

Electronic Supplementary Information

For

Spontaneous chiral resolution of $[\text{Co}^{\text{II}}(\text{N},\text{N},\text{O-L3})_2]$ complexes mediated by π - π interactions

Jin-Ji Wu, Man-Li Cao and Bao-Hui Ye*

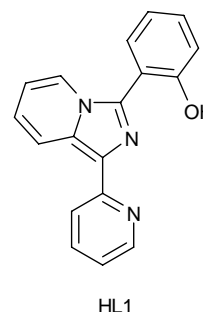
MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry and
Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China.

E-mail: cesybh@mail.sysu.edu.cn

1. Syntheses of ligands:

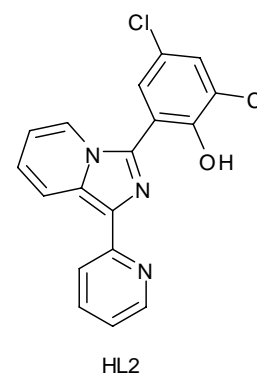
General methods. A mixture of 2,2'-dipyridyl ketone (0.92 g, 5.0 mmol), substituted benzaldehyde (15.0 mmol) and NH_4OAc (1.93 g, 25.0 mmol) were dissolved in 50 mL of glacial acetic acid. The mixture solution was stirred at 110 °C for 12 h under N_2 atmosphere. The reaction mixture was cooled to room temperature, and then poured into 250 mL of ice water. The formed solid was then filtered, dried and recrystallised with ethanol. If no solid appeared, the mixture was extracted with CHCl_3 and washed with brine and then water. The organic layer was collected and dried over Na_2SO_4 . Upon the removal of solvent, the residue was recrystallized with ethanol to afford analytically pure compound, or purified by chromatography on a Al_2O_3 column with $\text{EtOAc}:\text{hexane} = 1:10$ as an eluant.

1-(2-pyridyl)-3-(2-hydroxyphenyl)-imidazo[1,5-a]pyridine (HL1): Yield, 88.7%, white solid; $^1\text{H-NMR}$ (300 MHz; CDCl_3) δ 11.57 (br, s, 1H), 8.78 (d, 1H), 8.63 (m, 1H), 8.53 (d, 1H), 8.11 (d, 1H), 7.78 (d, 1H), 7.72 (d, 1H), 7.33 (t, 1H), 7.19 (d, 1H), 7.13 (t, 1H), 7.06-6.96 (m, 2H), 6.76 (t, 1H); ESI-MS $m/z = 288$ $[\text{M}+\text{H}]^+$; FT-IR (KBr, cm^{-1}), 3432(br), 1588(vs), 1525(s), 1515(vs), 1482(s), 1452(vs), 1386(s), 1325(s), 1296(s), 1012(s), 956(w), 933(w), 756(vs), 738(s), 707(s).



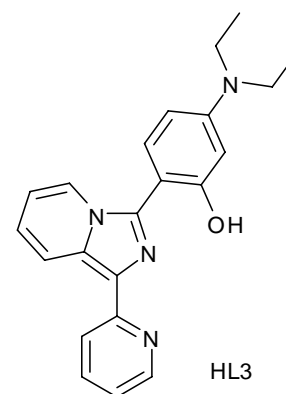
1-(2-pyridyl)-3-(3,5-dichloro-2-hydroxyphenyl)-imidazo[1,5-a]pyridine (HL2):

Yield, 86.3%, yellow solid; $^1\text{H-NMR}$ (300 MHz; CDCl_3) δ 8.84 (d, 1H), 8.63 (d, 1H), 8.49 (d, 1H), 8.07 (d, 1H), 7.73 (t, 1H), 7.68 (d, 1H), 7.40 (d, 1H), 7.15 (t, 1H), 7.06 (t, 1H), 6.89 (t, 1H); ESI-MS $m/z = 356$ $[M+H]^+$; FT-IR (KBr, cm^{-1}) 3437(w, br), 1634(w), 1591(vs), 1566(s), 1518(s), 1474(s), 1454(vs), 1433(s), 1406(s), 1372(s), 1349(s), 1310(s), 1281(s), 1271(s), 1250(vs), 1194(s), 1181(s), 1147(s), 1052(s), 1028(s), 842(s), 797(vs), 774(s), 752(s), 740(s), 724(vs), 691(s).



1-(2-pyridyl)-3-(4-diethylamino-2-hydroxyphenyl)-imidazo[1,5-a]pyridine (HL3):

Yield, 57.5%, yellow solid; $^1\text{H-NMR}$ (300MHz; CDCl_3) δ 11.90~11.60 (br, s, 1H), 8.74 (d, 1H), 8.62 (d, 1H), 8.46 (d, 1H), 8.11 (d, 1H), 7.74 (t, 1H), 7.63 (d, 1H), 7.11 (t, 1H), 6.93 (t, 1H), 6.69 (t, 1H), 6.46 (s, 1H), 6.36 (s, 1H), 3.42 (q, 4H), 1.24 (t, 6H); ESI-MS $m/z = 359$ $[M+H]^+$; IR (KBr, cm^{-1}) 3141(w), 2975(s), 2960(s), 1630(vs), 1589(vs), 1556(vs), 1534(vs), 1511(vs), 1482(vs), 1466(vs), 1444(s), 1414(s), 1403(vs), 1372(s), 1359(vs), 1337(s), 1300(s), 1271(s), 1222(s), 1200(s), 1147(s), 1110(s), 1089(s), 1019(s), 1006(s), 948(s), 825(s), 804(s), 783(s), 747(s), 736(s), 721(s), 702(s).



2. Syntheses of complexes

[Co(L1)₂].EtOH.0.5CH₃CN (1): HL1 (0.115 g, 0.4 mmol), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.047 g, 0.2 mmol) and 25% tetramethylammonium hydroxide (1.5 mL) were added to a mixture solution of ethanol-acetonitrile (12 mL, 1:1). The mixture was put into a 25 mL Teflon-lined Parr vessel and heated to 110 °C for 24 h. When the reactant was cooled to room temperature at a rate of 5 °C/h, the red plate crystals appeared and were collected by filtration and washed with CHCl_3 . Yield, 0.031 g, 12.2% on the basis of metal ion. EI-MS $m/z = 632$ $[M+1]^+$. FT-IR (KBr, cm^{-1}): 3452(br, w), 1600(vs), 1549(s), 1516(s), 1470(vs), 1427(s), 1321(s), 1255(s), 1188(w), 1142(w), 1043(w),

1007(w), 951(w), 843(w), 784(w), 742(s), 698(s), 595(w).

[Co(L2)₂·H₂O (2): HL2 (0.143 g, 0.4 mmol), Co(NO₃)₂·6H₂O (0.058 g, 0.2 mmol), 6mL ethanol and 6mL acetonitrile were put into a 25mL Teflon-lined Parr vessel. The mixture was heated to 165 °C for 24 h. When the reactant was cooled to room temperature at a rate of 5 °C/h, the dark red prismatical crystals appeared and were collected by filtration. Yield, 0.128 g, 82.8% on the basis of metal ion. EI-MS m/z = 770 [$M+1$]⁺. FT-IR (KBr, cm⁻¹): 3465(br, s), 3101(w), 1637(w), 1605(w), 1554(w), 1514(w), 1475(w), 1442(vs), 1342(w), 1240(s), 1173(w), 1141(w), 1028(w), 1004(w), 849(w), 787(w), 752(w), 698(w), 655(w).

[Fe(L2)₂] (3): HL2 (0.143 g, 0.4 mmol), FeCl₂·4H₂O (0.040 g, 0.2 mmol), 7 drops of aqueous solution of 25% tetramethylammonium hydroxide, 6mL ethanol and 6mL acetonitrile were put into a 25mL Teflon-lined Parr vessel. The mixture was heated to 120 °C for 24 h. When the reactant was cooled to room temperature at a rate of 5 °C/h, the red octahedral crystals appeared and were collected by filtration. Yield, 10.0% on the basis of metal ion. EI-MS m/z = 767 [$M+1$]⁺. FT-IR (KBr, cm⁻¹): 3088(w), 1637(w), 1607(s), 1550(w), 1518(s), 1476(w), 1453(w), 1437(vs), 1343(w), 1305(w), 1242(w), 1167(w), 1142(w), 1029(w), 966(w), 867(w), 791(s), 763(w), 741(s), 699(s), 657(w).

[Co(L3)₂] (4): HL3 (0.143 g, 0.4 mmol), Co(NO₃)₂·6H₂O (0.058 g, 0.2 mmol), 6 mL ethanol and 6 mL acetonitrile were put into a 25mL Teflon-lined Parr vessel. The mixture was heated to 120 °C for 24 h. When the reactant was cooled to room temperature at a rate of 5 °C/h, the dark red octahedral crystals appeared and were collected by filtration. Yield, 0.138 g, 89.4% on the basis of metal ion. EI-MS m/z = 774 [$M+1$]⁺. FT-IR (KBr, cm⁻¹): 3084(w), 2968(w), 2930(w), 2887(w), 1595(vs), 1550(w), 1510(w), 1481(vs), 1416(w), 1350(w), 1323(w), 1257(w), 1238(w), 1199(w), 1145(w), 1020(w), 945(w), 850(w), 823(w), 781(w), 738(w), 698(w), 652(w), 611(w).

3. Experimental method for CD spectra.

The solid state CD and Uv-vis spectra were recorded on a Jasco-810 circular dichroism spectropolarimeter at 20 °C. The CD spectra were measured on the resulting complexes as crystal (ca. 0.4 mg) in 100 mg of oven-dried KCl. The baseline correction was performed with the spectrum of a pure KCl disk, prepared in the same conditions. The displayed absorption spectra result from subtraction of spectrum of a standard KCl disk. Spectra were recorded for the wavelength range 250-700 nm for all the disks with the pathlength was 3 nm.

4. X-ray experiments

Diffraction intensities for [Co(L1)₂]-EtOH·0.5CH₃CN (**1**), [Co(L2)₂]-H₂O (**2**), [Fe(L2)₂] (**3**) and [Co(L3)₂] (**4**) were collected on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied using SADABS. The structures were solved by direct methods and refined with full-matrix least-squares technique using SHELXS-97 and SHELXTL-97 programs, respectively. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically (C-H 0.96 Å and N-H 0.86 Å). In complex **1**, the solvent molecules are highly disordered. The carbon atoms in EtOH might have two most probable positions (C3W, C4W and C5W, C6W) with the occupancies of 0.75 and 0.25. The occupancy of acetonitrile might be 0.5 due to the unstable refinement and high atomic displacement parameter (*U*) when it was 1. The bond lengths of the disordered molecules were chemically restrained. Most of the hydrogen atoms couldn't be located due to the disorder. In complex **2**, the water molecule was highly disorder and dispersed in the small tube, O1W (0,0,1/2) and O2W'(0,0,z) were located in two specific positions. The occupancies of O1W, O2W and O2W' are 1/6, respectively, according to the result chemical analysis. The hydrogen atoms couldn't be located due to the disorder.

5. Supplementary Figures

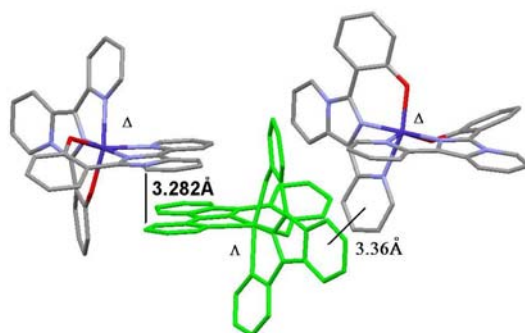


Fig. S1 Presentation of head-to-tail π - π interactions in **1**.

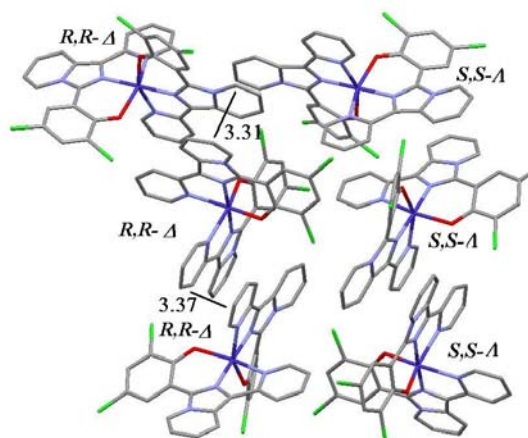


Fig. S2 View of homochiral R,R - Δ and S,S - Δ chains via head-to-head π - π interactions along the a -axis in **2**.

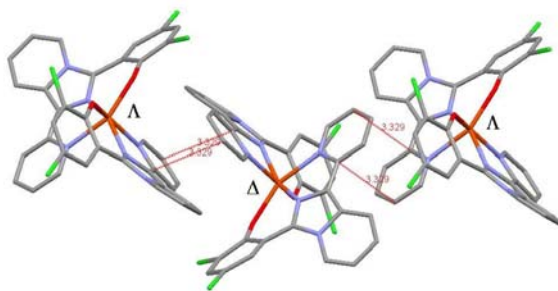


Fig. S3 View of a heterochiral chain via π - π interactions in **3** along the b -axis.

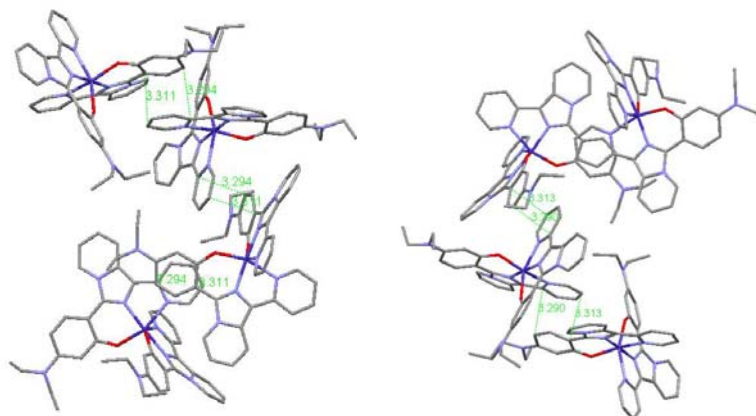


Fig. S4 Views of the *P* (**4-R**, left) and *M* (**4-S**, right) helices of **4** via π - π interactions along the *b*-axis.

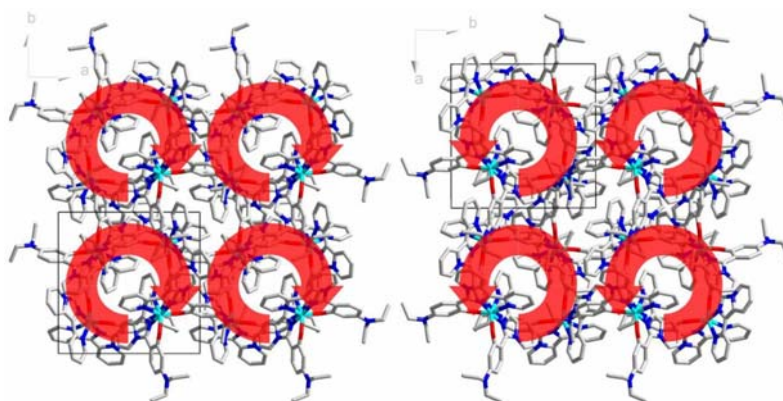


Fig. S5 Views of crystal packing of helical columns of unique *P* (**4-R**, left) and *M* (**4-S**, right) chirality along the *c*-axis.