Electronic Supplementary Information (ESI) for

Chiral coordination compounds with exceptional enantioselectivity

*Minju Lee and Kang Min Ok**

Department of Chemistry, Sogang University, 35 Baekbeom-ro, Mapo-gu, Seoul 04107, Republic of Korea

Table of Contents

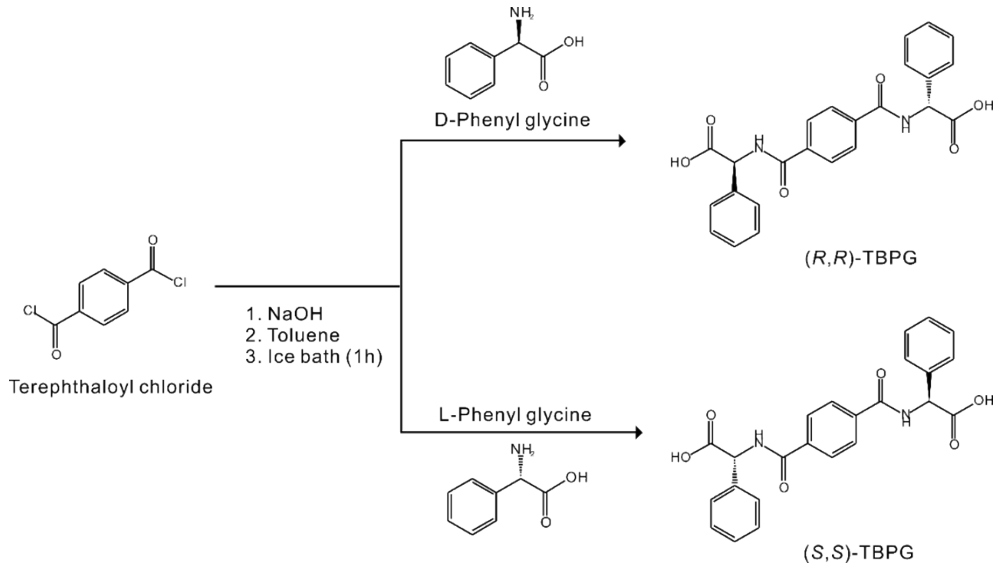
Experimental Procedures

Section S1. Materials and Methods

Materials. D-2-phenylglycine (99%, TCI), L-2-phenylglycine (98%, TCI), $Zn(NO_3)_2{\cdot}6H_2O$ (99%, Alfa Aesar), NaOH (98%, Alfa Aesar), Terephthaloyl chloride (99%, Sigma Aldrich), Toluene (99.8%, Samchun), HCl (35~37 wt% aq. solution, Samchun), *N*,*N*'-dimethylacetamide (DMA, 99%, Alfa Aesar), ethanol (99.9%, Samchun), and dimethyl sulfoxide-d_6 (99%, Sigma Aldrich) were purchased and used without further purification.

Synthesis of (*R*,*R*)-Terephthaloyl-bis-phenyl glycine [(*R*,*R*)-TBPG] and (*S*,*S*)-Terephthaloyl-bis-phenyl glycine [(*S*,*S*)-TBPG] ligands. The (*R*,*R*)-TBPG ligand was synthesized by a nucleophilic aromatic substitution reaction (Scheme S1). A 1.5 g (10.0 mmol) portion of D-phenyl glycine and 0.6 g (15.0 mmol) of NaOH were placed in a round bottom flask and dissolved in 20 mL of water by stirring in an ice bath to cool the solution to below 10 °C. And then, 1.0 g (5.0 mmol) of terephthaloyl chloride dissolved in 20 mL of toluene solution was added dropwise to the mixture. After the reaction mixture was stirred for 1 h, the aqueous layer was separated from the organic layer and acidified with concentrated HCl aqueous solution. The white product was collected by a vacuum filtration and dried. (*S*,*S*)-TBPG was synthesized by the same method as that of (*R*,*R*)-TBPG using L-phenyl glycine instead of D-phenyl glycine. (*R*,*R*)-TBPG and (*S*,*S*)-TBPG were obtained in 92.0% and 93.5.% yields, respectively.

Scheme S1. Synthesis of (*R,R*)-TBPG and (*S,S*)-TBPG



Synthesis of $[Zn_2((R,R)\text{-TBPG})_2(H_2O)_5]{\cdot}4H_2O$ [(*R*)-Zn] and $[Zn_2((S,S)\text{-TBPG})_2(H_2O)_5]{\cdot}4H_2O$ [(*S*)-Zn]. A 0.089 g (0.3 mmol) portion of $Zn(NO_3)_2{\cdot}6H_2O$, 0.130 g (0.3 mmol) of (*R*,*R*)-TBPG or (*S*,*S*)-TBPG, 1 mL of DMA, 1 mL of deionized water, and 1 mL of ethanol were put into a Teflon–lined autoclave. After closing, the autoclave was heated at 80 °C for 72 h and cooled to room temperature at a rate of 6 °C/h. The clear solution was transferred to a vial and colorless plate-shaped crystals begin to grow after about 5 hours through slow evaporation. After 24 h, the complete product was filtered and washed with deionized water. Colorless crystals of (*R*)-Zn and (*S*)-Zn were obtained in 43% and 41% yields, respectively.

Instrumentation. Colorless plate shape single crystals with the size of 0.168 mm × 0.153 mm × 0.037 mm for (*R*)-Zn and 0.164 mm × 0.157 mm × 0.104 mm for (*S*)-Zn were used for single crystal X-ray diffraction (SC-XRD) analysis. SC-XRD data were collected using a Bruker D8 QUEST diffractometer with a graphite monochromated Mo Kα radiation source (λ = 0.71703 Å) and a PHOTON-II CPAD detector at 100 K at the Advanced Bio-Interface Core Research Facility, Sogang University. The collected data were integrated by the SAINT program[1] and absorption correction was performed using the program SADABS.[2, 3] The crystal structures were solved and refined with SHELXS-2013 and SHELXL-2013, respectively, implemented in the WinGX-2014.[4-6] Since the solvent molecules were severely disordered, the SQUEEZE option in the PLATON[7, 8] software was performed. The detailed crystallographic data for (*R*)-Zn and (*S*)-Zn are tabulated in Table S1. The diffraction data for (*S*)-Zn-EtOH were obtained using a synchrotron radiation (0.63000 Å) on the 2D Supramolecular Crystallography (2D-SMC) beamline equipped with a Rayonix MX225HS CCD area detector at 100k in Pohang Acceleration Laboratory (PAL). The data were integrated and scaled by the program HKL-3000sm.[9] The crystal structures were solved and refined with SHELXS-2013[4] and SHELXL-2013,[5] respectively, implemented in the WinGX-2014.[6] Since the solvent molecules were severely disordered, the SQUEEZE option in the PLATON[7, 8] software was performed. The detailed crystallographic data and selected bond lengths and selected bond angles for (*S*)-Zn-EtOH are tabulated in Tables S7-9.

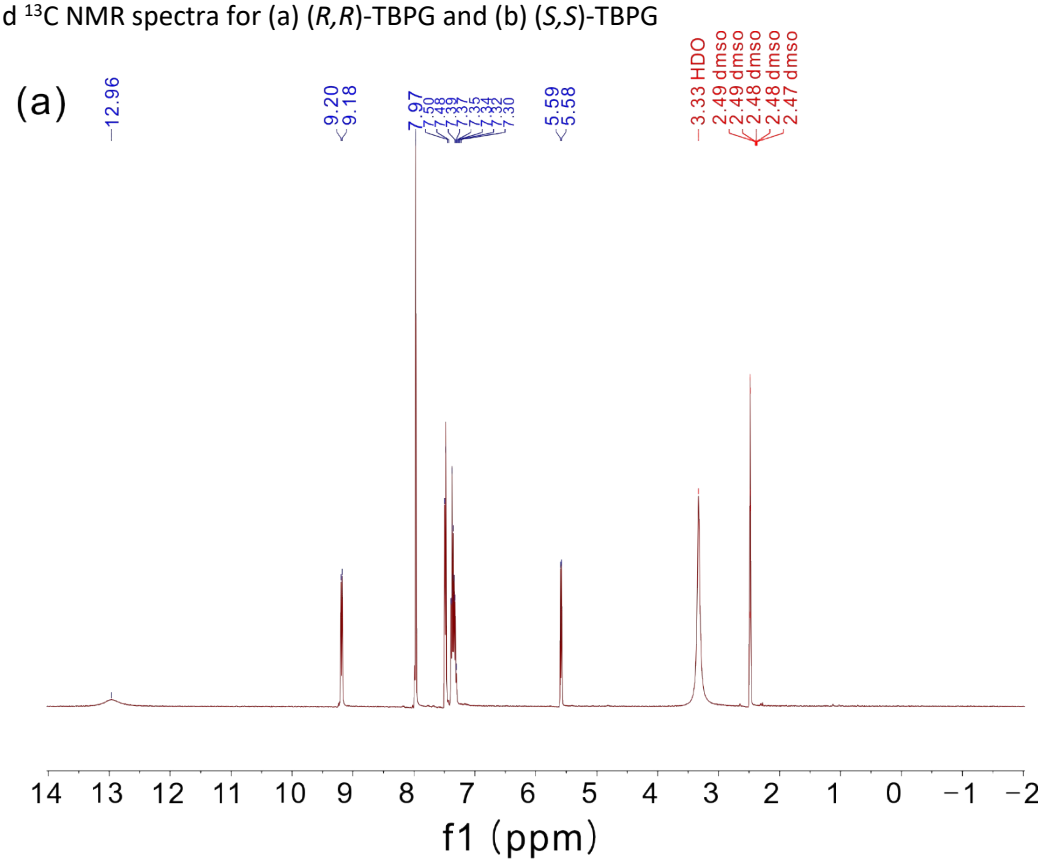
Table 1 Crystallographic Data for (*R*)-Zn and (*S*)-Zn

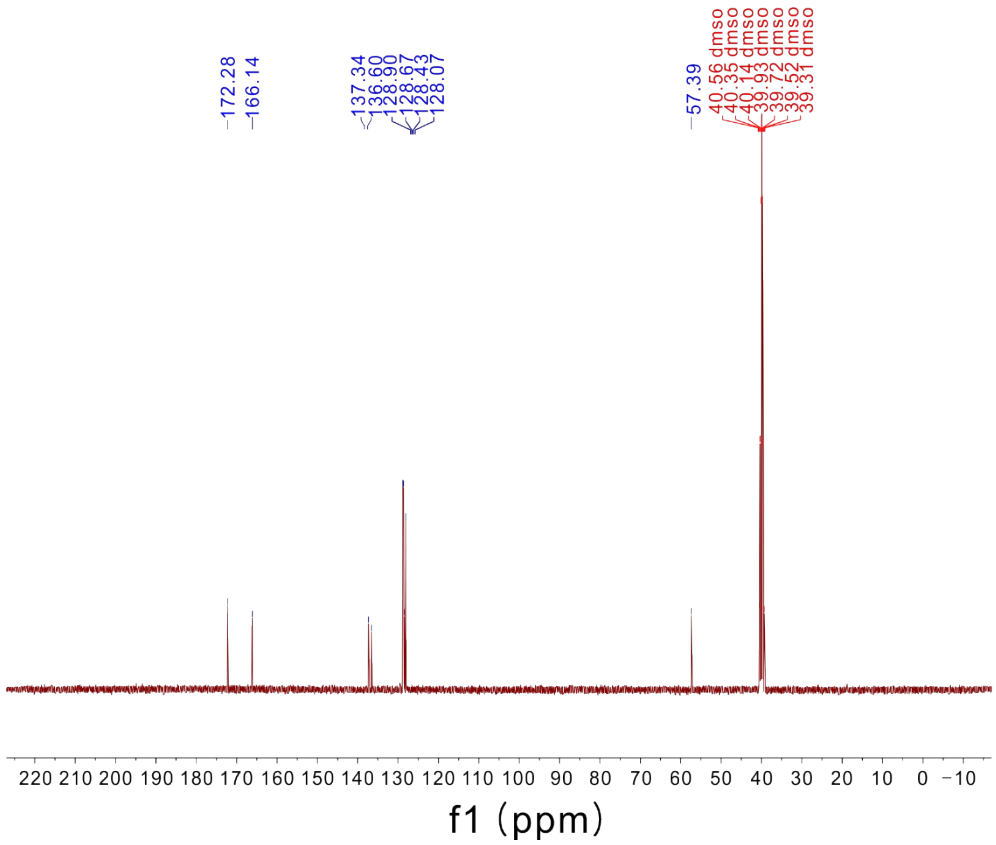
	(*R*)-Zn	(*S*)-Zn
fw	1153.69	1153.69
space group	$P2_1$	$P2_1$
a (Å)	12.0803(13)	12.0909(7)
b (Å)	16.6380(18)	16.6580(10)
c (Å)	14.6323(16)	14.6039(8)
β (°)	114.205(4)	114.138(2
V (Å^3)	2682.45(5)	2684.2(3)
Z	2	2
T (K)	100(2)	100(2)
λ (Å)	0.71073	0.71073
ρ_{calcd} (g/cm^3)	1.428	1.410
$R(F_o)^a$	0.0664	0.0461
$R_w(F_o^2)^b$	0.1047	0.0601
Flack *x*	0.042(6)	0.042(4)

$^aR(F) = \Sigma\, ||F_o| - |F_c|| \,/\, \Sigma\, |F_o|$. $^bR_w(F_o^2) = [\Sigma w(F_o^2 - F_c^2)^2 \,/\, \Sigma w(F_o^2)^2]^{1/2}$.

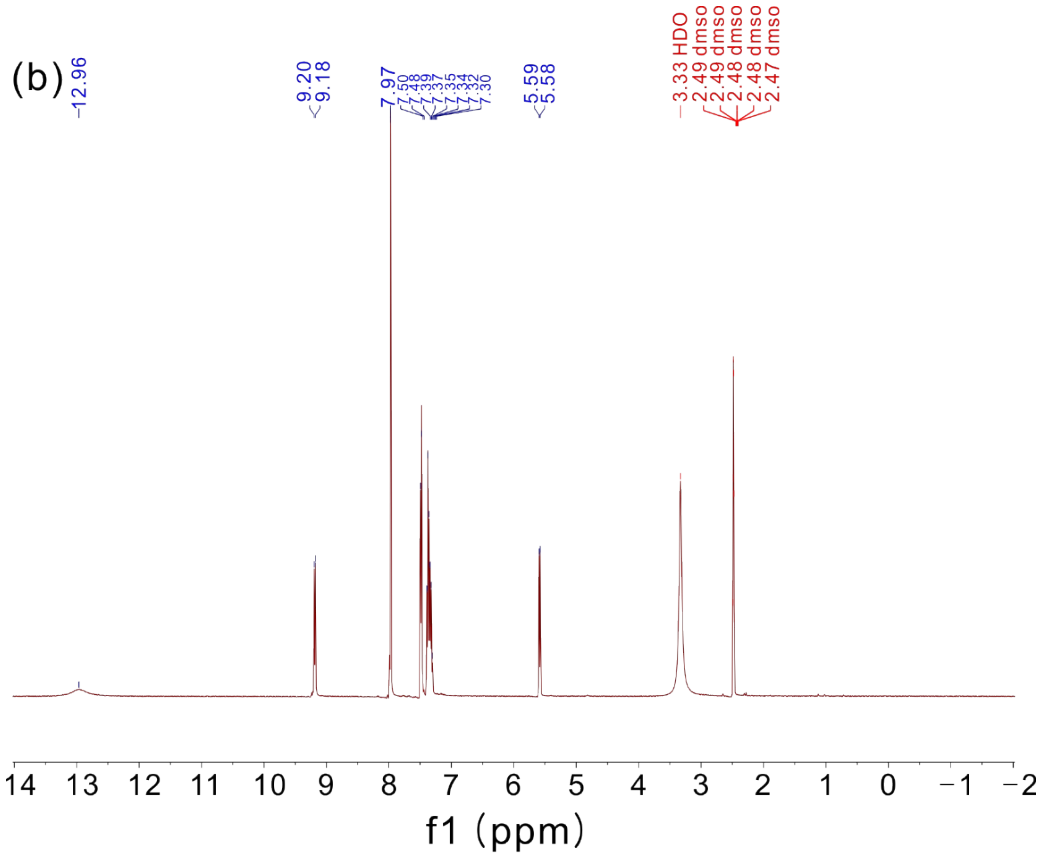
Powder X-ray diffraction (PXRD) data were collected on a Rigaku MiniFlex 600 using Cu Kα (*λ* = 1.5406 Å) radiation with 40 kV and 15 mA at room temperature. Polycrystalline samples were placed on the sample holders and then scanned in the 2θ range of 5−70° with a scan speed of 20° min^{-1} and a scan step width of 0.02°.
Thermogravimetric analysis (TGA) diagrams of the title compounds were obtained by using a SCINCO TGA-N1000 thermal analyzer. The polycrystalline samples were placed on alumina crucibles and heated from 25 °C to 900 °C at a rate of 10 °C min^{-1} under flowing air.
^{1}H-NMR and ^{13}C-NMR spectral data of the samples were measured with a Varian Inova 400 spectrometer at 400 and 100 MHz, respectively.
Energy Dispersive X-ray Spectrometer (EDX) data were measured with a Horiba Energy EX-250 instrument equipped on a Hitachi S-3400N scanning electron microscope. The EDX data matched well with the calculated atomic ratios obtained from SC-XRD.
Elemental analysis was measured with a Thermo Scientific Flash 2000 on Sn capsules. Elemental analysis for (*R*)-Zn, observed (calculated): C, 49.97% (49.88%); H, 4.72% (4.74%); N, 4.84% (4.91%); (*S*)-Zn, observed (calculated): C, 49.91% (49.88%); H, 4.84 (4.74%); N, 4.82% (4.91%).
Infrared (IR) spectra were measured with a Thermo Scientific Nicolet iS50 FT-IR spectrometer in the range of 400–4000 cm^{-1} with an attenuated total reflection (ATR) accessory.
UV-vis diffuse-reflectance spectra were measured with a Jasco V–660 spectrophotometer in the range of 200–800 nm. The band gap energy was calculated by the Kubelka-Munk function.[10]
Density functional theory (DFT) calculations for title compounds were performed to investigate the electronic structures using the Quantum Espresso package.[11] The ultrasoft pseudopotentials type[12] and the Perdew–Burke–Ernzerhof (PBE)[13] functionals were used for all elements (C, H, N, O, and Zn). The kinetic energy and charge density cutoff were set to 46.649 and 419.846 Ry, respectively. The self-consistent function (SCF) convergence thresholds were set to about 4.0 × 10^{-6} Ry and the k-points grids of Brillouin zone was set to 2 × 2 × 2.
Solid state circular dichroism (CD) spectra were measured with a JASCO-J-815 spectrophotometer in the range of 220–325 nm after purging with nitrogen gas. The scanning speeds for the measurements were 50 nm min^{-1}.
The fluorescence spectra were measured with a Hitachi F-7000 fluorescence spectrophotometer in the range of 600–800 nm. The scanning speeds for the measurements were 1200 nm min^{-1}. The solid-state fluorescence measurements for (*R*)-Zn were performed at room temperature. To investigate the selective sensing capacity of (*R*)-Zn for Histidine, the ground polycrystalline sample of (*R*)-Zn (10 mg) was dispersed in water (3 mL) by ultrasonication and then subsequently placed in a cuvette with 1 cm width for the measurements. All the titrations were carried out by adding L- and D-Histidine (10 mM) gradually. The fluorescence spectra were recorded at 298 K with the emission wavelength at 680 nm (λ_{ex} = 340 nm). Each measurement was repeated three times to obtain reliable data.
Powder second-harmonic generation (SHG) measurements were performed using a modified Kurtz nonlinear optical system.[14] Because the SHG efficiency depends on the particle size, the ground sample was sieved into specific particle size ranges (< 20, 20–45, 45–63, 63–75, 75–90, and 90–125 μm). Each sieved particle was put into separate capillary tubes. The tubes were irradiated by a DAWA Q-switched Nd:YAG laser (1064 nm), and the SHG light (532 nm) was received to a Hamamatsu photomultiplier tube and detected by a Tektronix TDS 1032 oscilloscope. A comprehensive SHG measurement was described earlier in the published paper.[15]

Fig. S1 ^{1}H and ^{13}C NMR spectra for (a) (*R,R*)-TBPG and (b) (*S,S*)-TBPG





(b)


12.96
9.20
9.18
7.97
7.50
7.48
7.39
7.37
7.35
7.34
7.32
7.30
5.59
5.58
3.33 HDO
2.49 dmso
2.49 dmso
2.48 dmso
2.48 dmso
2.47 dmso
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2
f1 (ppm)

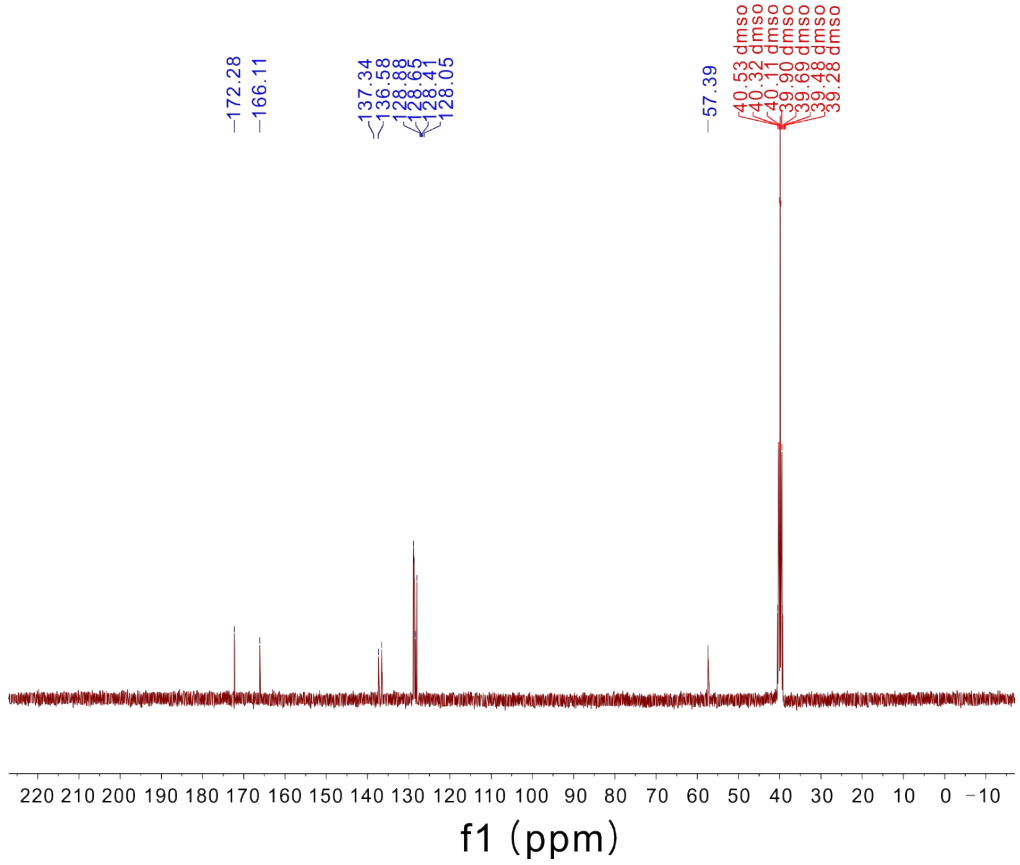

172.28
166.11
137.34
136.58
128.88
128.65
128.41
128.05
57.39
40.53 dmso
40.32 dmso
40.11 dmso
39.90 dmso
39.69 dmso
39.48 dmso
39.28 dmso
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

Fig. S2 Ball-and-stick model revealing coordination modes of Zn^{2+} cations and TBPG ligands in (*R*)-Zn (cyan, Zn; black, C; red, O).

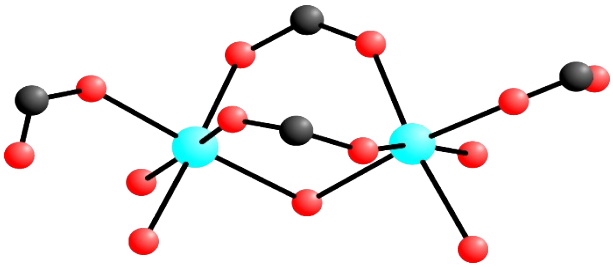


Table S2 Selected bond distances (Å) and selected bond angles (°) for *(R)*-Zn

Selected bond distances (Å)							
Zn(1)-O(4)	2.031(5)	Zn(2)-O(11)	2.287(6)	O(16)-C(48)	1.252(9)	C(37)-C(40)	1.494(10)
Zn(1)-O(17)#1	2.074(5)	O(4)-C(1)	1.252(8)	O(17)-C(48)	1.259(8)	C(41)-C(42)	1.42(5)
Zn(1)-O(13)#2	2.086(5)	O(5)-C(1)	1.257(9)	C(1)-C(2)	1.531(10)	C(41)-C(48)	1.548(10)
Zn(1)-O(1)	2.096(6)	O(6)-C(9)	1.244(9)	C(2)-C(3)	1.503(11)	N(1)-C(9)	1.319(9)
Zn(1)-O(3)	2.136(5)	O(7)-C(16)	1.244(8)	C(9)-C(10)	1.496(10)	N(1)-C(2)	1.474(9)
Zn(1)-O(2)#2	2.163(6)	O(8)-C(24)	1.258(9)	C(13)-C(16)	1.500(10)	N(2)-C(16)	1.323(9)
Zn(2)-O(12)	2.027(5)	O(9)-C(24)	1.267(9)	C(17)-C(18)	1.525(10)	N(2)-C(17)	1.468(9)
Zn(2)-O(16)#3	2.042(5)	O(12)-C(25)	1.267(8)	C(17)-C(24)	1.522(10)	N(3)-C(33)	1.341(9)
Zn(2)-O(9)	2.056(5)	O(13)-C(25)	1.248(9)	C(25)-C(26)	1.518(10)	N(3)-C(26)	1.455(9)
Zn(2)-O(10)	2.072(5)	O(14)-C(33)	1.232(9)	C(26)-C(27)	1.523(10)	N(4)-C(40)	1.341(9)
Zn(2)-O(2)	2.186(5)	O(15)-C(40)	1.231(10)	C(33)-C(34)	1.502(10)	N(4)-C(41)	1.464(9)

Selected bond angles (°)					
O(1)-Zn(1)-O(2)#2	90.3(2)	O(16)#3-Zn(2)-O(10)	92.0(2)	C(40)-N(4)-C(41)	122.4(7)
O(1)-Zn(1)-O(3)	85.1(2)	O(16)#3-Zn(2)-O(11)	174.5(2)	O(4)-C(1)-C(2)	116.1(6)
O(2)-Zn(2)-O(11)	89.6(2)	O(17)#1-Zn(1)-O(1)	92.9(2)	O(5)-C(1)-C(2)	116.7(6)
O(3)-Zn(1)-O(2)#2	92.7(2)	O(17)#1-Zn(1)-O(2)#2	89.3(2)	O(6)-C(9)-C(10)	119.5(7)
O(4)-Zn(1)-O(1)	85.7(2)	O(17)#1-Zn(1)-O(3)	177.2(2)	O(7)-C(16)-C(13)	119.2(6)
O(4)-Zn(1)-O(2)#2	173.1(2	O(17)#1-Zn(1)-O(13)#2	95.8(2)	O(8)-C(24)-C(17)	117.5(7)
O(4)-Zn(1)-O(3)	92.7(20	Zn(1)#4-O(2)-Zn(2)	111.4(2)	O(9)-C(24)-C(17)	116.7(6)
O(4)-Zn(1)-O(13)#2	90.29(19)	C(1)-O(4)-Zn(1)	130.6(5)	O(12)-C(25)-C(26)	115.5(6)
O(4)-Zn(1)-O(17)#1	85.2(2)	C(24)-O(9)-Zn(2)	128.4(5)	O(13)-C(25)-C(26)	117.0(6)
O(9)-Zn(2)-O(2)	171.6(2)	C(25)-O(12)-Zn(2)	131.3(5)	O(14)-C(33)-C(34)	121.7(6)
O(9)-Zn(2)-O(10)	92.4(2)	C(25)-O(13)-Zn(1)#4	132.7(5)	O(15)-C(40)-C(37)	121.3(7)
O(9)-Zn(2)-O(11)	83.1(2)	C(48)-O(16)-Zn(2)#5	134.5(5)	O(16)-C(48)-C(41)	117.1(6)
O(10)-Zn(2)-O(2)	91.0(2)	C(48)-O(17)-Zn(1)#6	132.0(5)	N(1)-C(2)-C(1)	110.2(6)
O(10)-Zn(2)-O(11)	84.9(2)	O(4)-C(1)-O(5)	127.0(7)	N(1)-C(2)-C(3)	114.2(6)
O(12)-Zn(2)-O(2)	87.9(2)	O(8)-C(24)-O(9)	125.8(7)	N(1)-C(9)-C(10)	117.7(6)
O(12)-Zn(2)-O(11)	83.9(2)	O(13)-C(25)-O(12)	127.5(7)	N(2)-C(16)-C(13)	119.1(6)
O(12)-Zn(2)-O(9)	87.2(2)	O(16)-C(48)-O(17)	127.2(7)	N(2)-C(17)-C(18)	112.7(6)
O(12)-Zn(2)-O(10)	168.7(2)	O(6)-C(9)-N(1)	122.7(7)	N(2)-C(17)-C(24)	109.7(6)
O(12)-Zn(2)-O(16)#3	99.3(2)	O(7)-C(16)-N(2)	121.7(7)	N(3)-C(26)-C(25)	110.7(6)
O(13)#2-Zn(1)-O(1)	170.1(2)	O(14)-C(33)-N(3)	121.4(7)	N(3)-C(26)-C(27)	112.6(6)
O(13)#2-Zn(1)-O(2)#2	94.4(2)	O(15)-C(40)-N(4)	121.3(7)	N(3)-C(33)-C(34)	116.9(6)
O(13)#2-Zn(1)-O(3)	86.0(2)	C(9)-N(1)-C(2)	122.2(6)	N(4)-C(40)-C(37)	117.4(7)
O(16)#3-Zn(2)-O(2)	94.9(2)	C(16)-N(2)-C(17)	119.7(6)	N(4)-C(41)-C(42)	110.6(13)
O(16)#3-Zn(2)-O(9)	92.6(2)	C(33)-N(3)-C(26)	120.4(6)	N(4)-C(41)-C(48)	107.3(6)

Symmetry operation : #1 x-1,y+1,z-1 #2 x,y+1,z #3 x-1,y,z-1 #4 x,y-1,z #5 x+1,y,z+1 #6 x+1,y-1,z+1

Table S3 Hydrogen bonds distances (Å) for *(R)*-Zn

D-H...A	d(D...A)	D-H...A	d(D...A)
N(1)-H(1)...O(18)#1	2.968(8)	O(10)-H(55)...O(7)#9	2.732(7)
N(2)-H(2A)...O(19)	3.477(9)	O(11)-H(56)...O(19)	2.812(9)
O(1)-H(48)...O(14)#7	2.734(7)	O(18)-H(58)...O(8)#8	2.868(8)
O(2)-H(50)...O(20)	2.600(8)	O(18)-H(59)...O(17)	2.825(7)
O(2)-H(51)...O(21)	2.634(8)	O(19)-H(60)...O(12)	2.762(8)
O(3)-H(52)...O(4)	3.016(7)	O(19)-H(61)...O(5) #8	2.840 (8)
O(3)-H(52)...O(5)	2.738(7)	O(20)-H(62)...O(6)#8	2.728(8)
O(3)-H(53)...O(6)#7	2.796(8)	O(20)-H(63)...O(11)	2.756(9)
O(10)-H(54)...O(8)	2.638(8)	O(21)-H(64)...O(7)#9	2.804(9)
Symmetry operation : #1 x-1,y+1,z-1 #7 -x+1,y+1/2,-z+1 #8 -x+1,y-1/2,-z+1 #9 -x,y-1/2,-z			

Table S4 Selected bond distances (Å) and selected bond angles (°) for *(S)*-Zn

Selected bond distances (Å)							
Zn(1)-O(4)	2.042(3)	Zn(2)-O(11)	2.284(4)	O(16)-C(48)	1.257(6)	C(37)-C(40)	1.501(7)
Zn(1)-O(17)#1	2.071(3)	O(4)-C(1)	1.252(6)	O(17)-C(48)	1.255(6)	C(41)-C(42)	1.47(4)
Zn(1)-O(13)#2	2.079(3)	O(5)-C(1)	1.248(6)	C(1)-C(2)	1.533(6)	C(41)-C(48)	1.540(7)
Zn(1)-O(1)	2.102(4)	O(6)-C(9)	1.252(5)	C(2)-C(3)	1.520(7)	N(1)-C(9)	1.318(6)
Zn(1)-O(3)	2.144(3)	O(7)-C(16)	1.242(6)	C(9)-C(10)	1.503(6)	N(1)-C(2)	1.475(6)
Zn(1)-O(2)	2.160(3)	O(8)-C(24)	1.250(5)	C(13)-C(16)	1.500(6)	N(2)-C(16)	1.336(6)
Zn(2)-O(12)	2.023(3)	O(9)-C(24)	1.270(5)	C(17)-C(18)	1.520(7)	N(2)-C(17)	1.465(6)
Zn(2)-O(16)#3	2.039(4)	O(12)-C(25)	1.259(5)	C(17)-C(24)	1.527(7)	N(3)-C(33)	1.343(6)
Zn(2)-O(9)	2.050(3)	O(13)-C(25)	1.245(6)	C(25)-C(26)	1.539(6)	N(3)-C(26)	1.461(5)
Zn(2)-O(10)	2.067(3)	O(14)-C(33)	1.222(6)	C(26)-C(27)	1.511(7)	N(4)-C(40)	1.342(6)
Zn(2)-O(2)#4	2.188(3)	O(15)-C(40)	1.225(6)	C(33)-C(34)	1.502(6)	N(4)-C(41)	1.461(6)

Selected bond angles (°)					
O(1)-Zn(1)-O(2)	90.23(14)	O(16)#3-Zn(2)-O(10)	91.90(14)	C(40)-N(4)-C(41)	121.3(4)
O(1)-Zn(1)-O(3)	85.13(14)	O(16)#3-Zn(2)-O(11)	174.54(14)	O(4)-C(1)-C(2)	115.6(4)
O(2)#4-Zn(2)-O(11)	89.85(13)	O(17)#1-Zn(1)-O(1)	93.01(14)	O(5)-C(1)-C(2)	117.0(4)
O(3)-Zn(1)-O(2)	92.87(13)	O(17)#1-Zn(1)-O(2)	88.89(13)	O(6)-C(9)-C(10)	119.0(4)
O(4)-Zn(1)-O(1)	85.69(14)	O(17)#1-Zn(1)-O(3)	177.44(13)	O(7)-C(16)-C(13)	120.1(4)
O(4)-Zn(1)-O(2)	172.90(13)	O(17)#1-Zn(1)-O(13)#2	95.56(14)	O(8)-C(24)-C(17)	117.7(4)
O(4)-Zn(1)-O(3)	92.57(13)	Zn(1)-O(2)-Zn(2)#2	111.44(15)	O(9)-C(24)-C(17)	116.1(4)
O(4)-Zn(1)-O(13)#2	90.43(12)	C(1)-O(4)-Zn(1)	130.2(3)	O(12)-C(25)-C(26)	115.0(4)
O(4)-Zn(1)-O(17)#1	85.53(13)	C(24)-O(9)-Zn(2)	128.4(3)	O(13)-C(25)-C(26)	117.5(4)
O(9)-Zn(2)-O(2)#4	172.02(13)	C(25)-O(12)-Zn(2)	131.7(3)	O(14)-C(33)-C(34)	121.7(4)
O(9)-Zn(2)-O(10)	92.10(13)	C(25)-O(13)-Zn(1)#4	132.7(3)	O(15)-C(40)-C(37)	121.2(4)
O(9)-Zn(2)-O(11)	83.18(13)	C(48)-O(16)-Zn(2)#5	134.5(3)	O(16)-C(48)-C(41)	117.1(4)
O(10)-Zn(2)-O(2)#4	91.17(13)	C(48)-O(17)-Zn(1)#6	132.5(3)	N(1)-C(2)-C(3)	113.6(4)
O(10)-Zn(2)-O(11)	85.03(14)	O(5)-C(1)-O(4)	127.4(4)	N(1)-C(2)-C(1)	110.6(4)
O(12)-Zn(2)-O(2)#4	87.90(13)	O(8)-C(24)-O(9)	126.2(4)	N(1)-C(9)-C(10)	117.6(4)
O(12)-Zn(2)-O(9)	87.52(13)	O(13)-C(25)-O(12)	127.4(4)	N(2)-C(16)-C(13)	119.3(4)
O(12)-Zn(2)-O(10)	169.13(14)	O(17)-C(48)-O(16)	126.7(5)	N(2)-C(17)-C(18)	113.1(4)
O(12)-Zn(2)-O(11)	84.14(13)	O(6)-C(9)-N(1)	123.4(4)	N(2)-C(17)-C(24)	110.1(4
O(12)-Zn(2)-O(16)#3	98.97(14)	O(7)-C(16)-N(2)	120.6(4)	N(3)-C(26)-C(27)	112.8(4)
O(13)#2-Zn(1)-O(1)	170.29(14)	O(14)-C(33)-N(3)	121.6(4)	N(3)-C(26)-C(25)	109.6(4)
O(13)#2-Zn(1)-O(2)	94.49(13)	O(15)-C(40)-N(4)	122.3(4)	N(3)-C(33)-C(34)	116.7(4)
O(13)#2-Zn(1)-O(3)	86.16(14)	C(9)-N(1)-C(2)	121.1(4)	N(4)-C(40)-C(37)	116.5(5)
O(16)#3-Zn(2)-O(2)#4	94.73(14)	C(16)-N(2)-C(17)	120.0(4)	N(4)-C(41)-C(42)	111.8(1)
O(16)#3-Zn(2)-O(9)	92.44(14)	C(33)-N(3)-C(26)	119.7(4)	N(4)-C(41)-C(48)	107.5(4)

Symmetry operation : #1 x-1,y-1,z-1 #2 x,y-1,z #3 x-1,y,z-1 #4 x,y+1,z #5 x+1,y,z+1 #6 x+1,y+1,z+1

Table S5 Hydrogen bonds distances (Å) for *(S)*-Zn

D-H...A	d(D...A)	D-H...A	d(D...A)
N(1)-H(1)...O(18)#1	2.967(5)	O(10)-H(55)...O(8)	2.626(5)
N(2)-H(2A)...O(19)	3.468(6)	O(11)-H(57)...O(19)	2.814(5)
O(1)-H(48)...O(14)#10	2.743(5)	O(18)-H(58)...O(17)	2.833(5)
O(2)-H(50)...O(20)	2.640(5)	O(18)-H(59)...O(8)#8	2.862(5)
O(2)-H(51)...O(21)	2.613(5)	O(19)-H(60)...O(5)#8	2.843(5)
O(3)-H(52)...O(6)#10	2.799(5)	O(19)-H(61)...O(12)	2.773(5)
O(3)-H(53)...O(4)	3.027(5)	O(20)-H(63)...O(7)#9	2.808(5)
O(3)-H(53)...O(5)	2.744(5)	O(21)-H(64)...O(6)#10	2.716(5)
O(10)-H(54)...O(7)#7	2.743(5)	O(21)-H(65)...O(11)#2	2.749(6)
Symmetry operation : #1 x-1,y-1,z-1 #2 x,y-1,z #7 -x,y+1/2,-z #8 -x+1,y+1/2,-z+1 #9 -x,y-1/2,-z #10 -x+1,y-1/2,-z+1			

Fig. S3 Experimental and calculated powder X-ray diffraction patterns of *(R)*-Zn and *(S)*-Zn

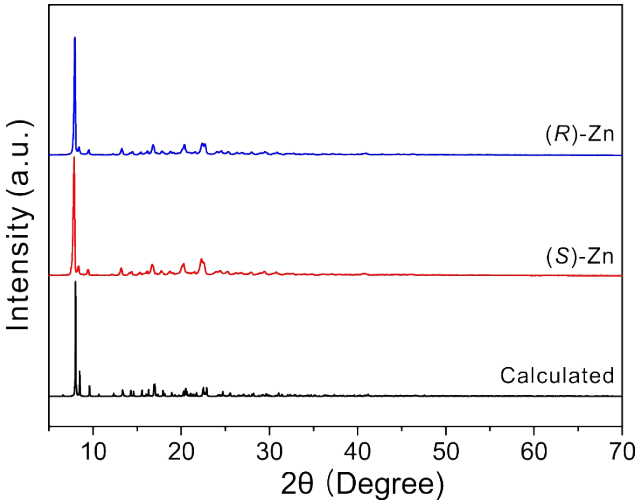


Fig. S4 SEM-EDX data for *(R)*-Zn and *(S)*-Zn

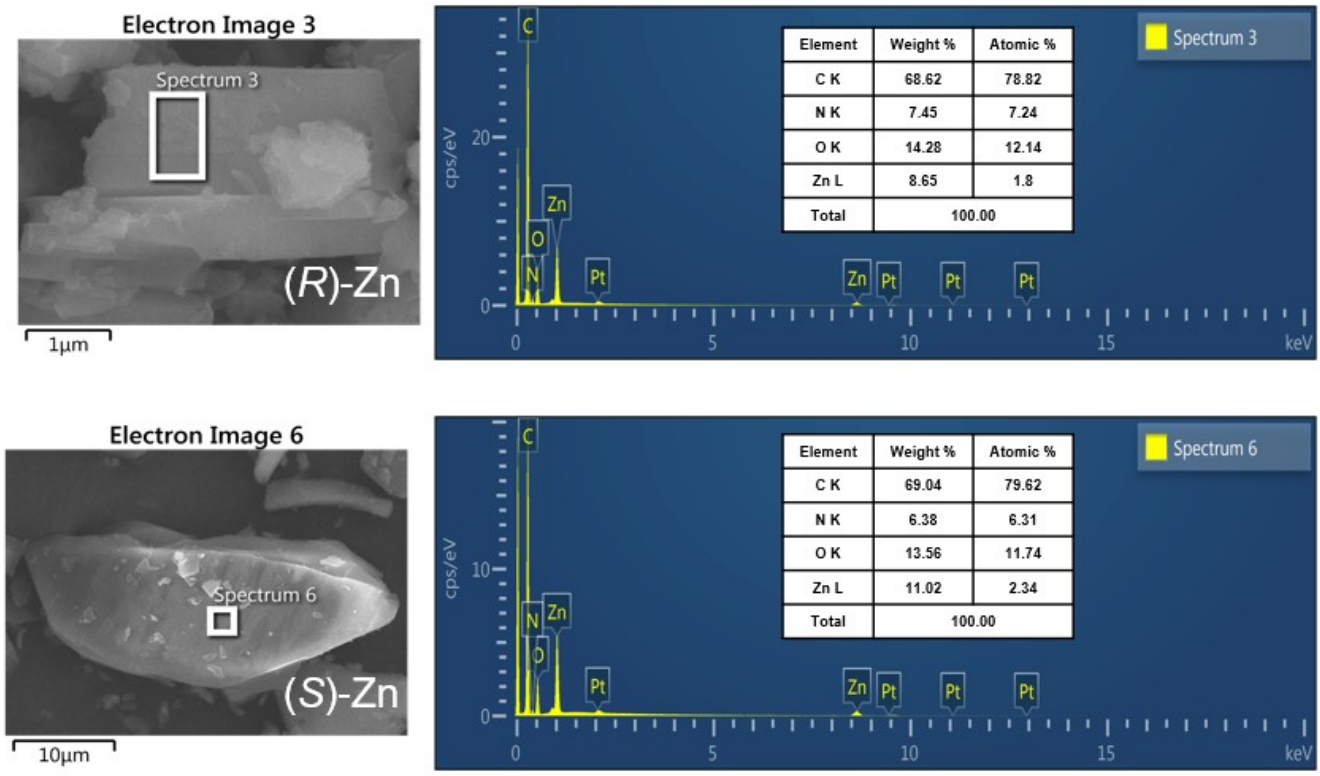


Fig. S5 IR spectra for (*R,R*)-TBPG, (*S,S*)-TBPG, (*R*)-Zn and (*S*)-Zn

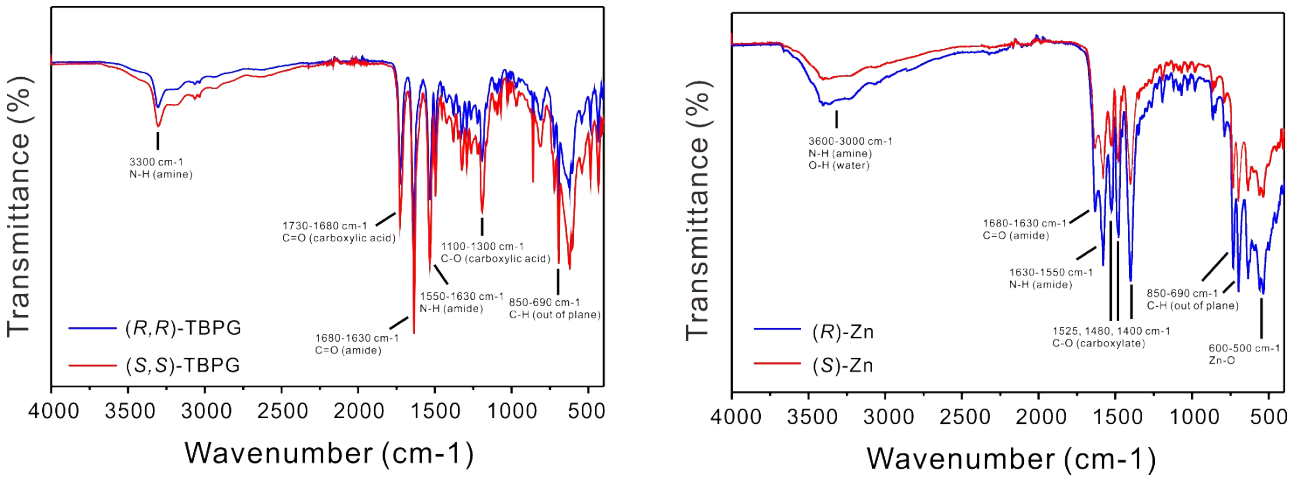


Fig. S6 UV-vis diffuse reflectance spectra for (*R,R*)-TBPG, (*S,S*)-TBPG, *(R)*-Zn and *(S)*-Zn

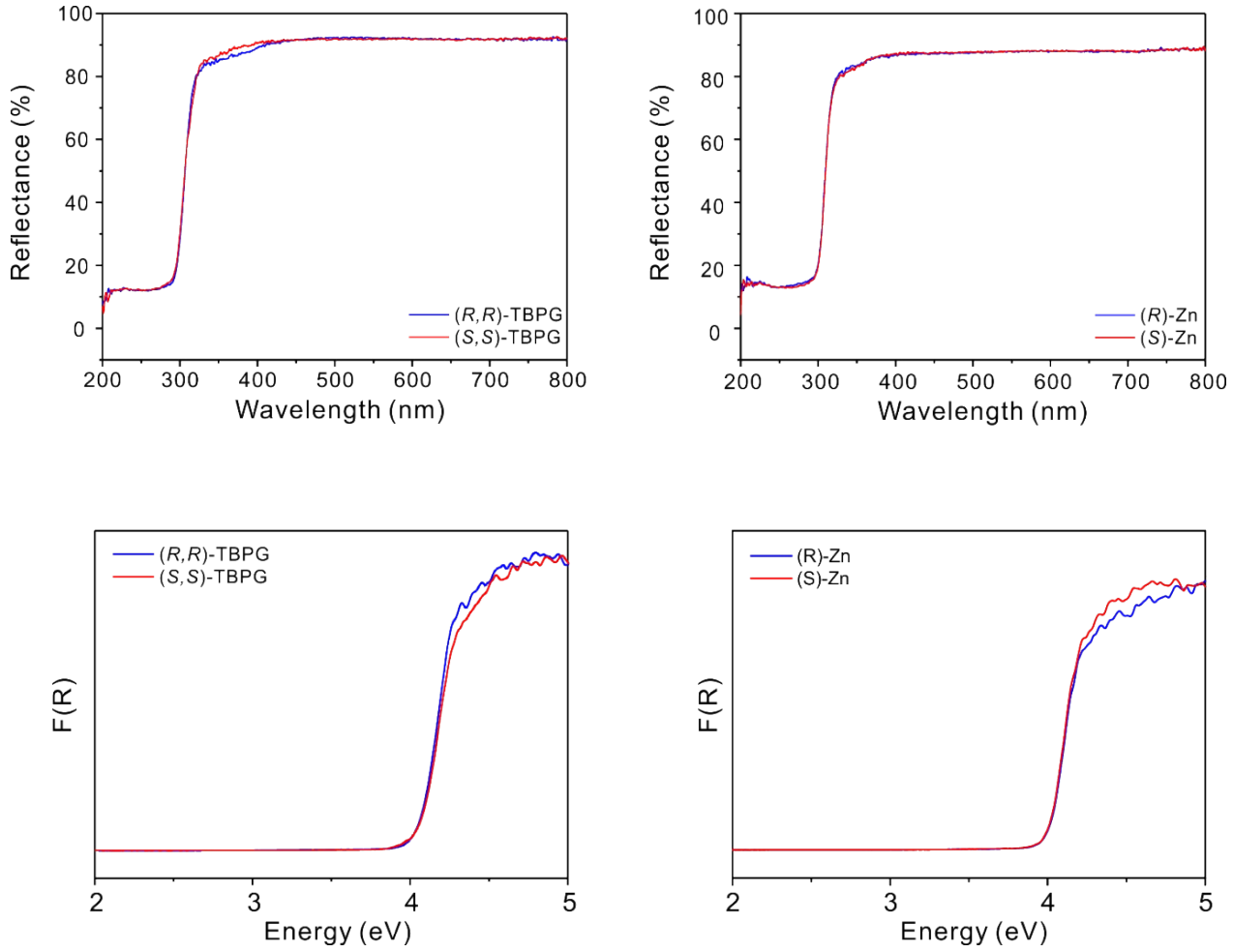


Fig. S7 TGA diagrams for *(R)*-Zn and *(S)*-Zn

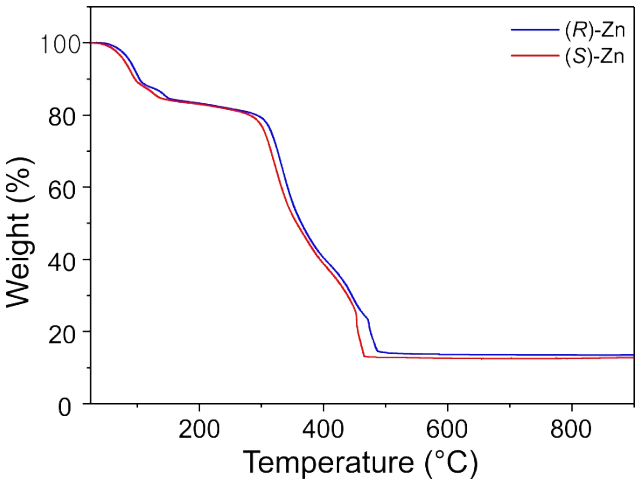


Fig. S8 PXRD patterns measured after heating the samples to 800 °C

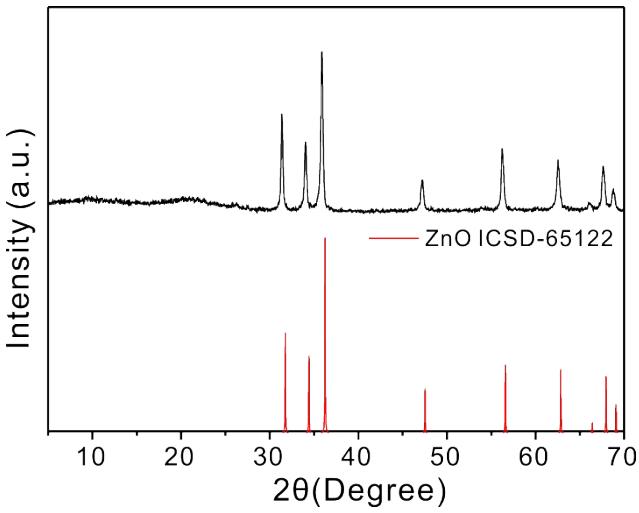
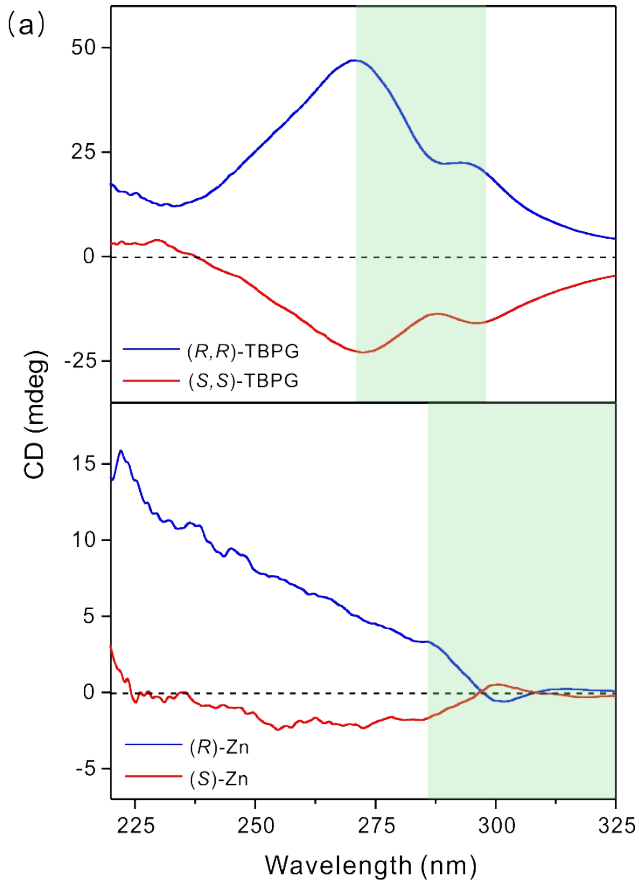


Fig. S9 (a) Solid-state CD spectra of (*R*,*R*)-TBPG, (S,*S*)-TBPG, (*R*)-Zn, and (*S*)-Zn. (b) Absorbance spectra of (*R*,*R*)-TBPG and (*R*)-Zn.



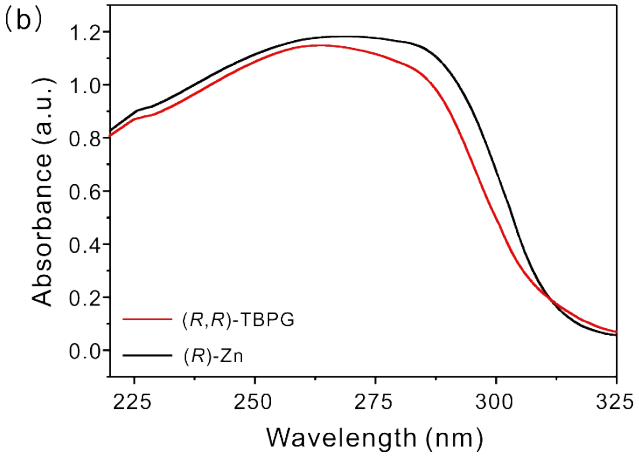


Fig. S10 Band structures for (a) *(R)*-Zn and (b) *(S)*-Zn. Arrows represent the optical transition from the valence band maximum to the conduction band minimum.

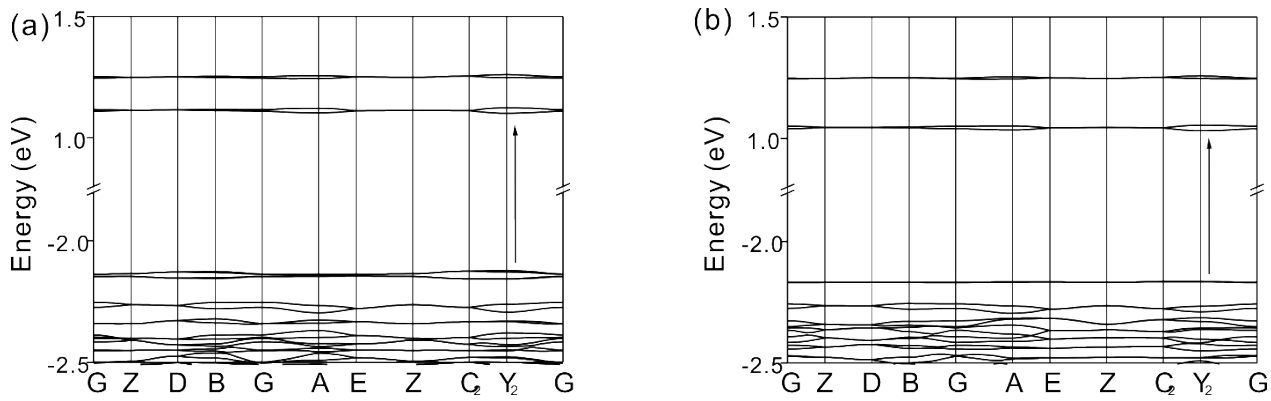


Fig. S11 Total and partial density of states for (a) (*R*)-Zn and (b) (*S*)-Zn

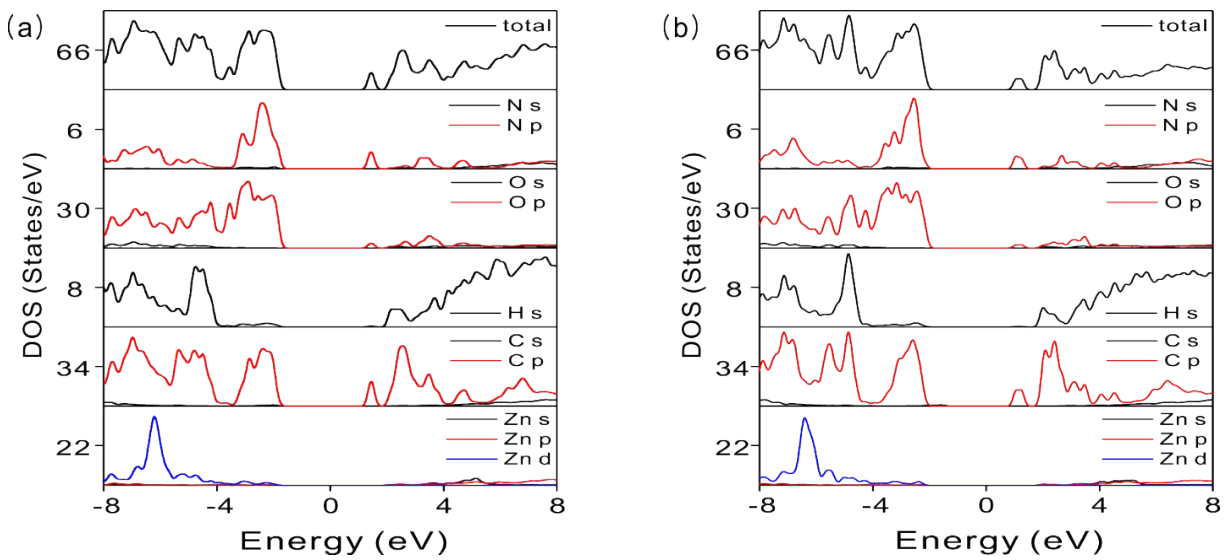


Fig. S12 Plots of SHG intensity versus particle size for (*R*)-Zn and (*S*)-Zn

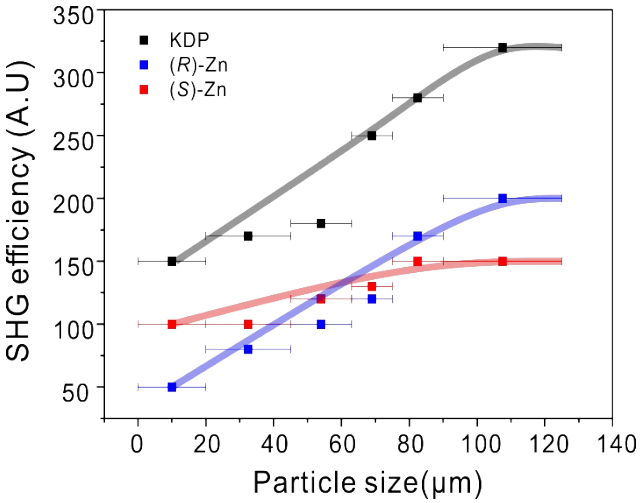


Table S6 Dipole moments for polyhedra in (*R*)-Zn and (*S*)-Zn

Compound	Unit	Magnitude	Dipole moment (D)		
			x	*y*	*z*
(*R*)-Zn	ZnO_6(1)	3.71D	-1.01	3.57	-0.06
	ZnO_6(2)	2.93 D	-0.05	-2.63	-1.28
	ZnO_6(3)	3.71 D	1.01	3.57	0.06
	ZnO_6(4)	2.93 D	0.05	-2.63	1.28
	Net	1.87D	0	1.87	0
(*S*)-Zn	ZnO_6(1)	2.85 D	-0.16	2.59	1.17
	ZnO_6(2)	3.62 D	0.82	-3.53	0.02
	ZnO_6(3)	2.85 D	0.16	2.59	-1.17
	ZnO_6(4)	3.62 D	-0.82	-3.53	-0.02
	Net	1.87 D	0	-1.87	0

Fig. S13 Net moments and dipole moments of ZnO_6 polyhedra in a unit cell

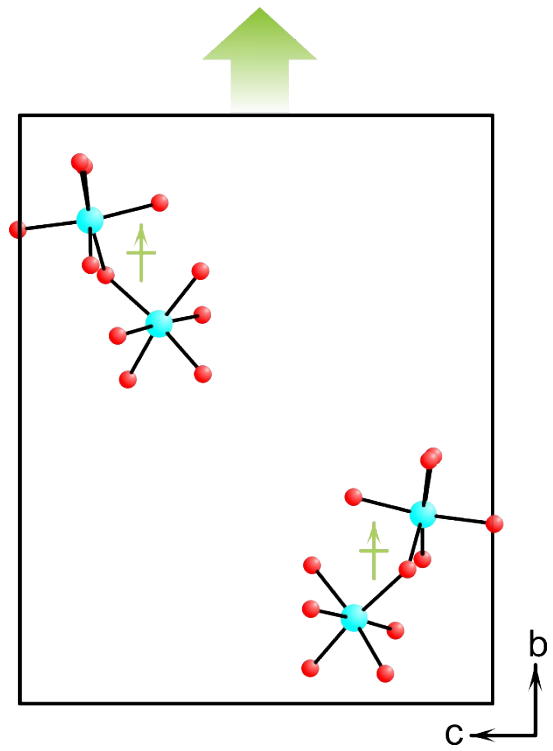


Fig. S14 PXRD patterns revealing the stability of (*R*)-Zn (a) in various solvents and (b) at various pH values.

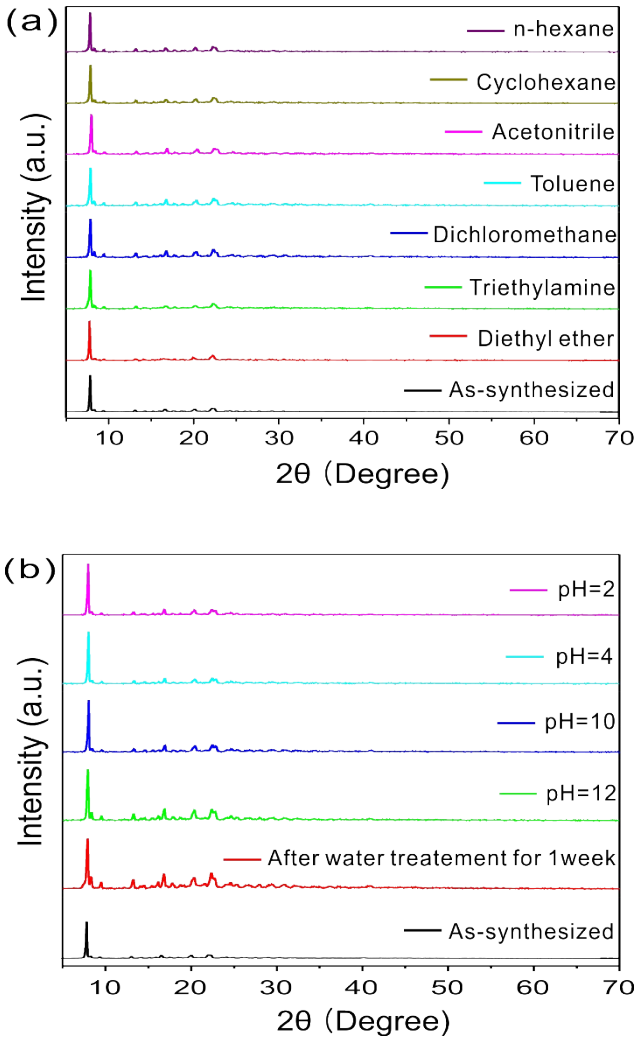


Table S7 Crystallographic Data for (*S*)-Zn-EtOH

	(*S*)-Zn-EtOH
fw	1178.72
space group	$P2_1$
a (Å)	12.177(2)
b (Å)	16.612(3)
c (Å)	14.691(3)
β (°)	114.36(3)
V (Å^3)	2707.2(11)
Z	2
T (K)	100(2)
λ (Å)	0.630
ρ_{calcd} (g/cm^3)	1.446
$R(F_o)^a$	0.0532
$R_w(F_o^2)^b$	0.0911
Flack *x*	0.023(9)

$^a R(F) = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o|$. $^b R_w(F_o^2) = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$.

Table S8 Selected bond distances (Å) and selected bond angles (°) for (*S*)-Zn-EtOH

Selected bond distances (Å)							
Zn(1)-O(4)	2.030(4)	O(4)-C(1)	1.254(6)	O(20)-C(49)	1.500(18)	C(41)-C(48)	1.525(8)
Zn(1)-O(17)#1	2. 057(4)	O(5)-C(1)	1.249(7)	C(1)-C(2)	1.547(9)	C(49)-C(50)	1.446(11)
Zn(1)-O(13)#2	2.069(4)	O(6)-C(9)	1.232(6)	C(2)-C(3)	1.514(9)	N(1)-C(9)	1.330(7)
Zn(1)-O(1)	2.132(5)	O(7)-C(16)	1.231(7)	C(9)-C(10)	1.516(8)	N(1)-C(2)	1.466(7)
Zn(1)-O(3)	2.135(4)	O(8)-C(24)	1.258(7)	C(13)-C(16)	1.495(8)	N(2)-C(16)	1.337(7)
Zn(1)-O(2)	2.157(5)	O(9)-C(24)	1.247(6)	C(17)-C(18)	1.533(9)	N(2)-C(17)	1.472(7)
Zn(2)-O(12)#3	2.029(4)	O(12)-C(48)	1.270(7)	C(17)-C(24)	1.529(8)	N(3)-C(33)	1.345(7)
Zn(2)-O(16)	2.052(4)	O(13)-C(48)	1.244(7)	C(25)-C(26)	1.578(8)	N(3)-C(26)	1.458(7)
Zn(2)-O(9)	2.060(4)	O(14)-C(33)	1.235(8)	C(26)-C(27)	1.44(4)	N(4)-C(40)	1.324(7)
Zn(2)-O(10)	2.073(4)	O(15)-C(40)	1.233(7)	C(33)-C(34)	1.498(8)	N(4)-C(41)	1.458(7)
Zn(2)-O(2)#4	2.181(4)	O(16)-C(25)	1.261(7)	C(37)-C(40)	1.501(8)		
Zn(2)-O(11)	2.231(5)	O(17)-C(25)	1.256(7)	C(41)-C(42)	1.532(9)		

Selected bond angles (°)					
O(1)-Zn(1)-O(2)	89.10(19)	O(16)-Zn(2)-O(11)	173.87(17)	O(5)-C(1)-C(2)	117.4(5)
O(1)-Zn(1)-O(3)	84.37(19)	O(17)#1-Zn(1)-O(1)	91.75(18)	O(6)-C(9)-C(10)	120.3(5)
O(2)#4-Zn(2)-O(11)	89.76(18)	O(17)#1-Zn(1)-O(2)	88.95(16)	O(7)-C(16)-C(13)	120.9(5)
O(3)-Zn(1)-O(2)	92.63(17)	O(17)#1-Zn(1)-O(3)	175.79(17)	O(8)-C(24)-C(17)	116.6(5)
O(4)-Zn(1)-O(1)	85.10(19)	O(17)#1-Zn(1)-O(13)#2	96.90(17)	O(9)-C(24)-C(17)	116.2(5)
O(4)-Zn(1)-O(2)	172.29(17)	Zn(1)-O(2)-Zn(2)#2	111.6(2)	O(12)-C(48)-C(41)	115.4(5)
O(4)-Zn(1)-O(3)	91.97(17)	C(1)-O(4)-Zn(1)	130.2(4)	O(13)-C(48)-C(41)	118.2(5)
O(4)-Zn(1)-O(13)#2	91.74(15)	C(24)-O(9)-Zn(2)	128.1(4)	O(14)-C(33)-C(34)	121.4(5)
O(4)-Zn(1)-O(17)#1	86.05(16)	C(25)-O(16)-Zn(2)	134.5(4)	O(16)-C(25)-C(26)	116.6(5)
O(9)-Zn(2)-O(2)#4	172.51(16)	C(25)-O(17)-Zn(1)#4	133.0(4)	O(17)-C(25)-C(26)	117.5(6)
O(9)-Zn(2)-O(10)	92.12(17)	C(48)-O(12)-Zn(2)#5	132.8(4)	O(20)-C(49)-C(50)	111.2(11)
O(9)-Zn(2)-O(11)	84.03(18)	C(48)-O(13)-Zn(1)#6	133.2(4)	N(1)-C(2)-C(3)	113.6(5)
O(10)-Zn(2)-O(2)#4	91.47(17)	O(5)-C(1)-O(4)	130.2(4)	N(1)-C(2)-C(1)	109.9(5)
O(10)-Zn(2)-O(11)	84.81(18)	O(8)-C(24)-O(9)	127.2(6)	N(1)-C(9)-C(10)	116.9(5)
O(12)#3-Zn(2)-O(2)#4	87.76(16)	O(13)-C(48)-O(12)	126.5(5)	N(2)-C(16)-C(13)	117.9(5)
O(12)#3-Zn(2)-O(9)	87.65(16)	O(17)-C(25)-O(16)	125.9(6)	N(2)-C(17)-C(18)	112.8(5)
O(12)#3-Zn(2)-O(10)	170.86(18)	O(6)-C(9)-N(1)	122.7(5)	N(2)-C(17)-C(24)	109.6(5)
O(12)#3-Zn(2)-O(11)	86.08(17)	O(7)-C(16)-N(2)	121.2(5)	N(3)-C(26)-C(27)	111.4(17)
O(12)-Zn(2)-O(16)#3	98.36(17)	O(14)-C(33)-N(3)	121.5(5)	N(3)-C(26)-C(25)	108.3(5)
O(13)#2-Zn(1)-O(1)	170.58(18)	O(15)-C(40)-N(4)	121.6(5)	N(3)-C(33)-C(34)	117.2(6)
O(13)#2-Zn(1)-O(2)	94.69(17)	C(9)-N(1)-C(2)	121.3(5)	N(4)-C(40)-C(37)	117.6(5)
O(13)#2-Zn(1)-O(3)	86.87(17)	C(16)-N(2)-C(17)	120.0(5)	N(4)-C(41)-C(42)	112.6(5)
O(16)-Zn(2)-O(2)#4	94.61(17)	C(33)-N(3)-C(26)	123.1(5)	N(4)-C(41)-C(48)	109.9(5)
O(16)-Zn(2)-O(9)	91.91(17)	C(40)-N(4)-C(41)	121.2(5)		
O(16)-Zn(2)-O(10)	90.78(17)	O(4)-C(1)-C(2)	115.8(5)		

Symmetry operation : #1 x-1,y-1,z-1 #2 x,y-1,z #3 x-1,y,z-1 #4 x,y+1,z #5 x+1,y,z+1 #6 x+1,y+1,z+1

Table S9 Hydrogen bonds distances (Å) for (*S*)-Zn-EtOH

D-H...A	d(D...A)	D-H...A	d(D...A)
N(1)-H(1)...O(18)#1	2.974(6)	O(18)-H(1D)...O(8)#8	2.857(6)
O(1)-H(10)...O(15)#7	2.717(6)	O(18)-H(1E)...O(17)	2.835(6)
O(1)-H(13)...O(3)	2.865(6)	O(18)-H(1E)...O(4)#4	3.000(6)
O(2)-H(9)...O(21)	2.566(7)	O(19)-H(1H)...O(12)	2.751(6)
O(3)-H(16)...O(5)	2.714(4)	O(19)-H(1F)...O(5)#8	2.839(6)
O(3)-H(1G)...O(6)#9	2.809(6)	O(21)-H(1B)...O(6)#9	2.744(7)
O(10)-H(1L)...O(7)#8	2.732(6)	C(50)-H(50A)...O(14)#7	2.779(8)
O(10)-H(1M)...O(8)	2.635(6)	O(50)-H(50B)...O(11)	2.755(8)
O(11)-H(1N)...O(19)#3	2.825(8)		

Symmetry operation : #1 x-1,y-1,z-1 #3 x,y,z-1 #4 x,y-1,z #7 -x,y+1/2,-z
#7 -x+1,y+1/2,-z+1 #8 -x+1,y+1/2,-z+1 #9 -x,y-1/2,-z

Fig. S15 Experimental and calculated powder X-ray diffraction patterns of (*S*)-Zn-EtOH

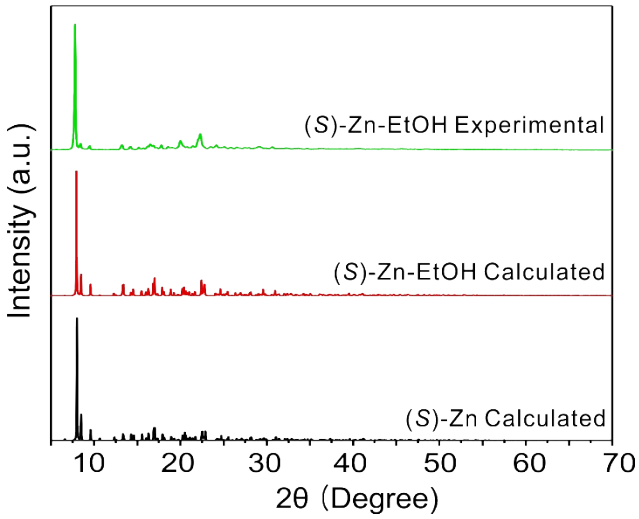
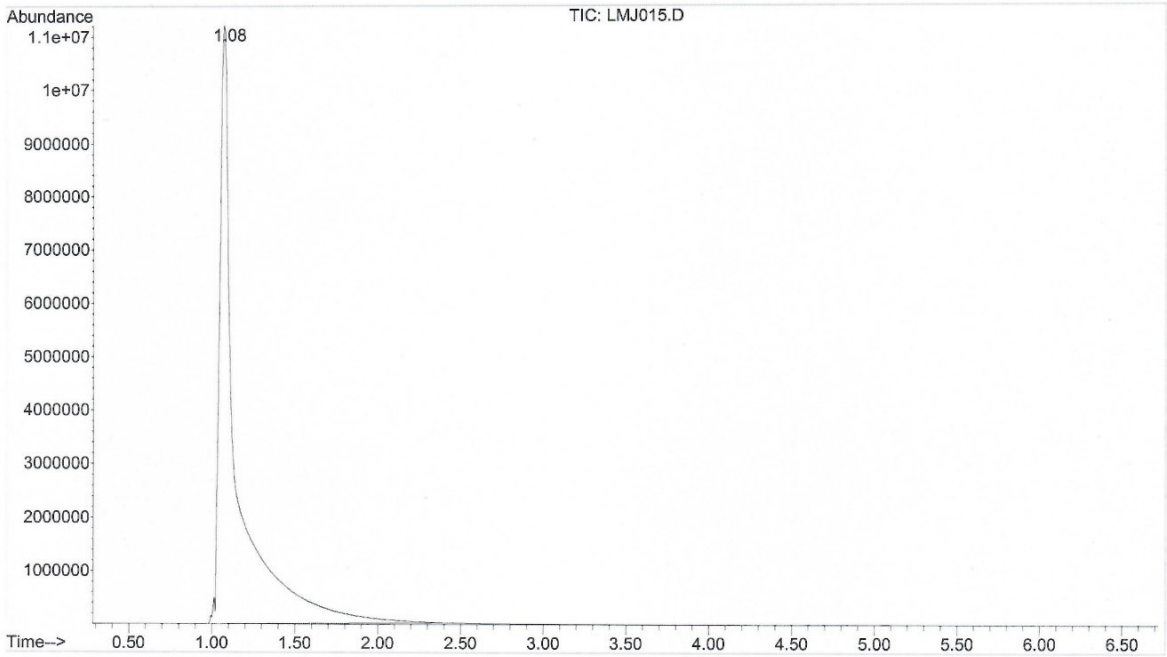
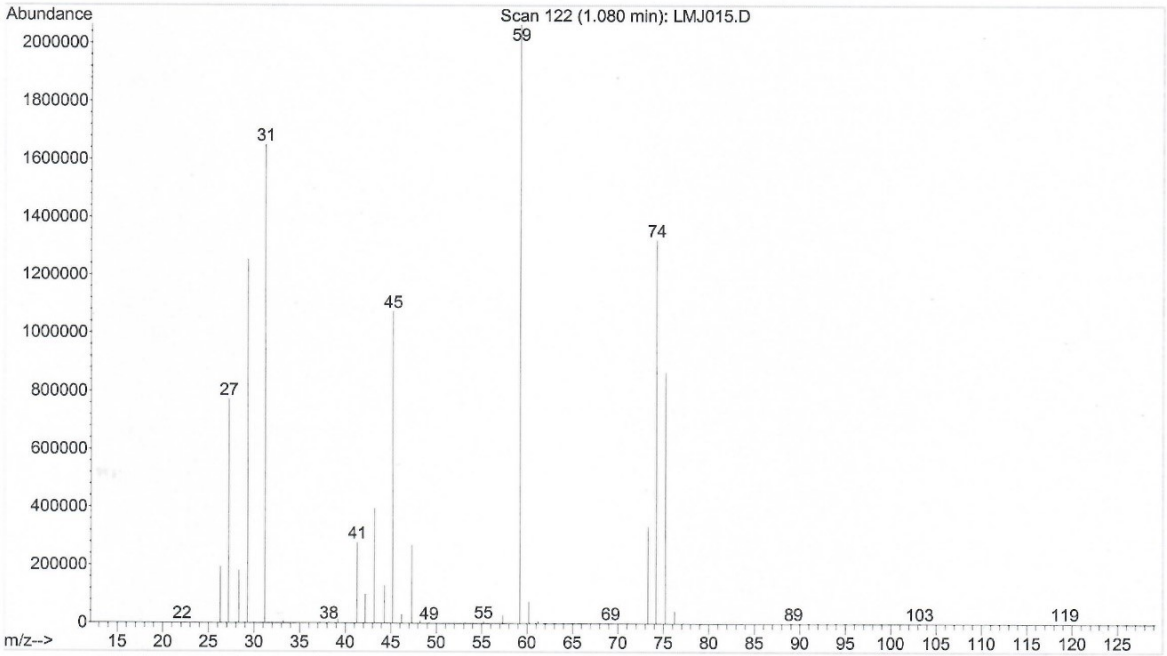


Fig. S16 GC-MS result of distilled diethyl ether





Area Percent Report

Data File : C:\MSDCHEM\1\DATA\LMJ015.D
Acq On : 14 Dec 2021 11:03
Sample : LMJ D_Ether
Misc : 60/10/10/240

Vial: 1
Operator: LHK
Inst : Instrumen
Multiplr: 1.00
Sample Amount: 0.00

MS Integration Params: autoint1.e

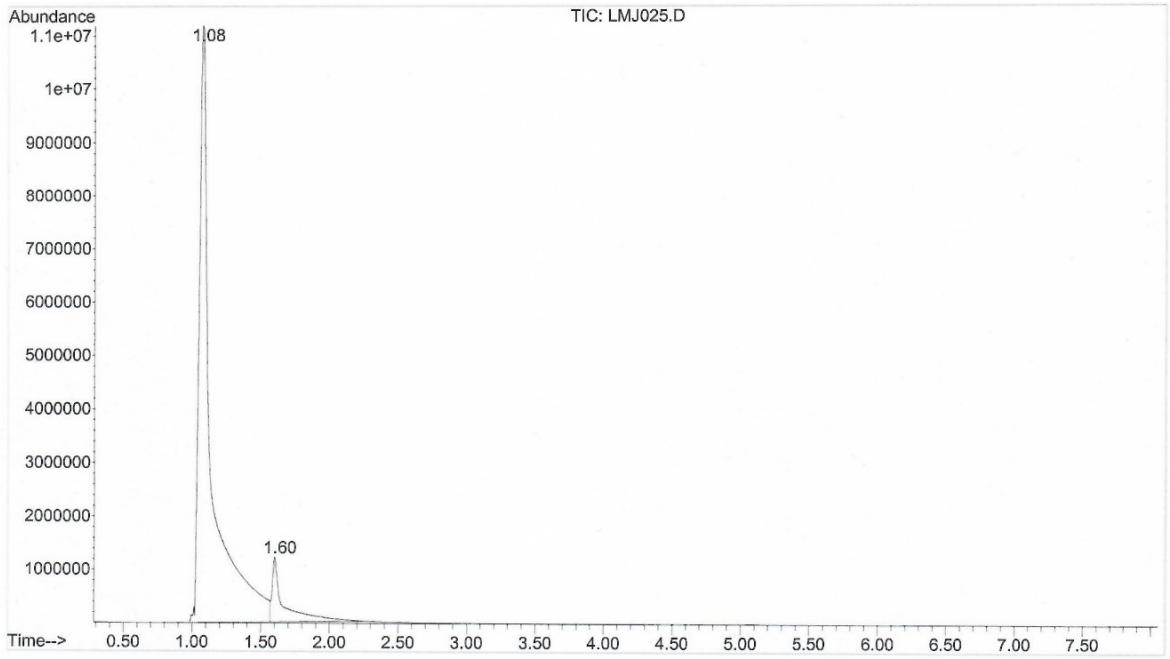
Method : C:\MSDCHEM\1\METHODS\DEFAULT.M (Chemstation Integrator)
Title :

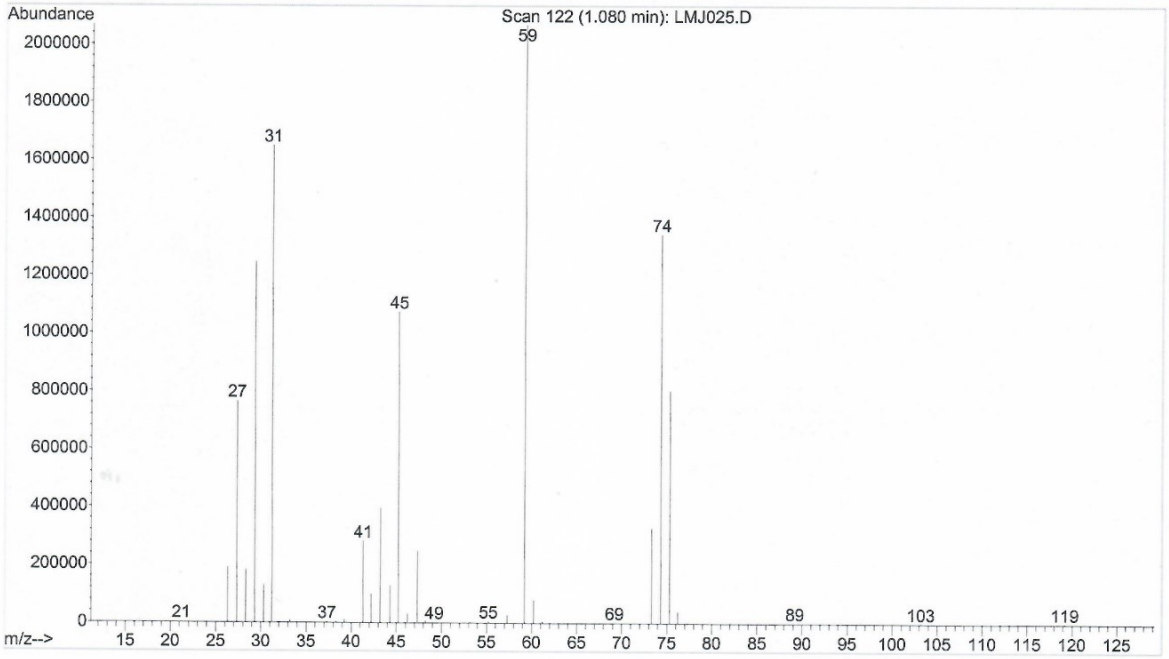
Signal : TIC

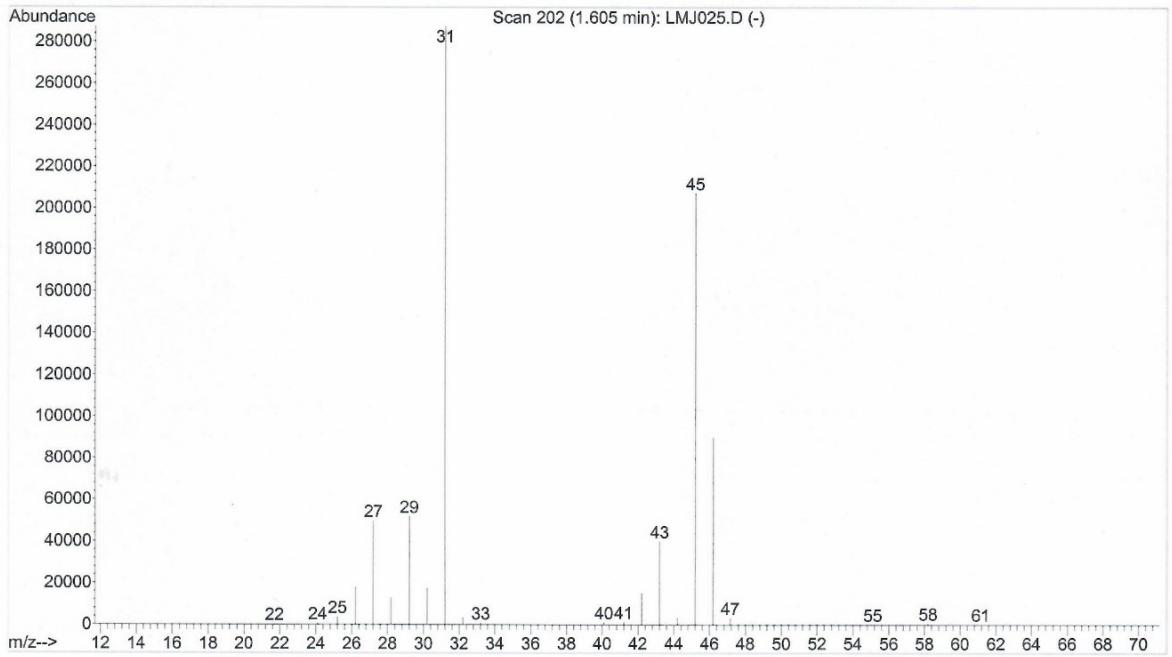
peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	1.080	105	122	330	BB 6	11191739	804600884	100.00%	100.000%

Sum of corrected areas: 804600884

Fig. S17 GC-MS result of distilled diethyl ether containing (*S*)-Zn crystal for 1 day







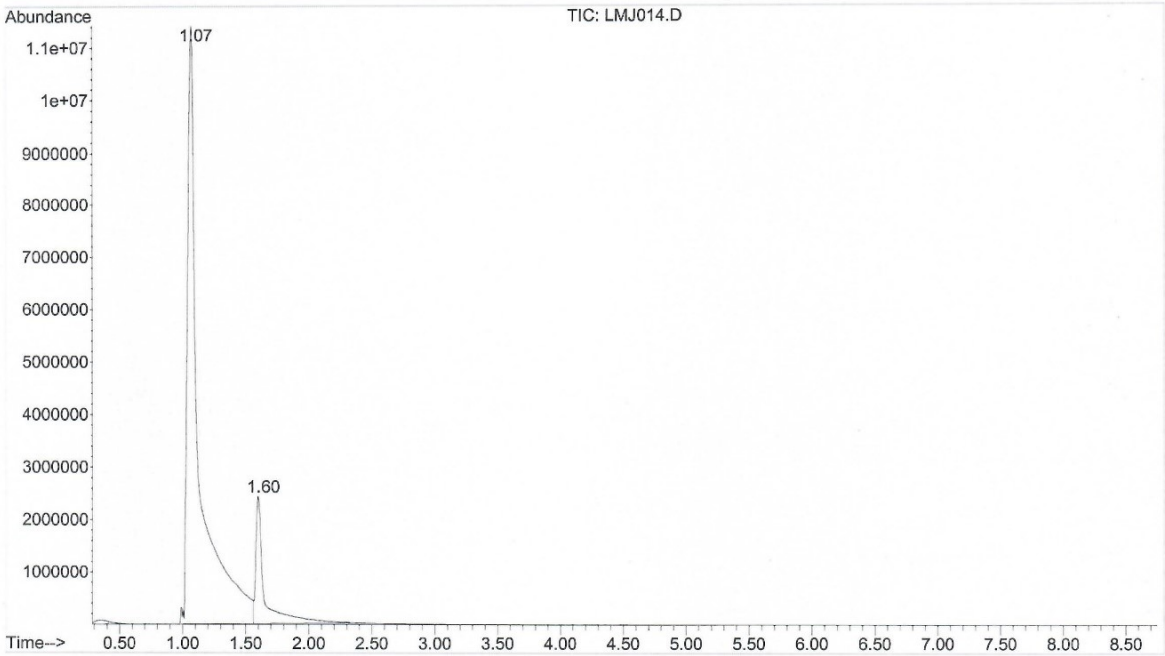
Area Percent Report

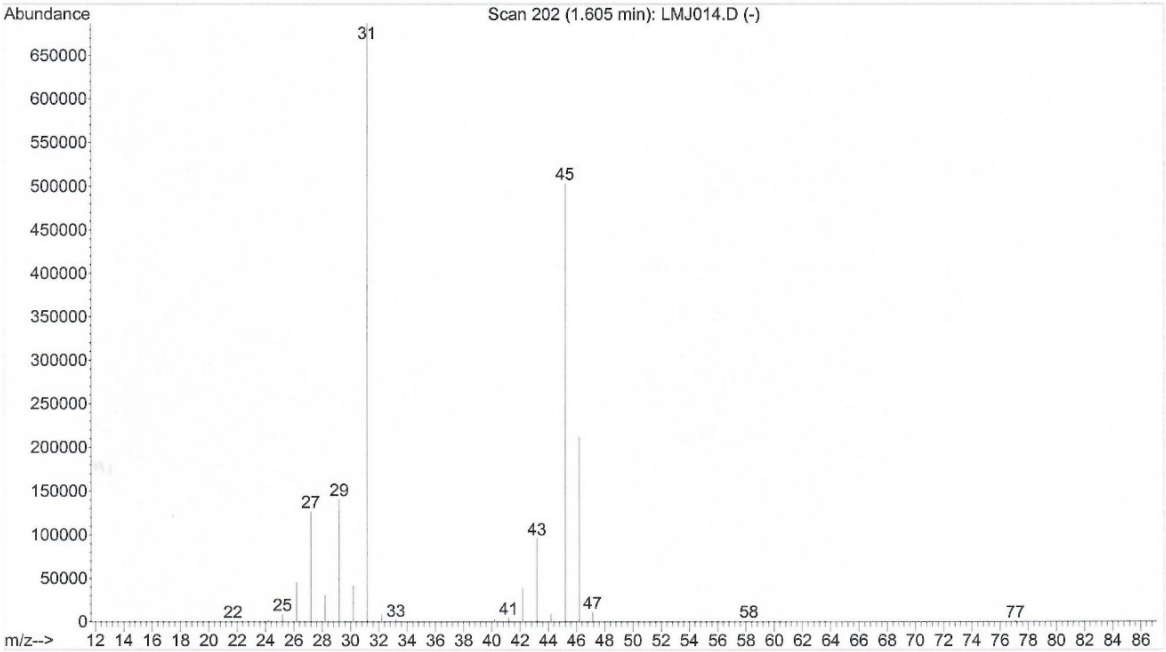
```
Data File : C:\MSDCHEM\1\DATA\LMJ025.D                    Vial: 1
Acq On    : 28 Dec 2021  14:26                        Operator: LHK
Sample    : LMJ D_ether_1d                            Inst    : Instrumen
Misc      : 60/10/10/240                              Multiplr: 1.00
                                                  Sample Amount: 0.00
MS Integration Params: autoint1.e

Method    : C:\MSDCHEM\1\METHODS\DEFAULT.M (Chemstation Integrator)
Title     :

Signal    : TIC
```

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	1.080	105	122	196	BV 5	11189299	695965201	100.00%	90.552%
2	1.605	196	202	305	VB	1211433	72614507	10.43%	9.448%

Sum of corrected areas: 768579707

Fig. S18 GC-MS result of distilled diethyl ether containing (*S*)-Zn crystal for 3 days





Area Percent Report

Data File : C:\MSDCHEM\1\DATA\LMJ014.D
Acq On : 14 Dec 2021 10:44
Sample : LMJ D_Ether 3d
Misc : 60/10/10/240

Vial: 1
Operator: LHK
Inst : Instrumen
Multiplr: 1.00
Sample Amount: 0.00

MS Integration Params: autoint1.e

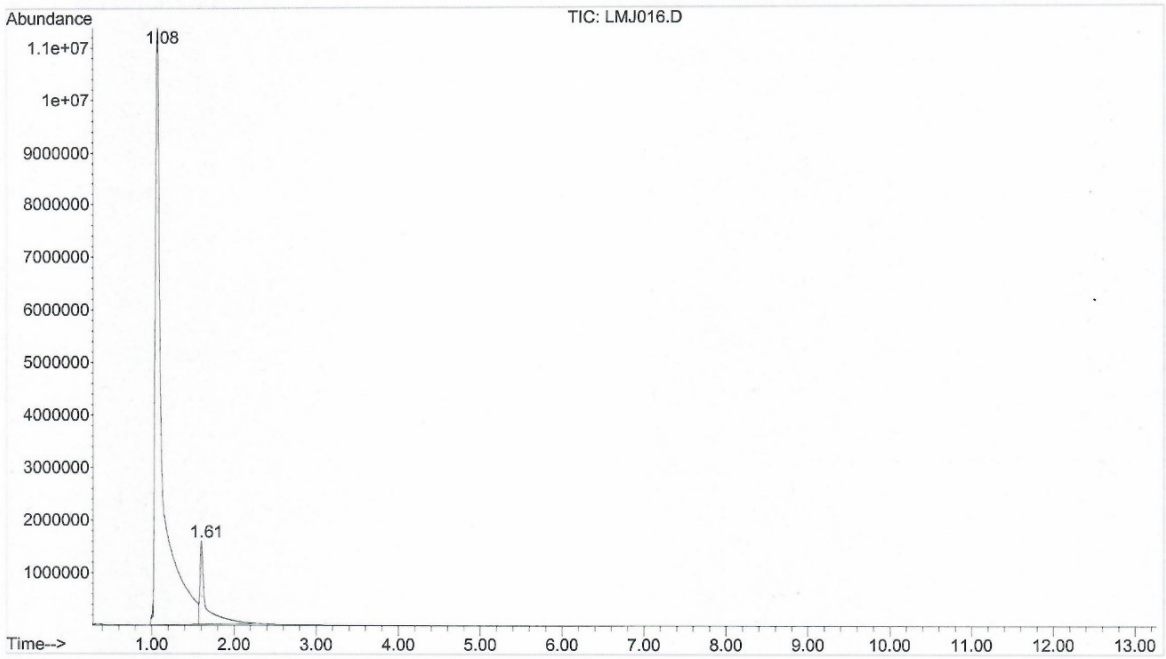
Method : C:\MSDCHEM\1\METHODS\DEFAULT.M (Chemstation Integrator)
Title :

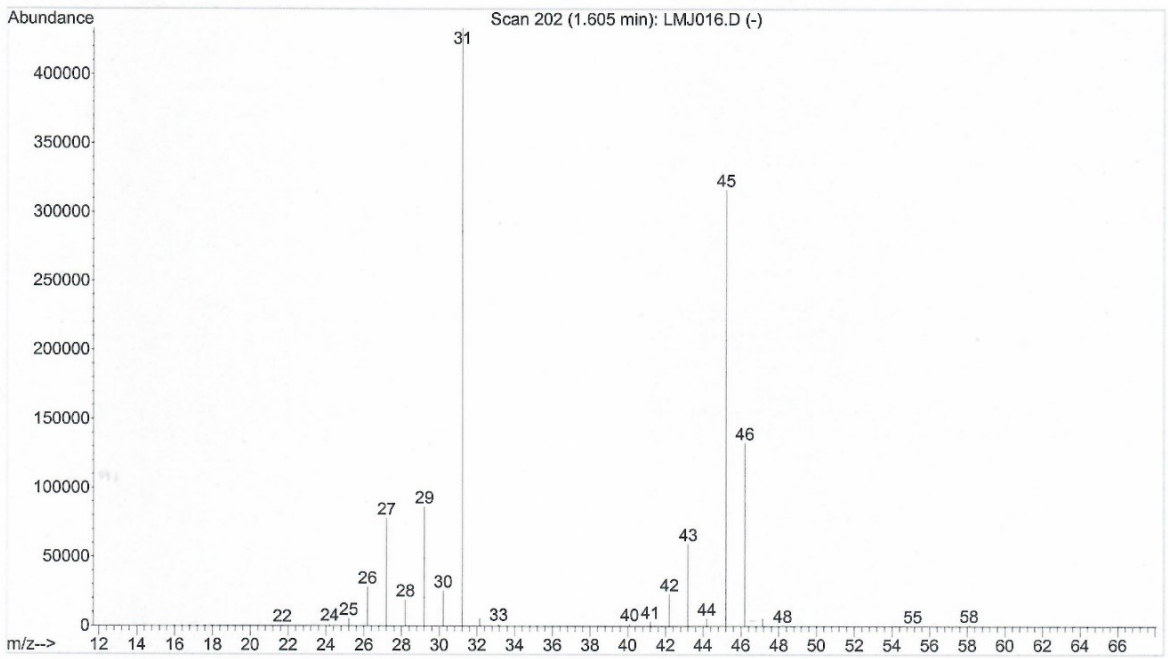
Signal : TIC

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	1.073	94	121	195	BV 5	11343887	736637667	100.00%	86.393%
2	1.605	195	202	318	VB	2413252	116019525	15.75%	13.607%

Sum of corrected areas: 852657192

Fig. S19 GC-MS result of distilled diethyl ether containing (*S*)-Zn crystal for 7 days





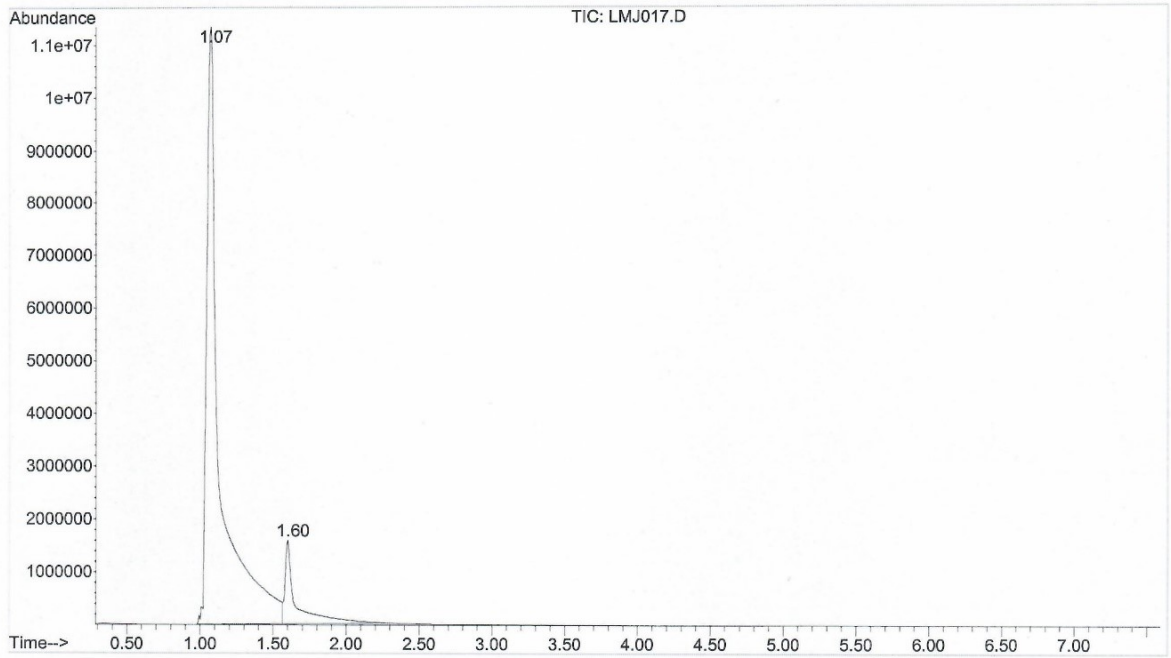
Area Percent Report

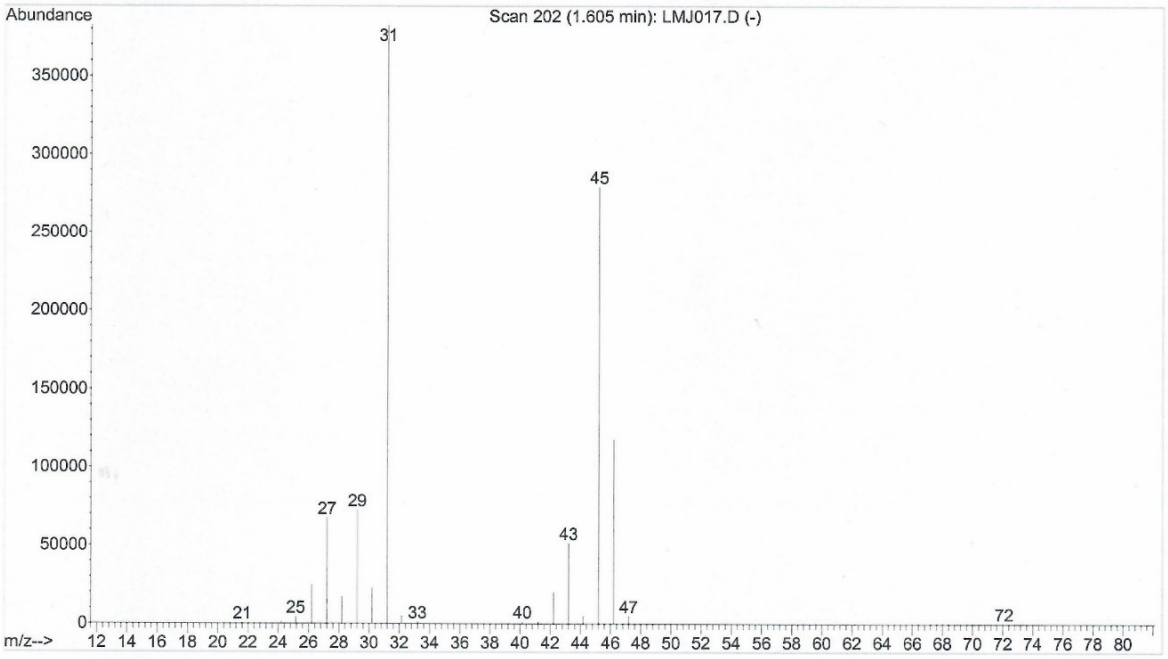
```
Data File : C:\MSDCHEM\1\DATA\LMJ016.D                    Vial: 1
Acq On    : 17 Dec 2021  10:28                        Operator: LHK
Sample    : LMJ D_ether_7d                            Inst    : Instrumen
Misc      : 60/10/10/240                              Multiplr: 1.00
                                                  Sample Amount: 0.00
MS Integration Params: autoint1.e

Method    : C:\MSDCHEM\1\METHODS\DEFAULT.M (Chemstation Integrator)
Title     :

Signal    : TIC
```

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	1.073	95	121	196	BV 5	11372559	705957412	100.00%	89.595%
2	1.605	196	202	309	VB	1568131	81984419	11.61%	10.405%

Sum of corrected areas: 787941831

Fig. S20 GC-MS result of distilled diethyl ether containing (*S*)-Zn crystal for 10 days





Area Percent Report

Data File : C:\MSDCHEM\1\DATA\LMJ017.D
Acq On : 20 Dec 2021 11:02
Sample : LMJ D_ether_10d
Misc : 60/10/10/240

Vial: 1
Operator: LHK
Inst : Instrumen
Multiplr: 1.00
Sample Amount: 0.00

MS Integration Params: autoint1.e

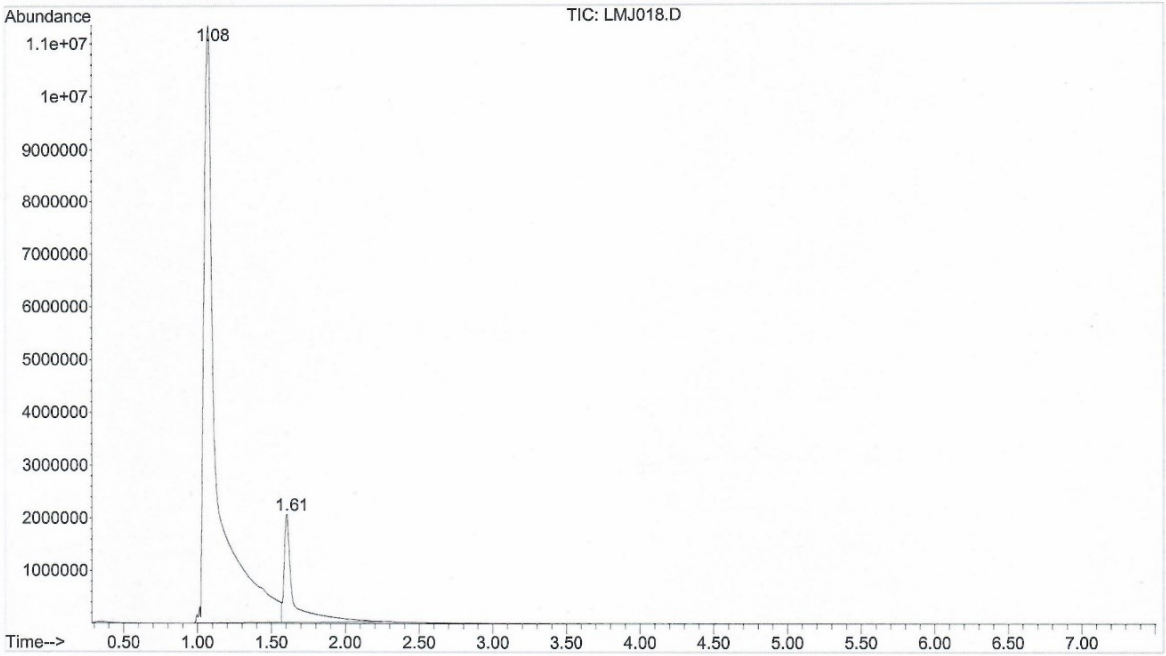
Method : C:\MSDCHEM\1\METHODS\DEFAULT.M (Chemstation Integrator)
Title :

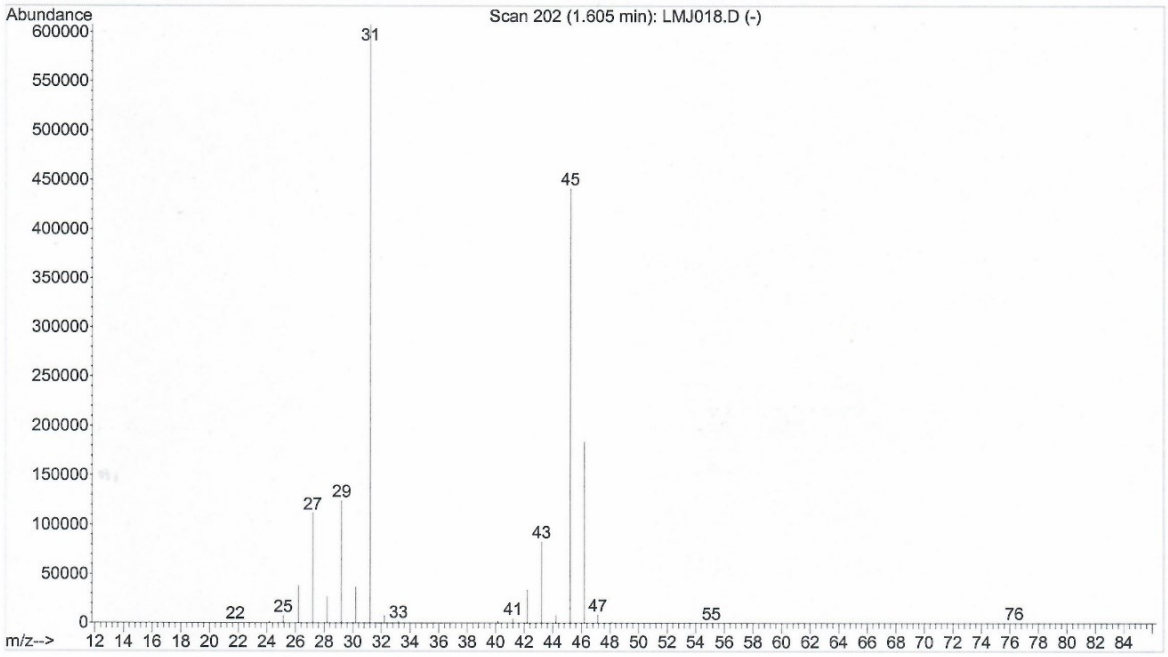
Signal : TIC

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	1.073	95	121	196	BV 4	11295725	702351997	100.00%	89.354%
2	1.599	196	201	310	VB	1558770	83683504	11.91%	10.646%

Sum of corrected areas: 786035501

Fig. S21 GC-MS result of distilled diethyl ether containing (*S*)-Zn crystal for 14 days





Area Percent Report

Data File : C:\MSDCHEM\1\DATA\LMJ018.D
Acq On : 24 Dec 2021 13:59
Sample : LMJ D_ether_14d
Misc : 60/10/10/240

Vial: 1
Operator: LHK
Inst : Instrumen
Multiplr: 1.00
Sample Amount: 0.00

MS Integration Params: autoint1.e

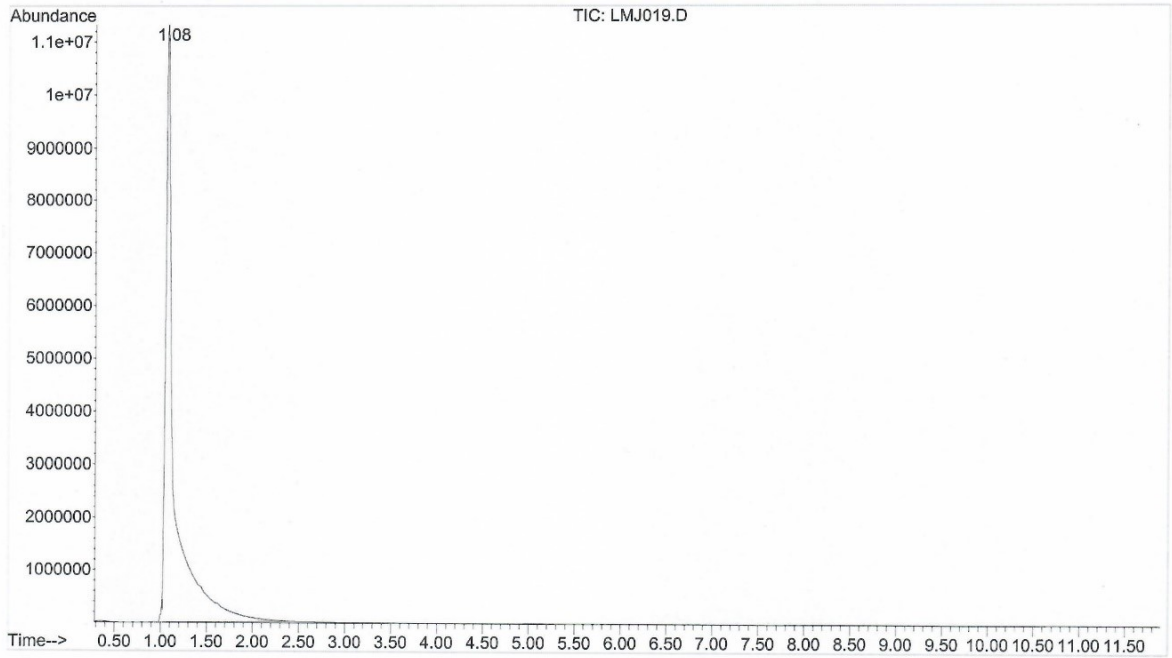
Method : C:\MSDCHEM\1\METHODS\DEFAULT.M (Chemstation Integrator)
Title :

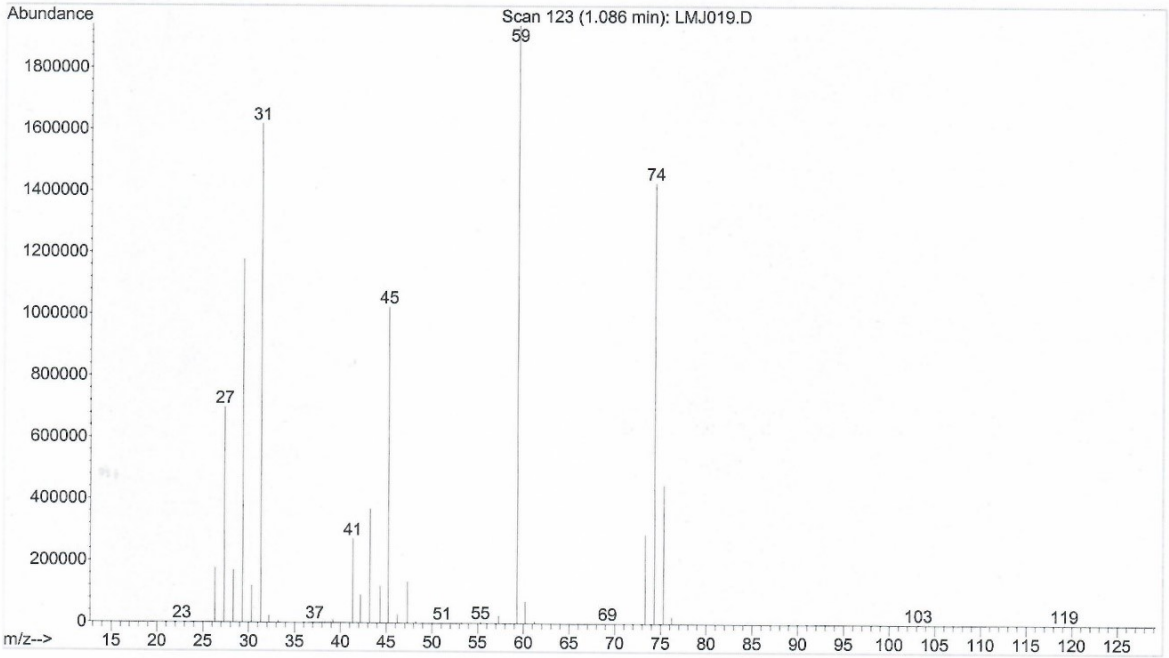
Signal : TIC

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	1.073	93	121	196	BV 5	11331447	682183556	100.00%	88.322%
2	1.605	196	202	305	VB	2046168	90196487	13.22%	11.678%

Sum of corrected areas: 772380043

Fig. S22 GC-MS result of distilled diethyl ether containing $Zn(NO_3)_2$ for 1 day





Area Percent Report

Data File : C:\MSDCHEM\1\DATA\LMJ019.D
Acq On : 27 Dec 2021 13:24
Sample : LMJ D_ether_Zn(NO3)2
Misc : 60/10/10/240

Vial: 1
Operator: LHK
Inst : Instrumen
Multiplr: 1.00
Sample Amount: 0.00

MS Integration Params: autoint1.e

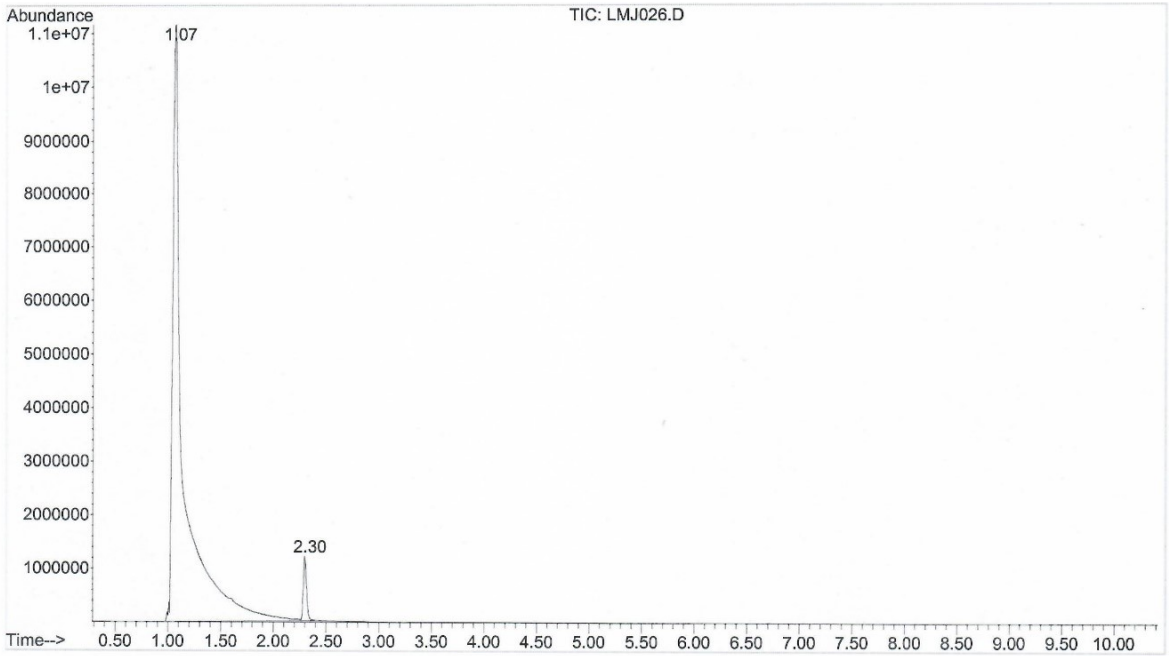
Method : C:\MSDCHEM\1\METHODS\DEFAULT.M (Chemstation Integrator)
Title :

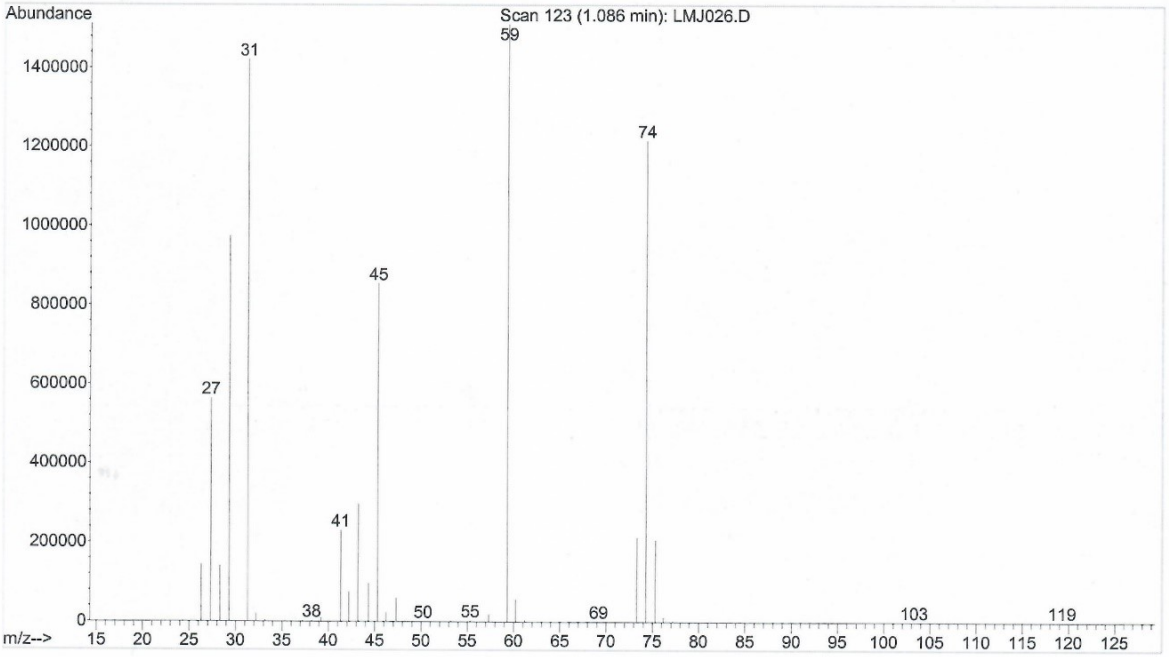
Signal : TIC

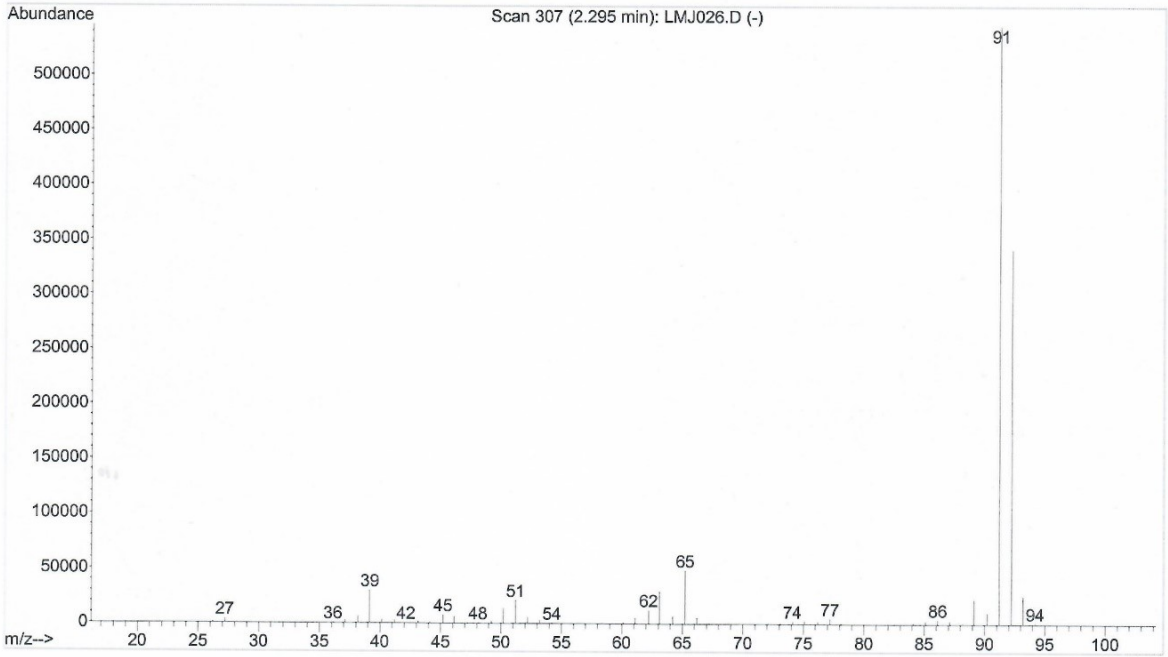
peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	1.080	97	122	329	BB 5	11328763	749202585	100.00%	100.000%

Sum of corrected areas: 749202585

Fig. S23 GC-MS result of distilled diethyl ether containing TBPG ligand for 1 day







Area Percent Report

```
Data File : C:\MSDCHEM\1\DATA\LMJ026.D                    Vial: 1
Acq On    : 28 Dec 2021  14:52                        Operator: LHK
Sample    : LMJ D_ether_ligand                        Inst    : Instrumen
Misc      : 60/10/10/240                              Multiplr: 1.00
                                                  Sample Amount: 0.00
MS Integration Params: autoint1.e

Method    : C:\MSDCHEM\1\METHODS\DEFAULT.M (Chemstation Integrator)
Title     :

Signal    : TIC
```

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	1.073	104	121	301	BV 4	11157777	797326498	100.00%	96.891%
2	2.302	301	308	329	VB	1181425	25585806	3.21%	3.109%

Sum of corrected areas: 822912304

Fig. S24 Fluorescence emission spectra of (*R*)-Zn and (*R*,*R*)-TBPG in the solid state

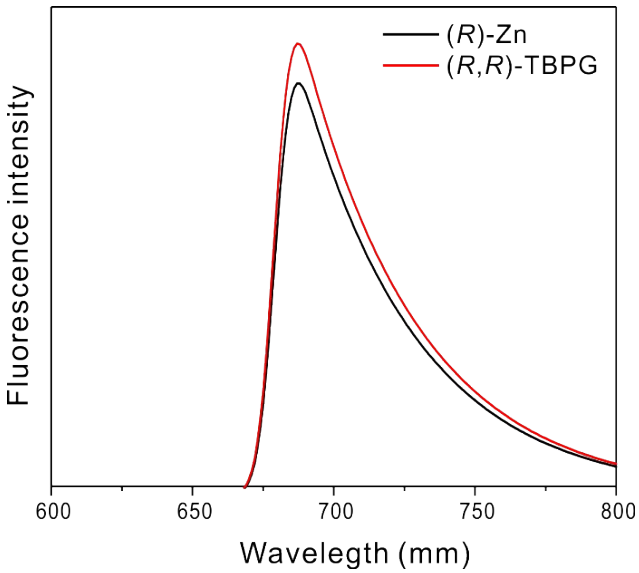


Fig. S25 PXRD patterns of (*R*)-Zn before and after the fluorescence measurements

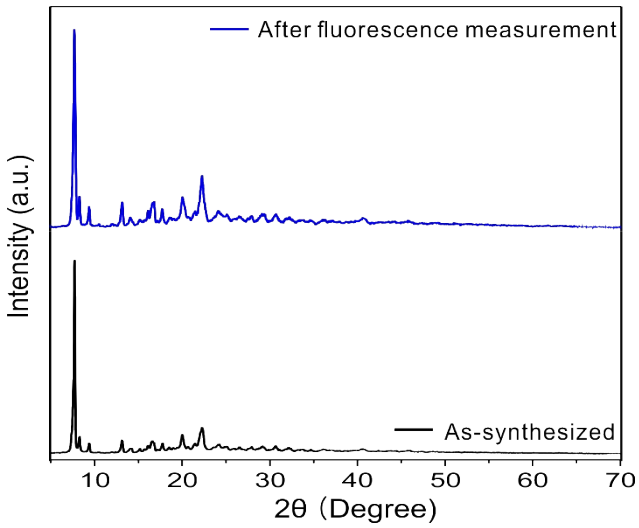


Fig. S26 Fluorescence emission spectra of (*R*,*R*)-TBPG upon addition of (a) D- and (b) L-histidine

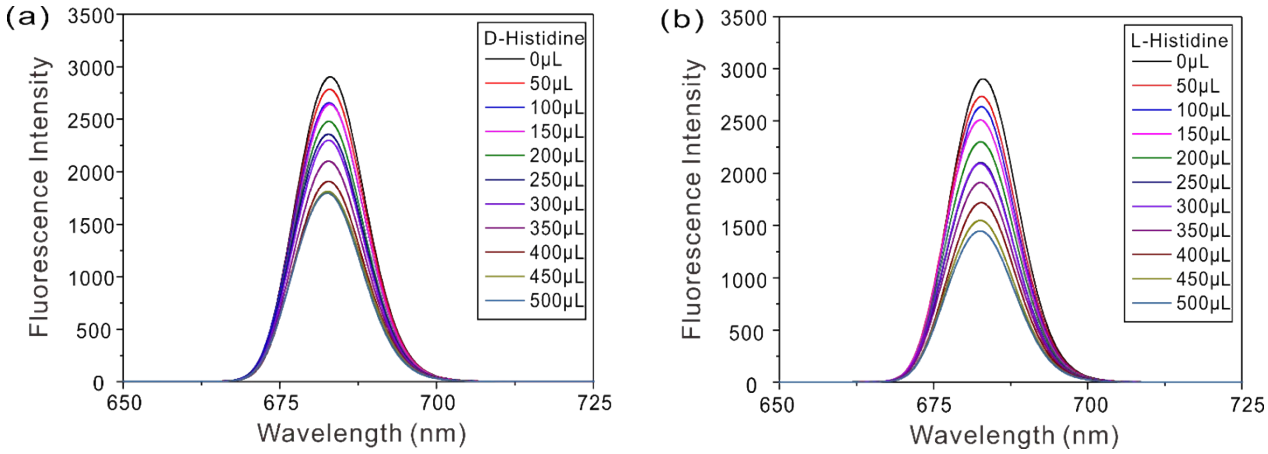


Fig. S27 Stern-Volmer (SV) plots of (*R*,*R*)-TBPG + D-histidine and (*R*,*R*)-TBPG + L-histidine

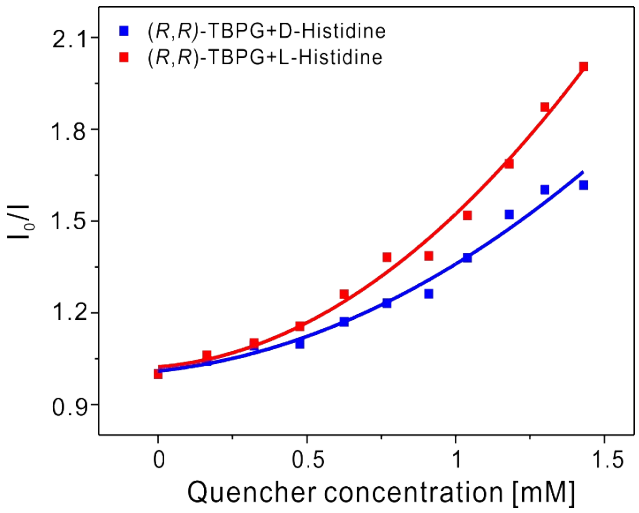


Fig. S28 Fluorescence emission spectra of (*R*)-Zn upon addition of imidazole

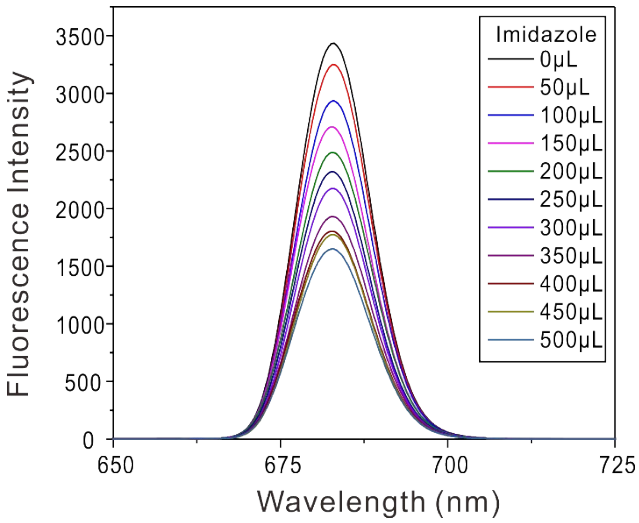


Fig. S29 Stern-Volmer (SV) plots of (*R*)-Zn + D-histidine, (*R*)-Zn + L-histidine and (*R*)-Zn + imidazole. The K_{SV} constant for (*R*)-Zn + imidazole is 7.6×10^2 M^{-1}.

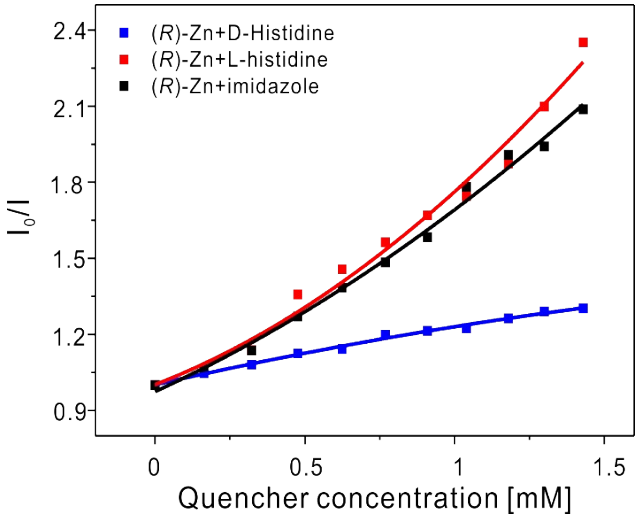


Fig. S30 ^{1}H NMR spectra for (*R*)-Zn in DMSO-d_6, (*R*)-Zn + Histidine in DMSO-d_6/D_2O and Histidine in D_2O

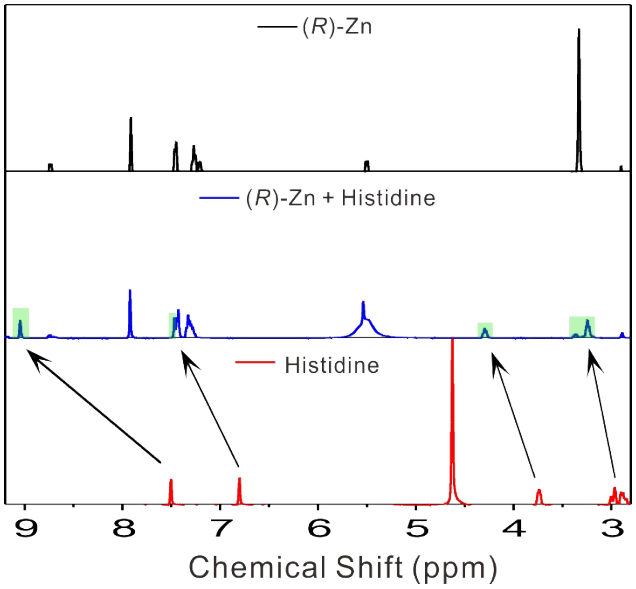


Fig. S31 Fluorescence emission spectra of (*S*)-Zn upon addition of (a) D- and (b) L-histidine

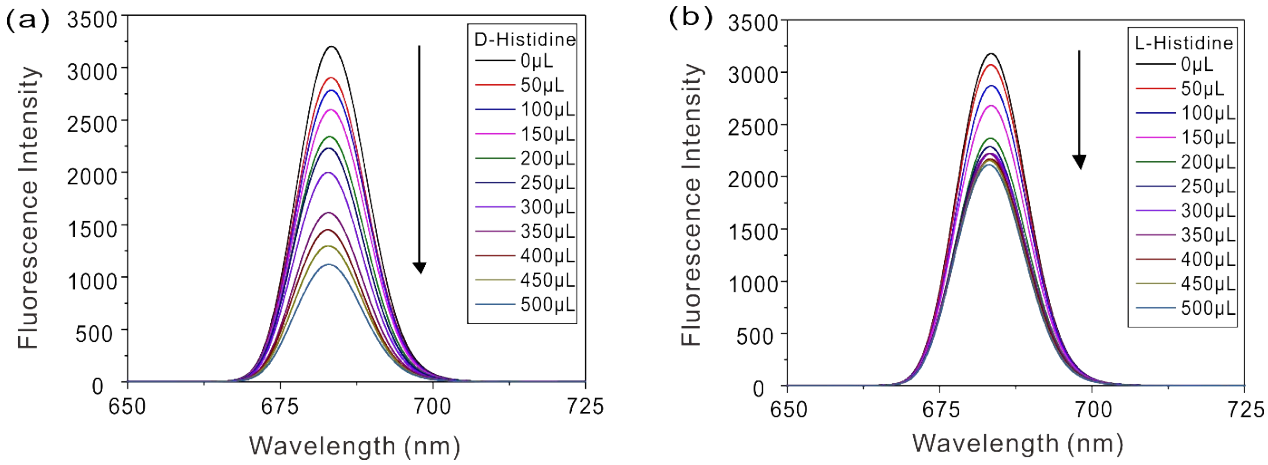
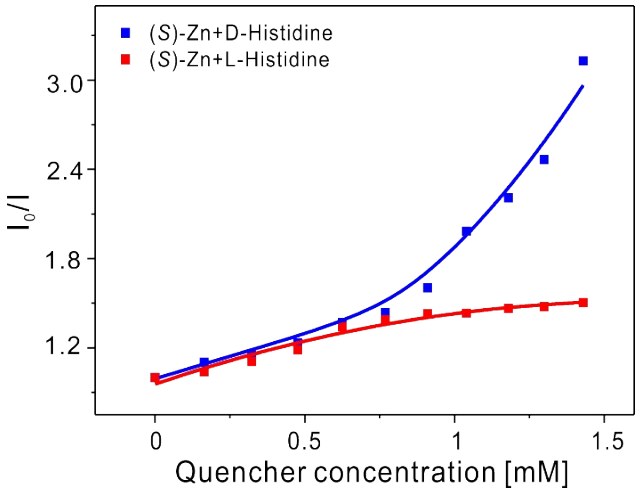


Fig. S32 Stern-Volmer (SV) plots of (*S*)-Zn + D-Histidine and (*S*)-Zn + *L*-Histidine. The K_{SV} constants for (*S*)-Zn + *D*-histidine and (*S*)-Zn + *L*-histidine are 1.5×10^3 M^{-1} and 3.5×10^2 M^{-1}, respectively, and enantioselectivity factor α is calculated to be 4.22.



References

1. SADABS, Siemens Industrial Automation Inc, *Madison, WI*, 1996.
2. Siemens, Area-Detector Control and Integration Software, *Siemens Analytical X-ray Instruments Inc., Madison, WI, USA*, 1996.
3. R. H. Blessing, An empirical correction for absorption anisotropy, *Acta Crystallogr., A, Found. Crystallogr.*, 1995, **51**, 33-38.
4. G. Sheldrick, SHELXS-2013/1, program for the solution of crystal structures, *Germany: University of Göttingen*, 2013.
5. G. M. Sheldrick, Crystal structure refinement with SHELXL, *Acta Crystallogr. C Struct. Chem.*, 2015, **71**, 3-8.
6. L. J. Farrugia, WinGX and ORTEP for Windows: an update, *J. Appl. Crystallogr.*, 2012, **45**, 849-854.
7. A. L. Spek, PLATON SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors, *Acta Crystallogr. C Struct. Chem.*, 2015, **71**, 9-18.
8. A. Spek, Single-crystal structure validation with the program PLATON, *J. Appl. Crystallogr.*, 2003, **36**, 7-13.
9. Z. Otwinowski and W. Minor, in *Methods Enzymol.*, Elsevier, 1997, vol. 276, pp. 307-326.
10. P. Kubelka, Ein Beitrag zur Optik der Farbanstriche (Contribution to the optic of paint), *Z. Tech. Phys.*, 1931, **12**, 593-601.
11. P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni and I. Dabo, QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials, *J. Phys.: Condens. Matter*, 2009, **21**, 395502.
12. D. Vanderbilt, Soft self-consistent pseudopotentials in a generalized eigenvalue formalism, *Phys. Rev. B*, 1990, **41**, 7892.
13. J. P. Perdew, K. Burke and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.*, 1996, **77**, 3865.
14. S. Kurtz and T. Perry, A powder technique for the evaluation of nonlinear optical materials, *J. Appl. Phys.*, 1968, **39**, 3798-3813.
15. K. M. Ok, E. O. Chi and P. S. Halasyamani, Bulk characterization methods for non-centrosymmetric materials: second-harmonic generation, piezoelectricity, pyroelectricity, and ferroelectricity, *Chem. Soc. Rev.*, 2006, **35**, 710-717.