SUPPORTING INFORMATION

Homochiral crystallization of single-stranded helical coordination polymers: generated by the structure of auxiliary ligands or spontaneous symmetry breaking

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Synthesis. All reagents and solvents were received from commercial supplies without further purification. (R)-2-amino-1-propanol, (S)-2-amino-1-propanol, 2-aminoethanol, o-vanillin, $CuCl_2$, $NaN(CN)_2$, NaOH and all the solvents were purchased from Alfa Aesar, respectively. The Schiff base ligands R-H_2L^1, S-H_2L^1, H_2L^2 were synthesized according to literature procedures.

Synthesis of [Cu(R-HL^1)($\mu_{1,5}$-dca)]$_n$ (1). A mixture of $CuCl_2{\cdot}4H_2O$ (0.207 g, 1 mmol), R-H_2L^1 (0.208 g, 1 mmol), $NaN(CN)_2$ (0.089 g, 1mmol) and NaOH (0.040 g, 1 mmol) in 20 mL of methanol/ethanol/water (1:2:1) was stirred for 0.5 h. The resulting dark blue solution was left unperturbed to a slow evaporation of the solvent. After three days, dark green block-shaped crystals, suitable for X-ray diffraction analysis, were obtained. Elemental analysis (%): Calc. for $C_{13}H_{14}CuN_4O_3$: C, 46.22; H, 4.18; N, 16.59. Found: C, 46.53; H, 4.37; N, 16.21. IR (KBr pellet, cm^{-1}): 3107*m*, 2318*vs*, 2242*vs*, 2188*vs*, 1641*s*, 1601*m*, 1445*m*, 1322*m*, 1301*m*, 1247*m*, 1027*m*, 975*m*, 871*w*, 742*m*, 630*w*, 567*w*.

Synthesis of [Cu(S-HL^1)($\mu_{1,5}$-dca)]$_n$ (2). This compound was prepared using the same procedure as that described above for the synthesis of using S-H_2L^2 in place of R-H_2L^1. Elemental analysis (%): Calc. for $C_{13}H_{14}CuN_4O_3$: C, 46.22; H, 4.18; N, 16.59. Found: C, 46.46; H, 4.32; N, 16.25. IR (KBr pellet, cm^{-1}): 3135*m*, 2321*vs*, 2259*vs*, 2200*vs*, 1620*s*, 1587*m*, 1429*m*, 1380*m*, 1289*m*, 1199*m*, 1067*m*, 954*m*, 857*w*, 739*m*, 637*w*, 580*w*.

Synthesis of [Cu(HL^2)($\mu_{1,5}$-dca)]$_n$ (3). A mixture of $CuCl_2{\cdot}4H_2O$ (0.207 g, 1 mmol), H_2L^2 (0.193g, 1 mmol), $NaN(CN)_2$ (0.089 g, 1mmol) and NaOH (0.040 mg, 1 mmol) in 20 mL of methanol/ethanol/water (1:2:1) was stirred for 3 h. The resulting dark blue solution was left unperturbed to a slow evaporation of the solvent. After 24 hours, dark green block-shaped crystals,

suitable for X-ray diffraction analysis, were obtained. Elemental analysis (%): Calc. for $C_{12}H_{12}CuN_4O_3$ (1): C, 44.51; H, 3.74; N, 17.30. Found: C, 44.19; H, 3.81; N, 17.62. IR (KBr pellet, cm^{-1}): 3119*m*, 2320*vs*, 2252*vs*, 2193*vs*, 1643*s*, 1601*m*, 1441*m*, 1397*m*, 1299*m*, 1217*m*, 1075*m*, 968*m*, 856*w*, 740*m*, 638*w*, 573*w*.

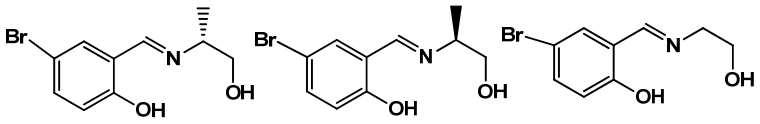
Crystallography. Single crystals of the complexes were selected and mounted on a Bruker ApexII CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å), operating in ω–2θ scanning mode using suitable crystals for data collection. Lorentz-polarization correction was applied to the data. The structure was solved by direct methods (SHELX-97) and refined by full-matrix least-squares procedures on F^2 using SHELX-97. Hydrogen atoms were added theoretically and refined with riding model position parameters and fixed isotropic thermal parameters. Experimental details for the structural determinations are summarized in Table 1S.

Physical Measurements. Fourier transform infrared (FTIR) spectra (KBr disk) were measured with a Vertex 70 FTIR on a spectrophotometer (4000–400 cm^{-1}). Elemental analyses for C, H and N were obtained from a Perkin-Elmer 2400 elemental analyzer. Circular dichroism (CD) spectra were measured as KBr pellet with a J-715 spectropolarimeter in the range of 200-900 nm at 298 K.

Table S1. Crystallographic Data and Structure Refinement for Complexes 1-3.

	1	**2**	**3**
Empirical Formula	$C_{13}H_{14}CuN_4O_3$	$C_{13}H_{14}CuN_4O_3$	$C_{12}H_{12}CuN_4O_3$
Formula weight	337.82	337.82	323.80
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	9.586(2)	9.589(2)	9.596(2)
b (Å)	10.713(2)	10.709(2)	10.990(2)
c (Å)	13.527(3)	13.528(3)	12.258(3)
α, β, γ (°)	90, 90, 90	90, 90, 90	90, 90, 90
V (Å^3)	1389.1(5)	1389.2(5)	1292.7(4)
Z	4	4	4
T (K)	293(2)	293(2)	293(2)
ρ_{calcd} (g cm^{-3})	1.615	1.615	1.664
Abs. coefficient (mm^{-1})	1.588	1.588	1.702
F(000)	692	692	660
θ Range (°)	2.43 < θ < 28.27	2.43 < θ < 28.28	2.49 < θ < 27.86
Reflections collected	10202	10187	13542
unique reflns, R_{int}	3428, 0.0199	3422, 0.0195	3082, 0.0446
GOF on F^2	1.038	1.027	0.960
Final R indices [I > 2σ(I)]	R [a)] = 0.0235, wR [b)] = 0.0607	R [a)] = 0.0235, wR [b)] = 0.0627	R [a)] = 0.0243, wR [b)] = 0.0512
R indices (all data)	R = 0.0272, wR = 0.0623	R = 0.0255, wR = 0.0635	R = 0.0298, wR = 0.0518
Flack parameter	0.011(10)	0.014(10)	0.009(18)

a) $R=\Sigma||F_0|-|F_c||/\Sigma|F_0|$ b) $wR=[\Sigma w(F_0^2-F_c^2)^2/\Sigma(wF_0^4)]^{1/2}$



R-H_2L^3 S-H_2L^3 H_2L^4

Scheme S1. The structures of the bromine-substituted chelate ligands (R-H_2L^3, S-H_2L^3, H_2L^4).

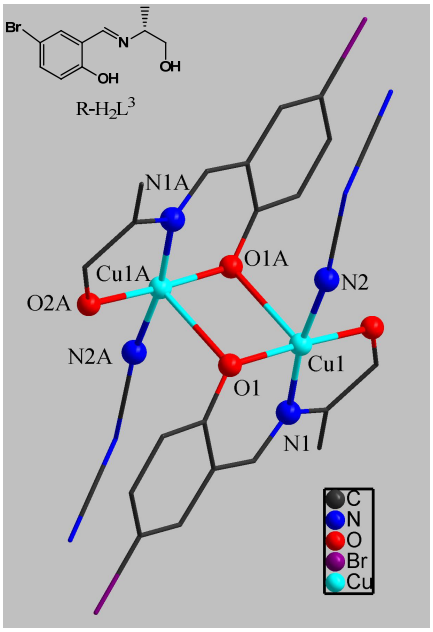


Figure S1. A perspective view of structure for **[Cu(R-HL^3)($N(CN)_2$)]$_2$ (4).** Hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Cu1–O1 1.910(6), Cu1–N1 1.932(7), Cu1–N2 1.932(7), Cu1–O2 1.963(7), Cu1–O1A 2.580(7), O1–Cu1–N1 94.3(3), N2–Cu1–O2 91.4(3), N1–Cu1–O2 81.9(3), O1–Cu1–O1A 88.7(3), N2–Cu1–O1A 91.0(3), N1–Cu1–O1A 95.3(3), O2–Cu1–O1 91.8(3) (symmetry code A: $-x+2, -y+1, -z$). This compound was prepared using the same procedure as that described above for the synthesis of using R-H_2L^3 in place of R-H_2L^1. Elemental analysis (%): Calc. for $C_{24}H_{22}Br_2Cu_2N_8O_4$ (1): C, 37.27; H, 2.87; N, 14.49. Found: C, 37.61; H, 2.55; N, 14.28. IR (KBr pellet, cm^{-1}): 2972*m*, 2316*vs*, 2255*vs*, 2179*vs*, 1637*s*, 1590*m*, 1456*m*, 1378*m*, 1293*m*, 1177*m*, 1040*m*, 830*m*, 796*w*, 672*m*, 645*w*, 550*w*.

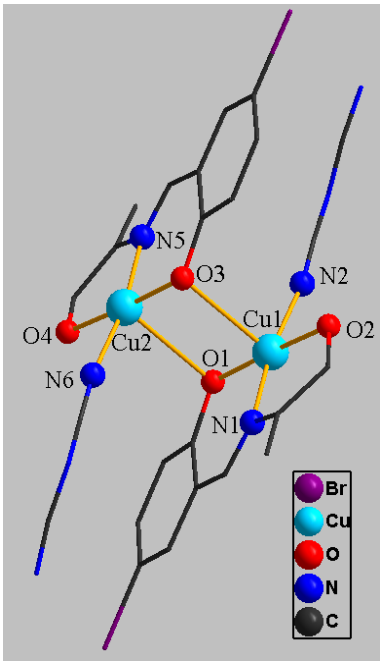


Figure S2. A perspective view of structure for **[Cu(S-HL^3)(N(CN)$_2$)]$_2$ (5)**. Hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Cu1–O1 1.915(10), Cu1–N2 1.949(14), Cu1–N1 1.949(13), Cu1–O2 1.971(11), Cu2–O3 1.914(10), Cu2–N5 1.938(13), Cu2–N6 1.941(14), Cu2–O4 1.960(11), O1–Cu1–N2 92.4(5), O1–Cu1–N1 94.2(5), N2–Cu1–N1 171.2(6), O1–Cu1–O2 176.8(5), N2–Cu1–O2 90.8(5), N1–Cu1–O2 82.6(5), O3–Cu2–N5 94.1(5), O3–Cu2–N6 91.9(5), N5–Cu2–N6 171.0(6), O3–Cu2–O4 175.4(5), N5–Cu2–O4 81.3(5), N6–Cu2–O4 92.7(5). This compound was prepared using the same procedure as that described above for the synthesis of using S-H_2L^4 in place of H_2L^1. Elemental analysis (%):Calc. for $C_{24}H_{22}Br_2Cu_2N_8O_4$ (1): C, 37.27; H, 2.87; N, 14.49. Found: C, 37.59; H, 2.66; N, 14.17. IR (KBr pellet, cm^{-1}): 3124*m*, 2333*vs*, 2262*vs*, 2183*vs*, 1653*s*, 1611*m*, 1451*m*, 1387*m*, 1289*m*, 1227*m*, 1065*m*, 948*m*, 866*w*, 730*m*, 628*w*, 563*w*.

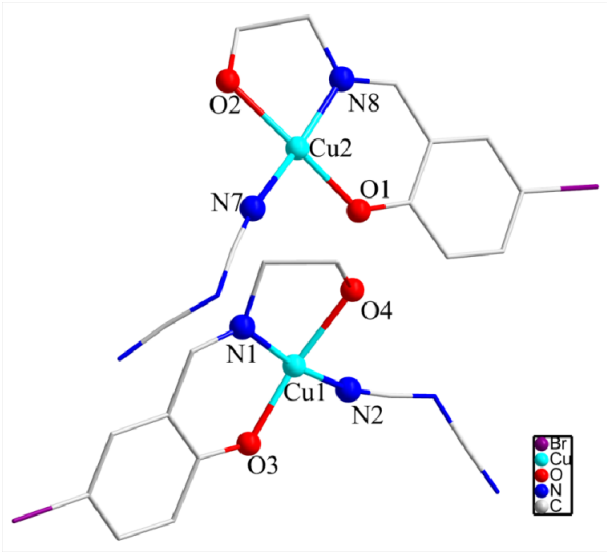


Figure S3. A perspective view of structure for **$[Cu(HL^4)(N(CN)_2)]_2$ (6).** Hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Cu1–O3 1.8829(15), Cu1–N1 1.9205(18), Cu1–N2 1.943(2), Cu1–O4 2.0256(17), Cu2–O1 1.8796(16), Cu2–N8 1.9160(18), Cu2–N7 1.947(2), Cu2–O2 2.0212(18), O3–Cu1–N1 94.07(7), O3–Cu1–N2 94.56(8), N1–Cu1–O4 82.72(7), N2–Cu1–O4 90.07(8), O1–Cu2–N8 94.72(8), O1–Cu2–N7 91.45(9), N8–Cu2–O2 82.41(8), N7–Cu2–O2 92.66(9). This compound was prepared using the same procedure as that described above for the synthesis of using H_2L^3 in place of H_2L^1. Elemental analysis (%): Calc. for $C_{22}H_{18}Br_2Cu_2N_8O_4$ (1): C, 35.45; H, 2.43; N, 15.03. Found: C, 35.10; H, 2.61; N, 14.89. IR (KBr pellet, cm^{-1}): 2964*m*, 2307*vs*, 2252*vs*, 2187*vs*, 1636*s*, 1521*m*, 1458*m*, 1375*m*, 1318*m*, 1175*m*, 1087*m*, 928*m*, 883*w*, 683*m*, 648*w*, 565*w*.

Table S2. Crystallographic Data and Structure Refinement for Complexes **4-6.**

	4 (CCDC 933907)	**5** (CCDC 933908)	**6** (CCDC 933909)
Empirical Formula	$C_{24}H_{22}Br_2Cu_2N_8O_4$	$C_{24}H_{22}Br_2Cu_2N_8O_4$	$C_{22}H_{18}Br_2Cu_2N_8O_4$
Formula weight	773.40	773.40	745.34
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	*P*-1	*P*-1	$P2_1/c$
a (Å)	8.224(2)	9.518(4)	13.724(3)
b (Å)	9.513(2)	11.058(4)	13.478(3)
c (Å)	10.460(2)	14.814(6)	15.482(7)
α, β, γ (°)	64.03(3), 71.43(3), 83.95(3)	92.275(7), 105.925(7), 109.584(6)	90, 117.98(2), 90
V (Å^3)	696.8(2)	1397.6(10)	2529.0(14)
Z	1	2	4
T (K)	153(2)	296(2)	153(2)
ρ_{calcd} (g cm^{-3})	1.843	1.838	1.958
Abs. coefficient (mm^{-1})	4.440	4.427	4.889
F(000)	382	764	1464
θ Range (°)	$2.27 < \theta < 28.38$	$1.44 < \theta < 28.23$	$1.68 < \theta < 28.30$
Reflections collected	5161	10226	18375
unique reflns, R_{int}	3445, 0.0211	6831, 0.0304	6272, 0.0204
GOF on F^2	1.034	0.969	1.057
Final R indices [I > 2σ(I)]	R [a)] = 0.0759, wR [b)] = 0.1943	R [a)] = 0.0659, wR [b)] = 0.1619	R [a)] = 0.0271, wR [b)] = 0.0656
R indices (all data)	R = 0.0843, wR = 0.1973	R = 0.1529, wR = 0.1906	R = 0.0426, wR = 0.0707

a) $R=\Sigma||F_0|-|F_c||/\Sigma|F_0|$ b) $wR=[\Sigma w(F_0^2-F_c^2)^2/\Sigma(wF_0^4)]^{1/2}$

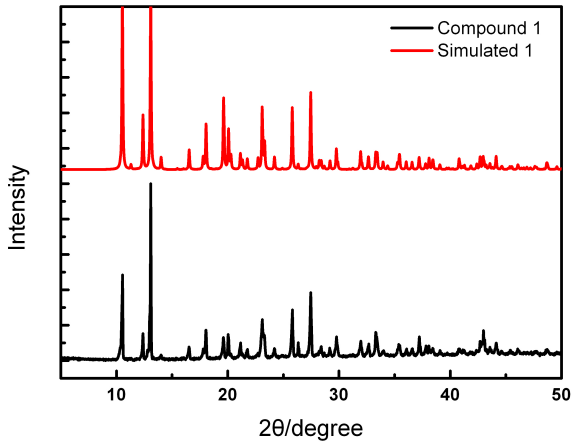


Figure S4. PXRD patterns and simulated data from Crystallographic Information File for compound **1**

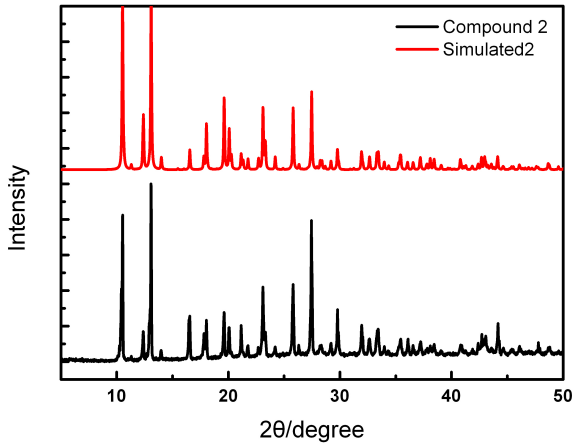


Figure S5. PXRD patterns and simulated data from Crystallographic Information File for compound **2**

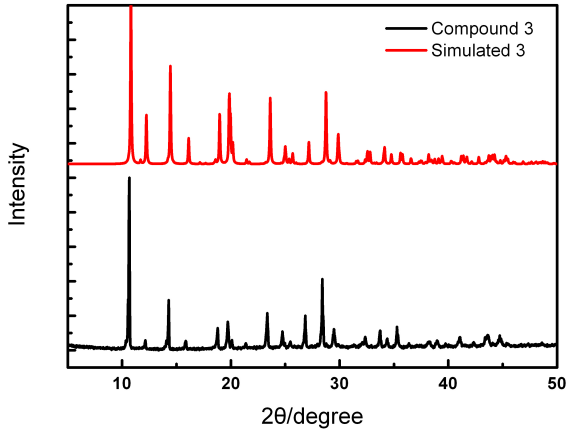


Figure S6. PXRD patterns and simulated data from Crystallographic Information File for compound **3**

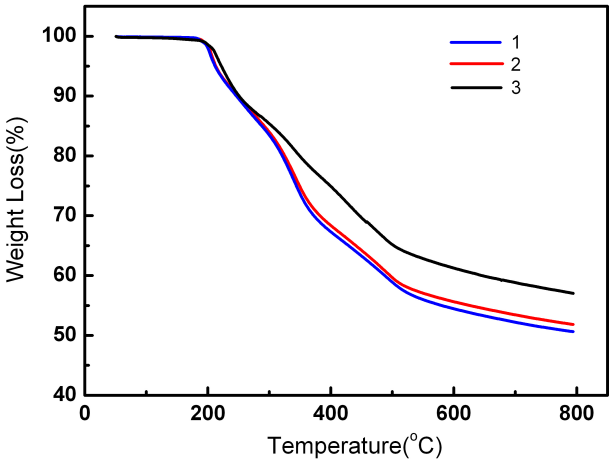


Figure S7. The TGA curves for compound **1-3**.

Table S3 Selected bond lengths [Å] and angles [°] for **1-3**

Compound 1			
Cu1-N1	1.9302(16)	N1-Cu1-O3	82.31(6)
Cu1-N2	1.9426(18)	O2-Cu1-O3	159.62(6)
Cu1-N4 #1	2.475(2)	N2-Cu1-O3	91.41(7)
Cu1-O2	1.9332(13)	N1-Cu1-N4 #2	90.49(8)
Cu1-O3	2.0457(14)	O2-Cu1-N4 #2	105.21(8)
N1-Cu1-O2	93.20(6)	N2-Cu1-N4 #2	88.88(9)
N1-Cu1-N2	173.61(7)	O3-Cu1-N4 #2	94.74(8)
O2-Cu1-N2	93.10(6)		
Compound **2**			
Cu1-N1	1.9318(15)	N1-Cu1-O3	82.26(6)
Cu1-N2	1.9421(17)	O2-Cu1-O3	159.60(6)
Cu1-N4 #1	2.473(2)	N2-Cu1-O3	91.38(6)
Cu1-O2	1.9352(13)	N1-Cu1-N4 #2	90.57(8)
Cu1-O3	2.0471(14)	O2-Cu1-N4 #2	105.31(8)
N1-Cu1-O2	93.19(6)	N2-Cu1-N4 #2	88.91(8)
N1-Cu1-N2	173.55(7)	O3-Cu1-N4 #2	94.65(8)
O2-Cu1-N2	93.15(6)		
Compound **3**			
Cu1-N1	1.9196(19)	N1-Cu1-O3	82.05(8)
Cu1-N2	1.928(2)	N2-Cu1-O3	91.52(7)
Cu1-N4 #1	2.359(2) #1	O2-Cu1-O3	161.94(6)
Cu1-O2	1.9356(15)	N1-Cu1-N4 #2	89.28(8)
Cu1-O3	2.0412(16)	N2-Cu1-N4 #2	92.07(8)
N1-Cu1-N2	173.57(9)	O2-Cu1-N4 #2	95.49(7)
N1-Cu1-O2	93.41(8)	O3-Cu1-N4 #2	101.89(7)
N2-Cu1-O2	92.72(7)		

Symmetry transformations used to generate equivalent atoms: #1: 2-x, y+1/2, -z+1/2; #2: 2-x, y-1/2, -z+1/2

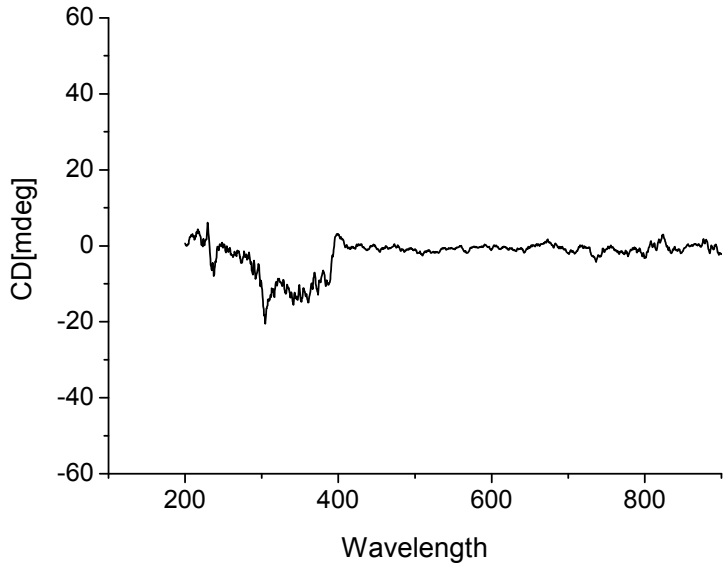


Figure S8 The complex **3** was prepared under static (unstirred) condition, solid-state CD measurements for the result bulk materials