Supporting Information

Anion-controlled self-assembly of two NLO-active dinuclear and molecular square Cu(II) enantiomeric pairs: from antiferromagnetic to ferromagnetic coupling

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Experimental Section

1. Materials and methods

All chemicals are of reagent grade and used as purchased without further purification. Linear bis-bidentate chiral ligands L_R and L_S were synthesized according to similar procedures.[1] Elemental analyses for C, H and N were performed on a Perkin-Elmer 240 C analyzer. The IR spectra were registered on a TENSOR27 Bruker Spectrophotometer from KBr pellets in the region of $4000-400$ cm^{-1}. The solid-state CD spectra were recorded on a JASCO J-810 Spectropolarimeter from KCl pellets (1% Wt.) at room temperature. Magnetic susceptibility measurements were carried out on respective crystalline samples with a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer in the temperature range of 2–300 K. Diamagnetic corrections were carried out considering both the sample holder as the background and the diamagnetism of the constituent atoms estimated from

Pascal's constant. The second-order nonlinear optical (NLO) activity were tested by the method of Kurtz and Perry using a Nd:YAG laser (1064 nm) with an input pulse of 350 mV. KDP powders were measured as a reference to assess the SHG efficiencies of Cu(II) enantiomeric pairs. The backscattered SHG light was collected by a spherical concave mirror and passed through a filter that transmits only 532 nm radiation. X-ray single crystal diffraction measurements of the title complexes were carried out on a Bruker SMART Apex II CCD-based diffractometer at 291(2) K. The structures were solved by direct methods and refined with full-matrix least-squares techniques using *SHELXS*-97 and *SHELXL*-97 programs. Anisotropic thermal parameters were refined for all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions and refined riding on their parent atoms. The crystallographic data are given in Table S1.

2. Synthesis of *R*-1 (CuL$_R$Cl$_4$2H$_2$O)

A mixture of CuCl$_2$·2H$_2$O (35 mg, 0.2 mmol) and (−)-2,5-bis(4,5-pinene-2-pyridyl)pyrazine (L$_R$) (42 mg, 0.1 mmol) in 10 mL CHCl$_3$/CH$_3$CN (1:1 = v/v) was stirred for 20 min. at room temperature, then filtered, and the filtrate was placed undisturbed for several days. Pale green block crystals of **R-1** were obtained in 82% yield (based on Cu). Elementary analysis (%) calcd. for **R-1** (C$_{28}$H$_{34}$Cl$_4$N$_4$O$_2$Cu$_2$): C, 46.23; H, 4.71; N, 7.70. Found: C, 46.31; H, 4.82; N, 7.79. IR (KBr, cm^{-1}): 3420(b, s), 3020(w), 2950(s), 1618(s), 1480(s), 1416(m), 1170(w), 1053(w), 627(w).

3. Synthesis of *S*-1 (CuL$_S$Cl$_4$2H$_2$O)

S-1 was obtained as pale green crystals by a method similar to that of **R-1**, except that (+)-2,5-bis(4,5-pinene-2-pyridyl)pyrazine (L$_S$) was used instead of (−)-2,5 - bis(4,5-pinene-2-pyridyl)pyrazine (L$_R$). Yield: 77% (based on Cu).   Elementary analysis (%) calcd. for **S-1** (C$_{28}$H$_{34}$Cl$_4$N$_4$O$_2$Cu$_2$): C, 46.23; H, 4.71; N, 7.70. Found: C,

46.28; H, 4.79; N, 7.81. IR (KBr, cm^{-1}): 3423(b, s), 3018(w), 2953(s), 1615(s), 1482(s), 1415(m), 1172(w), 1052(w), 628(w).

4. Synthesis of *R*-2 [Cu$_4$(L$_R$)$_4$(NO$_3$)$_8$·11H$_2$O]

A mixture of Cu(NO$_3$)$_2$·6H$_2$O (60 mg, 0.2 mmol) and (−)-2,5-bis(4,5-pinene-2-pyridyl)pyrazine (L$_R$) (42 mg, 0.1 mmol) in 10 mL CHCl$_3$/CH$_3$CN (1:1 = v/v) was stirred for 20 min. at room temperature, then filtered, and the filtrate was placed undisturbed for several days. Deep blue block crystals of *R*-2 were obtained in 75% yield (based on Cu). Elementary analysis (%) calcd. for *R*-2 (C$_{112}$H$_{142}$N$_{24}$O$_{35}$Cu$_4$): C, 50.98; H, 5.42; N, 12.74. Found: C, 50.92; H, 5.51; N, 12.82. IR (KBr, cm^{-1}): 3388(b, w), 2930(s), 1617(w), 1480(s), 1394(m), 1362(m), 1289(s), 1191(m), 1053(w), 957(w), 829(w).

5. Synthesis of *S*-2 [Cu$_4$(L$_S$)$_4$(NO$_3$)$_8$·11H$_2$O]

S-2 was obtained as deep blue crystals by a method similar to that of *R*-2, except that (+)-2,5-bis(4,5-pinene-2-pyridyl)pyrazine (L$_S$) was employed instead of (−)-2,5-bis(4,5-pinene-2-pyridyl)pyrazine (L$_R$). Yield: 73% (based on Cu). Elementary analysis (%) calcd. for *S*-2 (C$_{112}$H$_{142}$N$_{24}$O$_{35}$Cu$_4$): C, 50.98; H, 5.42; N, 12.74. Found: C, 51.03; H, 5.37; N, 12.80. IR (KBr, cm^{-1}): 3386(b, w), 2932(s), 1619(w), 1478(s), 1395(m), 1361(m), 1288(s), 1190(m), 1055(w), 956(w), 829(w).

Reference

1. T. Bark, H. Stoekli-Evans and A. V. Zelewsky, *J. Chem. Soc., Perkin Trans. 1,* 2002, 1881.

Table S1. X-ray crystallographic data for **R-/S-1** and **R-/S-2**

	R-1	**S-1**	**R-2**	**S-2**
Chemical formula	$C_{28}H_{34}Cl_4N_4O_2Cu_2$	$C_{28}H_{34}Cl_4N_4O_2Cu_2$	$C_{112}H_{142}N_{24}O_{35}Cu_4$	$C_{112}H_{142}N_{24}O_{35}Cu_4$
Formula weight	727.47	727.47	2638.66	2638.66
Crystal system	Triclinic	Triclinic	Tetragonal	Tetragonal
Space group	$P1$	$P1$	$I4$	$I4$
a/Å	5.7707(2)	5.7686(5)	13.8636(9)	13.5331(17)
b/Å	7.0509(3)	7.0486(5)	13.8636(9)	13.5331(17)
c/Å	19.2841(8)	19.2564(16)	34.6936(18)	35.6444(14)
α/º	90.775(3)	90.725(6)	90.00	90.00
β/º	93.694(3)	93.641(7)	90.00	90.00
γ/º	105.743(3)	105.836(7)	90.00	90.00
V/Å^3	753.25(5)	751.37(10)	6668.1(9)	6528.1(17)
Z	1	1	2	2
D/g cm^{-3}	1.604	1.608	1.314	1.342
μ/mm^{-1}	1.800	1.805	0.711	0.726
GOF	1.008	1.141	1.054	1.019
$R_1{}^a$/$_wR_2{}^b$	0.0278/0.0377	0.0668/0.1690	0.0532/0.1319	0.0571/0.1351
Flack parameter	0.009(14)	0.02(4)	0.07(2)	0.048(17)

[a] $R_1 = \sum||Fo|-|Fc||/\sum|Fo|$. [b] $_wR_2 = [\sum w(Fo^2 - Fc^2)^2/\sum w(Fo^2)^2]^{1/2}$

Table S2. Hydrogen-bonding geometry parameters (Å, °) for **R-1**

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O2–H2A···Cl2	0.605	2.823	3.268	133.25
O2–H2B···Cl4	0.829	2.547	3.337	159.78
O1–H1A···Cl1	0.724	2.581	3.277	162.1
O1–H1B···Cl3	0.864	2.506	3.333	160.66
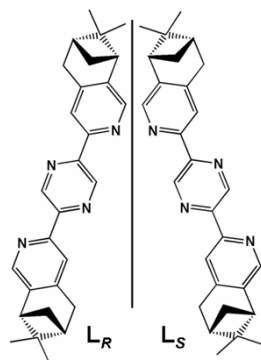
Fig. S1 Enantiomeric rigid linear bis-bidentate ligands **L_R** and **L_S**
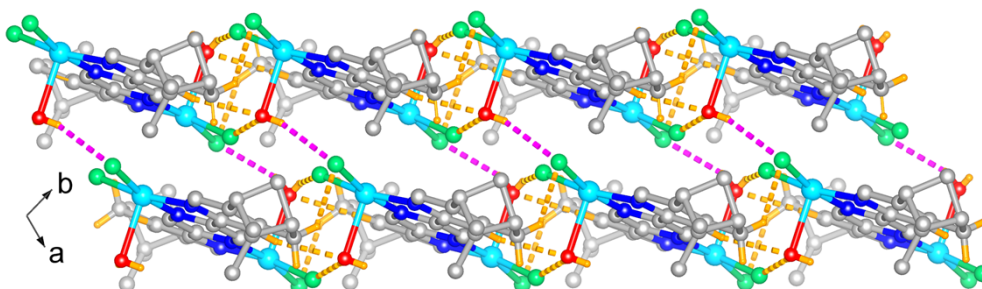
Fig. S2 Hydrogen-bonding interactions in **R-1**, showing the two-dimensional supramolecular array (Cu = cyan, Cl = green, N = blue, O = red, C = gray, H = orange).
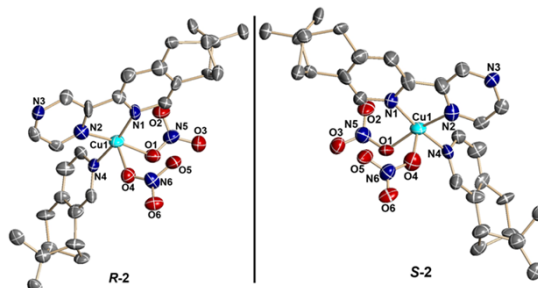
Fig. S3 ORTEP representation (50% probability ellipsoids) and enantiomeric pair of the asymmetric units of **R-2/S-2**; hydrogen atoms and lattice water molecules are omitted for clarity.
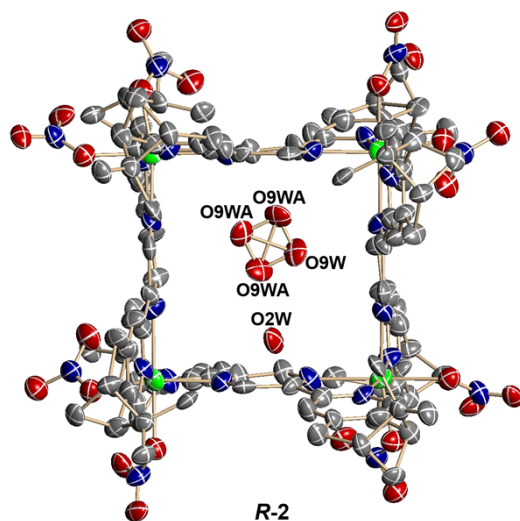
Fig. S4 Side view of the molecular structure for **R-2**, showing a perfect square shape of four Cu(II) ions.
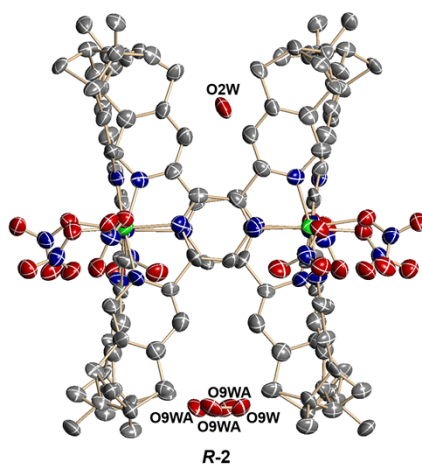

Fig. S5 down view of the molecular structure for **R-2**, showing the water molecules occupying the centers of two entrances to **R-2** square box up and down, respectively.
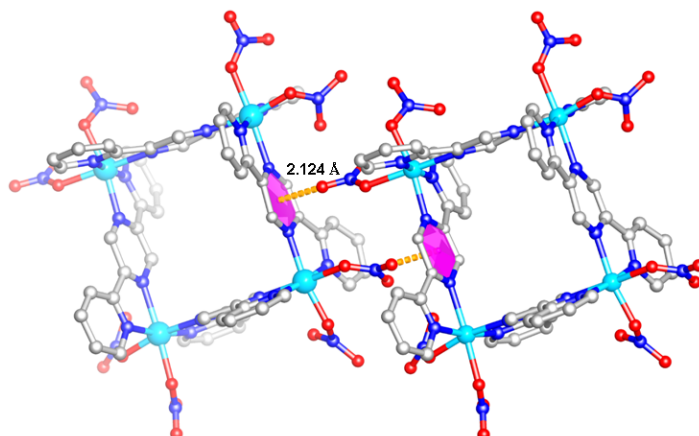

Fig. S6 schematic representation of the intermolecular interactions of NO_3–O (lone pair)$\cdots\pi$ (pyrazine ring) (O$\cdots$Cg = 2.124 Å) in **R-2**. Pinene moieties of L_R, H atoms and water molecules are omitted for clarity.
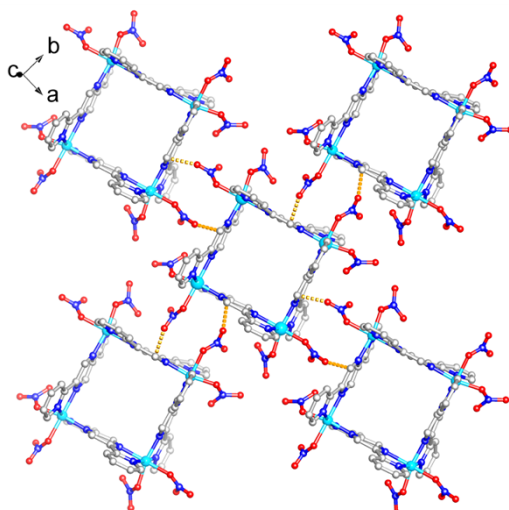
Fig. S7 Two-dimensional supramolecular array of **R-2** via NO_3–O (lone pair)$\cdots\pi$ (pyrazine ring) interactions (Cu = cyan, N = blue, O = red, C = gray). Pinene moieties of L_R, H atoms and water molecules are omitted for clarity.
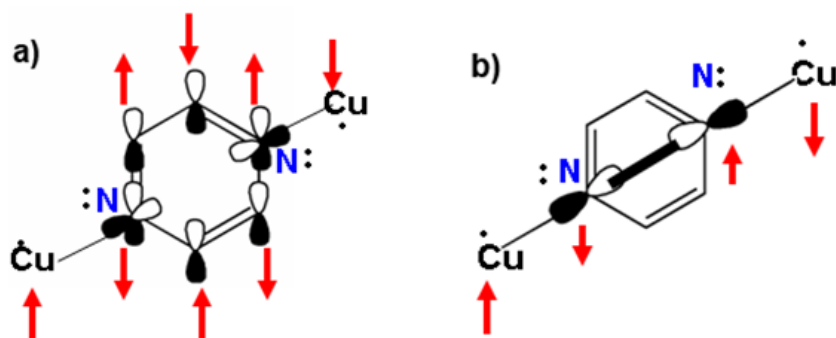

Fig. S8 Magnetic interaction paths in **R-1**. (a) Spin-polarization mechanism *via* π-bonds. The phases of $2P_z$ atomic orbitals are arbitrary; (b) Direct dσ-nσ magnetic exchange path.