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ELECTRONIC SUPPLEMENTARY DATA

for

Spontaneous Resolution of Chiral Metal Mandelates by Stereochemical Control

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Synthesis

*Elemental analysis calcd (%) for **1R** and **1S***: C, 61.75; H, 5.00; N, 4.97. Found: C, 61.95; H, 5.03; N, 5.11. IR data (KBr) (400-4000 cm-1): 3438 (m), 3031(m), 2897(w), 2601(m), 1592(s), 1428(w), 1379(s), 1269(m), 1224(w), 1189(w), 1049(s), 1027(m), 949(w), 845(w), 801(w), 749(m), 698(s), 651(w), 597(m), 547(m), 499(w).

*Elemental analysis calcd (%) for **2***: C, 61.23; H, 4.89; N, 6.80. Found: C, 61.50; H, 5.01; N, 6.77. IR data (KBr) (400-4000 cm-1): 3459(m), 3050(m), 3023(m), 2937(m), 2858(w), 2819(w), 2685(w), 1948(w), 1791(w), 1640(s), 1617(s), 1493(w), 1447(w), 1427(w), 1382(s), 1224(w), 1194(w), 1094(m), 1064(s) 1027(m), 942(w), 806(s), 733(s), 699(s), 619(w), 584(m), 526(m).

*Elemental analysis calcd (%) for **3**:* C, 61.75; H, 5.00; N, 4.97. Found: C, 61.86; H, 5.05; N, 4.95. IR data (KBr) (400-4000 cm-1): 3435 (m), 3029(m), 2901(w), 2603(m), 1590(s), 1428(w), 1375(s), 1267(m), 1222(w), 1185(w), 1046(s), 1024(m), 945(w), 840(w), 810(w), 694(s), 649(w), 602(m), 547(m).

Synthesis of **Λ-**[Fe(II)(*R*-Hopa)$_2$(bpp)] **4R** and **Δ-**[Fe(II)(*S*-Hopa)$_2$(bpp)] **4S**: NaOH (0.010 g, 0.25 mmol) was added to an water/ethanol solution of *rac*-H_2opa (0.038 g, 0.25 mmol) with stirring. And then bpp (0.025 g 0.125 mmol) and $FeCl_2 \cdot 4H_2O$ (0.025 g, 0.125 mmol) were added with stirring, the suspension was poured into a 23 ml Teflon reactor, which was heated at 160 ^oC for 48 hours and then cooled to room temperature at a rate of 5 ^oC/h. Golden crystals were obtained after washing and drying in air. Yield, 30%. Elemental analysis calcd (%): C, 62.60; H, 5.07; N, 5.03. Found: C, 62.72; H, 4.98; N, 5.12. IR data (KBr) (400-4000 cm^{-1}): 3425(m), 3030(m), 2927(w), 2604(m), 1610(s), 1429(w), 1379(s), 1270(m), 1226(w), 1193(w), 1052(s), 1023(m), 948(w), 800(w), 752(m), 697(s), 655(w), 597(m), 547(m), 499(w).

Synthesis of **Λ-**[Co(II)(*R*-Hopa)$_2$(bpp)] **5R** and **Δ-**[Co(II)(*S*-Hopa)$_2$(bpp)] **5S**: Similar procedure to that of [Fe(II)(*R*-Hopa)$_2$(bpp)] was carried out except $CoCl_2 \cdot 6H_2O$ (0.030 g, 0.125 mmol) was used in place of $FeCl_2 \cdot 4H_2O$. Yield, 28%. Elemental analysis calcd (%): C, 62.26; H, 5.04; N, 5.01. Found: C, 62.31; H, 4.97; N, 5.05. IR data (KBr) (400-4000 cm^{-1}): 3436 (m), 3029(m), 2894(w), 2598(m), 1590(s), 1430(w), 1382(s), 1270(m), 1226(w), 1191(w), 1051(s), 1025(m), 947(w), 842(w), 798(w), 751(m), 696(s), 655(w), 596(m), 546(m), 499(w).

Synthesis of **Λ-**[Ni(II)(*R*-Hopa)$_2$(bpp)] **6R** and **Δ-**[Ni(II)(*S*-Hopa)$_2$(bpp)] **6S**: Compounds were prepared by a similar procedure to that of [Fe(II)(*R*-Hopa)$_2$(bpp)] except $NiCl_2 \cdot 6H_2O$ (0.030 g, 0.125 mmol) was used. Yield, 35%. Elemental analysis calcd (%): C, 62.28; H, 5.05; N, 5.01. Found: C, 62.34; H, 5.03; N, 5.09. IR data (KBr) (400-4000 cm^{-1}): 3438 (m), 3031(m), 2897(w), 2601(m), 1592(s), 1428(w), 1379(s), 1269(m), 1224(w), 1189(w), 1049(s), 1027(m), 949(w), 845(w), 801(w), 749(m), 698(s), 651(w), 597(m), 547(m), 499(w).

Synthesis of **Λ-**[Zn(II)(*R*-Hopa)$_2$(bpp)] **7R** and **Δ-**[Zn(II)(*S*-Hopa)$_2$(bpp)] **7S**:
Method A: complexes were prepared by a similar procedure to that of [Fe(II)(*R*-Hopa)$_2$(bpp)] except that $ZnCl_2$ (0.017 g, 0.125 mmol) was used instead. Yield, 45%.

Method B: Ammonia was added to the methanol and water (1:1) solution of $Zn(NO_3)_2 \cdot 6H_2O$ (0.074 g, 0.25 mmol), until the solution was clear. Then *rac*-H_2opa (0.076 g, 0.50 mmol) and bpp (1,3-di(4-pyridyl) propane) (0.050 g 0.25 mmol) were added to the above solution. Diamond-like colorless crystals of **7R** and **7S** were obtained after five days. Yield, 88%. Elemental analysis calcd (%): C, 61.55; H, 4.99; N, 4.95. Found: C, 61.62; H, 4.95; N, 5.04. IR data (KBr) (400-4000 cm^{-1}): 3434 (m), 3028(m), 2893(w), 2599(m), 1592(s), 1430(w), 1383(s), 1271(m), 1226(w), 1191(w), 1054(s), 1025(m), 947(w), 842(w), 799(w), 752(m), 697(s), 656(w), 598(m), 547(m), 499(w).

Crystallographic Data:

Crystal data for **Λ**-[Fe(II)(*R*-Hopa)$_2$(bpp)] **4R** (293 K): $C_{29}H_{28}O_6N_2Fe$, M = 556.38, hexagonal, space group $P6_522$ (no. 179), a = 11.643(1) Å, b = 11.643(1) Å, c = 32.956(7) Å, U = 3869.0(9) Å^3, Z = 6, ρ_{calcd} = 1.433 g cm^{-3}, μ(MoKα) = 0.632 mm^{-1}. A total of 7089 reflections collected, 2746 independent reflections (R_{int} = 0.0281) with 2191 ($I > 2\sigma(I)$) observed data. R_1 = 0.0713 ($I > 2\sigma(I)$), wR_2 = 0.1793 (for all data), Flack parameter x = 0.02(6).

Crystal data for *Δ*-[Fe(II)(*S*-Hopa)$_2$(bpp)] **4S** (150 K): $C_{29}H_{28}O_6N_2Fe$, M = 556.38, hexagonal, space group $P6_122$ (no. 178), a = 11.565(1) Å, b = 11.565(1) Å, c = 32.789(2) Å, U = 3798.2(5) Å^3, Z = 6, ρ_{calcd} = 1.459 g cm^{-3}, μ(MoKα) = 0.644 mm^{-1}. A total of 9634 reflections collected, 3235 independent reflections (R_{int} = 0.0341) with 2125 ($I > 2\sigma(I)$) observed data. R_1 = 0.0422 ($I > 2\sigma(I)$), wR_2 = 0.1107 (for all data), Flack parameter x = 0.01(3).

Crystal data for *Λ*-[Co(II)(*R*-Hopa)$_2$(bpp)] **5R** (293 K): $C_{29}H_{28}O_6N_2Co$, M = 559.46, hexagonal, space group $P6_522$ (no. 179), a = 11.595 (2) Å, b = 11.595 (2) Å, c = 33.068 (9) Å, U = 3850 (1) Å^3, Z = 6, $\rho\chi_{calcd}$ = 1.448 g cm^{-3}, μ(MoKα) = 0.716 mm^{-1}. A total of 7061 reflections collected, 2563 independent reflections (R_{int} = 0.0655) with 1746 ($I > 2\sigma(I)$) observed data. R_1 = 0.1025 ($I > 2\sigma(I)$), wR_2 = 0.2551 (for all data), Flack parameter x = 0.11(8).

Crystal data for *Δ*-[Co(II)(*S*-Hopa)$_2$(bpp)] **5S** (293 K): $C_{29}H_{28}O_6N_2Co$, M = 559.46, hexagonal, space group $P6_122$ (no. 178), a = 11.583 (2) Å, b = 11.583 (2) Å, c = 33.05(1) Å, U = 3841(1) Å^3, Z = 6, ρ_{calcd} = 1.451 g cm^{-3}, μ(MoKα) = 0.718 mm^{-1}. A total of 6403 reflections collected, 2359 independent reflections (R_{int} = 0.0609) with 1534 ($I > 2\sigma(I)$) observed data. R_1 = 0.0537 ($I > 2\sigma(I)$), wR_2 = 0.1282 (for all data), Flack parameter x = 0.00(4).

Crystal data for *Λ*-[Ni(II)(*R*-Hopa)$_2$(bpp)] **6R** (293 K): $C_{29}H_{28}O_6N_2Ni$, M = 559.24, hexagonal, space group $P6_522$ (no. 179), a = 11.518(1) Å, b = 11.518(1) Å, c = 33.162(4) Å, U = 3809.6(6) Å^3, Z = 6, ρ_{calcd} = 1.463 g cm^{-3}, μ(MoKα) = 0.812 mm^{-1}. A total of 9642 reflections collected, 2315 independent reflections (R_{int} = 0.0472) with 1999 ($I > 2\sigma(I)$) observed data. R_1 = 0.0854 ($I > 2\sigma(I)$), wR_2 = 0.2066 (for all data), Flack parameter x = 0.04(6).

Crystal data for *Δ*-[Ni(II)(*S*-Hopa)$_2$(bpp)] **6S** (150 K): $C_{29}H_{28}O_6N_2Ni$, M = 559.24, hexagonal, space group $P6_122$ (no. 178), a = 11.4711(1) Å, b = 11.4711(1) Å, c = 33.0791(4) Å, U = 3769.59(7) Å^3, Z = 6, ρ_{calcd} = 1.478 g cm^{-3}, μ(MoKα) = 1.521 mm^{-1}. A total of 9433 reflections collected, 1814 independent reflections (R_{int} = 0.0296) with 1343 ($I > 2\sigma(I)$) observed data. R_1 = 0.0280 ($I > 2\sigma(I)$), wR_2 = 0.0506 (for all data), Flack parameter x = -0.01(4).

Crystal data for *Λ*-[Zn(II)(*R*-Hopa)$_2$(bpp)] **7R** (150 K): $C_{29}H_{28}O_6N_2Zn$, M = 565.90, hexagonal, space group $P6_522$ (no. 179), a = 11.595 (2) Å, b = 11.595 (2) Å, c = 33.068 (9) Å, U = 3850 (1) Å^3, Z = 6, ρ_{calcd} = 1.464 g cm^{-3}, μ(MoKα) = 1.004 mm^{-1}. A total of 10870 reflections collected, 2949 independent reflections (R_{int} = 0.0374) with 2066 ($I > 2\sigma(I)$) observed data. R_1 = 0.0662 ($I > 2\sigma(I)$), wR_2 = 0.1712 (for all data), Flack parameter x = 0.00 (5).

Crystal data for *Λ*-[Zn(II)(*S*-Hopa)$_2$(bpp)] **7S** (293 K): $C_{29}H_{28}O_6N_2Zn$, M = 565.90, hexagonal, space group $P6_122$ (no. 178), a = 11.606 (1) Å, b = 11.606 (1) Å, c = 33.043 (5) Å, U = 3854.3(8) Å^3, Z = 6, ρ_{calcd} = 1.463 g cm^{-3}, μ(MoKα) = 1.003 mm^{-1}. A total of 10274 reflections collected, 2816 independent reflections (R_{int} = 0.0412) with 2165 ($I > 2\sigma(I)$) observed data. R_1 = 0.0506 ($I > 2\sigma(I)$), wR_2 = 0.1196 (for all data), Flack parameter x = 0.02 (2).

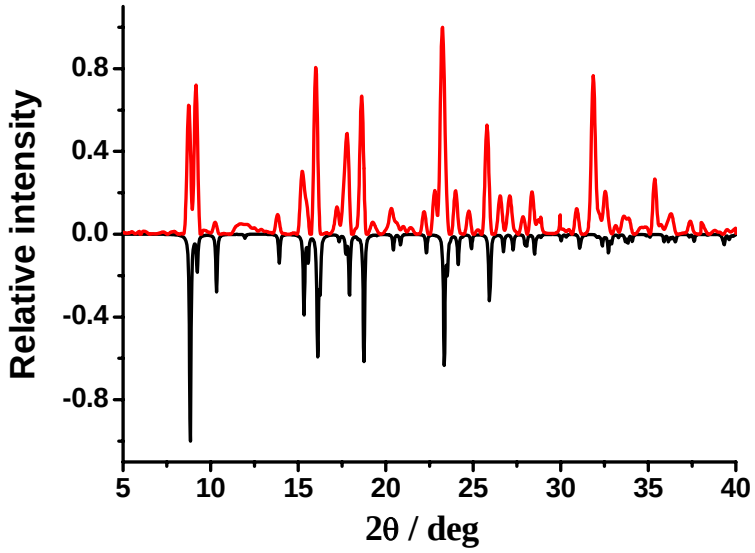

Fig. S1 Simulated (black line) and experimental (red line) powder XRD patterns of [Cu(*R*-Hopa)$_2$(bpp)]$_n$ **1R** and [Cu(*S*-Hopa)$_2$(bpp)]$_n$ **1S**.

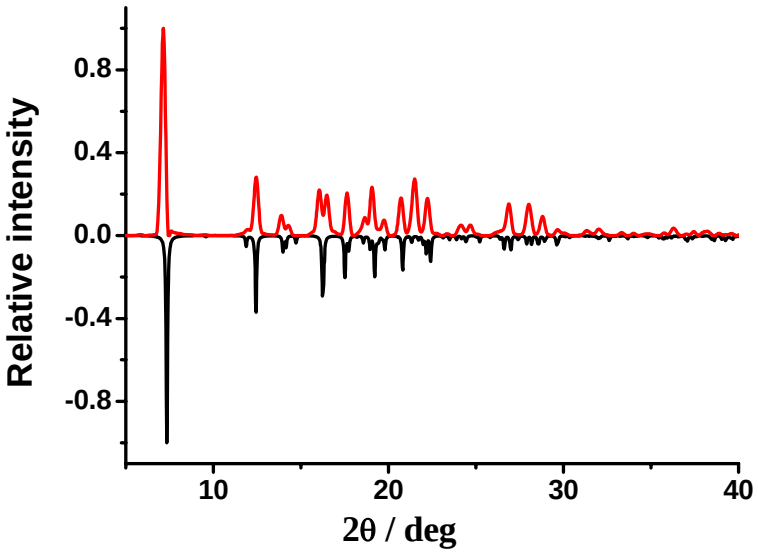

Fig. S2 Simulated (black line) and experimental (red line) powder XRD patterns of [Cu(*rac*-Hopa)$_2$(bpp)]$_n$ **2**.

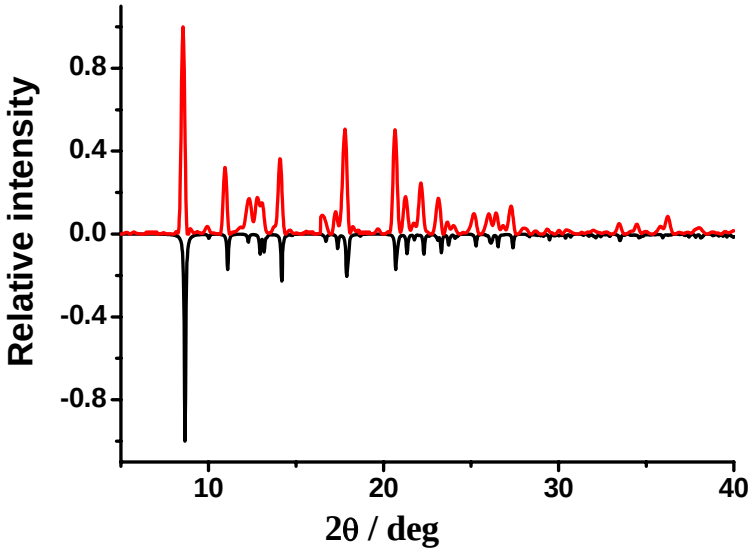

Fig. S3 Simulated (black line) and experimental (red line) powder XRD patterns of $[Cu_2(rac\text{-}opa)_2(bpp)]_n$ **3**.

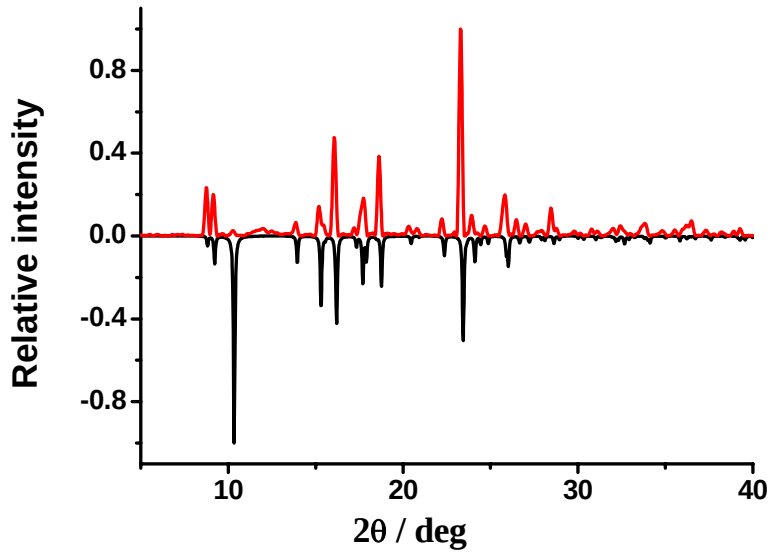

Fig. S4 Simulated (black line) and experimental (red line) powder XRD patterns of $[Fe(R\text{-}Hopa)_2(bpp)]_n$ **4R** and $[Fe(S\text{-}Hopa)_2(bpp)]_n$ **4S**.

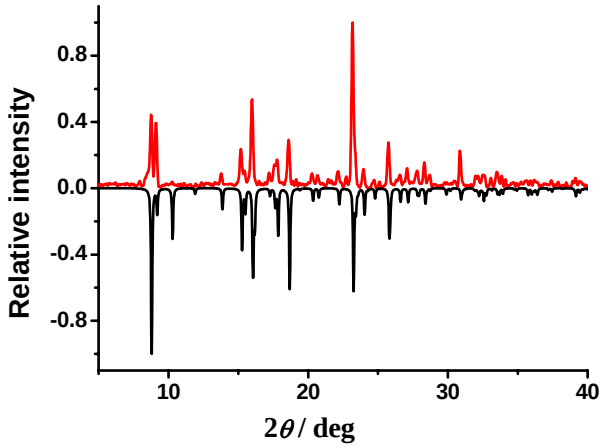

Fig. S5 Simulated (black line) and experimental (red line) powder XRD patterns of [Co(*R*-Hopa)$_2$(bpp)]$_n$ (**5R**) and [Co(*S*-Hopa)$_2$(bpp)]$_n$ (**5S**).

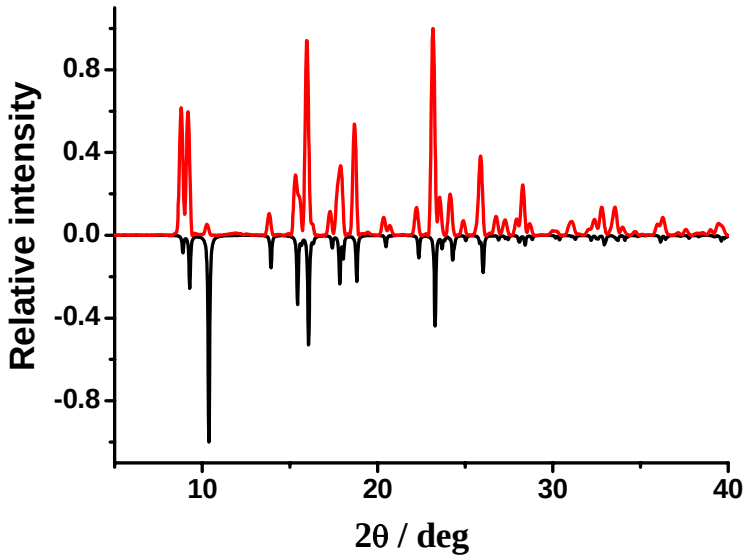

Fig. S6 Simulated (black line) and experimental (red line) powder XRD patterns of [Ni(*R*-Hopa)$_2$(bpp)]$_n$ (**6R**) and [Ni(*S*-Hopa)$_2$(bpp)]$_n$ (**6S**).

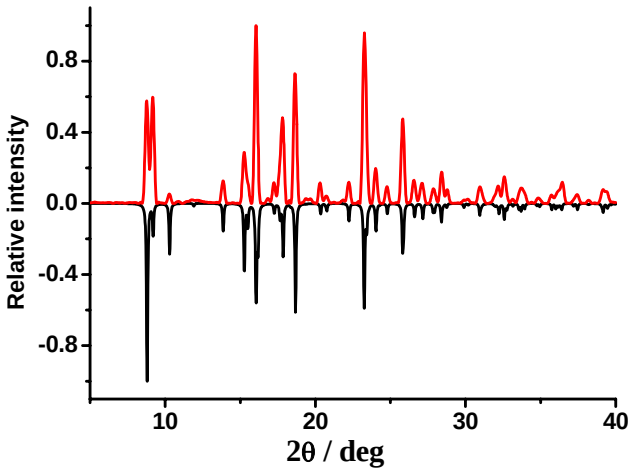

Fig. S7 Simulated (black line) and experimental (red line) powder XRD patterns of [Zn(*R*-Hopa)$_2$(bpp)]$_n$ (**7R**) and [Zn(*S*-Hopa)$_2$(bpp)]$_n$ (**7S**).

Table S1. Bond distances of the metal ions in racemic compounds of [Cu(*rac*-opa)(bpp)] **2** and [Cu(*rac*-Hopa)$_2$(bpp)] **3**

	M-O1 (*α*-OH)	**M-O2 (COO)**	**M-N (bpp)**
2 (SP)	1.924(3)	1.941(3)	1.999(3)
	1.945(3)		2.323(4)
3 (Oh)	2.312(5)	1.951(4)	2.027(6)
	2.315(5)	1.968(4)	2.033(6)

Table S2 Bond distances of the metal ions in the octahedral geometry for the chiral compounds of [M(Hopa)$_2$(bpp)]$_n$

	M-O1 (*α*-OH)	**M-O2 (COO)**	**M-N (bpp)**
1R (Cu)	2.131(4)	1.983(3)	2.148(5)
1S (Cu)	2.134(3)	1.981(3)	2.166(8)[a]
4R (Fe)	2.165(2)	2.061(2)	2.174(3)
4S (Fe)	2.156(2)	2.056(2)	2.162(7)[a]
5R (Co)	2.113(3)	2.049(3)	2.128(4)
5S (Co)	2.117(3)	2.042(3)	2.107(15)[a]
6R (Ni)	2.059(3)	2.043(3)	2.080(4)
6S (Ni)	2.054(2)	2.032(1)	2.066(12)[a]
7R (Zn)	2.131(3)	2.066(2)	2.138(3)
7S (Zn)	2.142(3)	2.052(2)	2.130(14)[a]

[a] bpp is disordered at two positions in all *S*-Mandelate compounds. Here the average distances are considered.