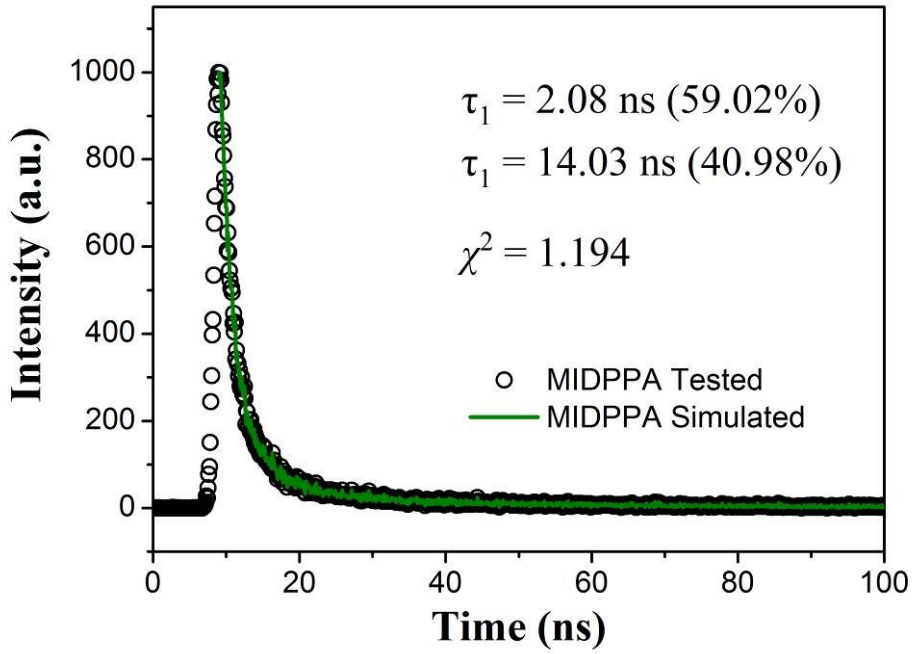


Fig. S6. The fitted decay curve monitored at 530 nm for free MIDPPA ligand in the solid state at room temperature. The sample was excited at 405 nm. Blank circles: experimental data; Solid line: fitted by Fit = $A + B_1 \times \exp(-t / \tau_1) + B_2 \times \exp(-t / \tau_2)$.

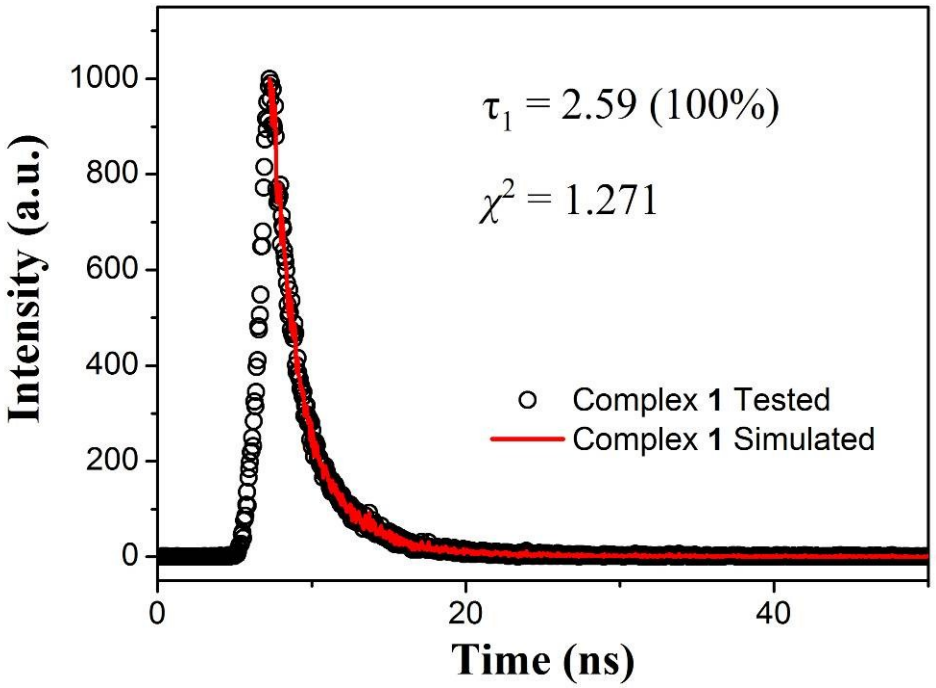


Fig. S7. The fitted decay curve monitored at 540 nm for complex **1** in the solid state at room temperature. The sample was excited at 405 nm. Blank circles: experimental data; Solid line: fitted by Fit = $A + B_1 \times \exp(-t / \tau_1) + B_2 \times \exp(-t / \tau_2)$.

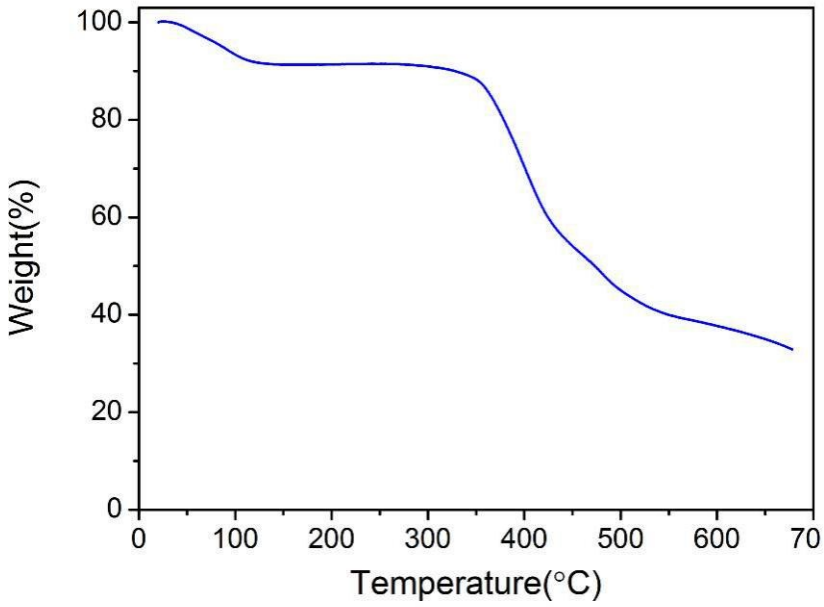


Fig. S8. Thermo-gravimetric plots of complex **1**.

References

S1 Zhang, M.–D.; Shi, Z.–Q.; Chen, M.–D.; Zheng, H.–G. Chiral crystallization and optical properties of three metal complexes based on two non–centrosymmetric tripodal ligands *Dalton Trans.*, **2015**, *44*, 5818–5825.

S2 Bruker (2005). *APEX2*, *SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

S3 Blatov, V. A. Nanocluster analysis of intermetallic structures with the program package TOPOS. *Struct. Chem.* **2012**, *23*, 955–963.