Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information (ESI) for the manuscript:

Single chain magnet behaviour in an enantiopure chiral cobalt(II)-copper(II) one-dimensional compound

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Experimental Section

Materials. All chemicals were of reagent grade quality, and they were purchased from commercial sources and used as received.

H_2Et_2-(*M*)-binaba. The proligand was prepared in a standard manner from the condensation of (*M*)-(+)-1,1'-bis(2-naphthylamine) (1.42 g, 5 mmol) and ethyl oxalyl chloride (2.2 mL, 10 mmol) in THF, and it was isolated as the diethyl ester derivative (2.36 g, 97%). Elemental analysis calcd (%) for $C_{28}H_{24}N_2O_6$ (484 g mol^{-1}): C 69.42, H 4.96, N 5.79; found: C 69.32, H 4.12, N 5.99; ^{1}H NMR ([D_6]DMSO): 1.12 (t, 6H; $2CH_3$), 4.09 (q, 4H; $2CH_2O$), 6.99 (d, 2H; 4-H and 4'-H of $C_{20}H_{12}N_2$), 7.35 (t, 2H; 5-H and 5'-H of $C_{20}H_{12}N_2$), 7.54 (t, 2H; 8-H and 8'-H of $C_{20}H_{12}N_2$), 8.07 (t, 4H; 6-H, 6'-H, 7-H and 7'-H of $C_{20}H_{12}N_2$), 8.21 (d, 2H; 3-H and 3'-H of $C_{20}H_{12}N_2$),9.79 (s, 2H; 2NH; IR (KBr): ν = 3253 (N–H), 3021, 3001, 2979 (C–H), 1721, 1677 cm^{-1} (C–O).

(nBu$_4$N)$_2${[Cu[(*M*)-binaba]}$\cdot 2H_2O$ (1). Complex **1** was obtained following a reported procedure[1] by reaction of the proligand H_2Et_2-(*M*)-binaba (0.48 g, 1 mmol) with $CuCl_2 \cdot 2H_2O$ (0.17 g, 1 mmol) using a 1.0 M methanol solution of nBu$_4$NOH (4 mL, 4 mmol) as a base in water, and it was isolated as its dihydrated tetrabuthylammonium salt (0.81 g, 80 %). Elemental analysis calcd (%) for $C_{56}H_{88}CuN_4O_8$ (1007.5 g mol^{-1}): C 66.73, H 8.74, N 5.56; found: C 66.28, H 8.01, N 5.59; IR (KBr): ν = 3003, 2959, 2915 (C–H), 1708, 1688cm^{-1} (C–O). Crystals Well-formed small dark green prisms of 1 suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a concentrated solution of **1** in a 1:1 EtOH/ACN mixture at r.t.

CoCu[(*M*)-binaba](DMF)$_2$ $\cdot$ DMF (2): Well-formed deep green cubic prisms of **2** suitable for single-crystal X-ray diffraction with synchrotron radiation were obtained by slow diffusion in an H-shaped tube of DMF solutions containing stoichiometric amounts of **1** (0.20 g, 0.20 mmol) in one arm, and $Co(NO_3)_2$ $6H_2O$ (0.06 g, 0.20 mmol) in the other one. They were isolated by filtration on paper and air-dried. Analysis calculated for $C_{33}H_{33}CoCuN_5O_9$ (766.1 g mol^{-1}) C, 52.06; H, 4.47; N, 9.49. Found: C,

[1] Bräuer, B.; Weigend, F.; Fittipaldi, M.; Gatteschi, D.; Reijerse, E. J.; Guerri, A.; Ciattini, S.; Salvan, G. and Rüffer, T. *Inorg. Chem*. **2008**, *47*, 6633.

52.12; H, 4.02; N, 9.89; IR (KBr) 3065, and 2962 (CH), 1664, 1624 and 1584 (CO) cm^{-1}.

Physical Techniques. Elemental analyses (C, H, N) were performed at the Service Central d'Analyze du CNRS in Vernaisson (France). ^{1}H NMR spectra were recorded at room temperature on a Bruker AC 200 (200.1 MHz) spectrometer. [D_6]DMSO was used as solvent and internal standard (δ 2.50 ppm). IR spectra were recorded on a Bio-Rad FTS165 spectrophotometer as KBr pellets.

Crystal Structure Data Collection and Refinement. Crystal data for **2**: $C_{33}H_{33}CoCuN_5O_9$, $M_r = 766.11$, orthorhombic, space group $C222_1$, $a = 10.566(2)$, $b = 15.364(3)$, $c = 19.755(4)$ Å, $V = 3207.0(11)$ $Å^3$, $T = 293(2)$ K, $\lambda = 0.7513$ Å, $Z = 4$, $\rho_{calc} = 1.587$ g cm^{-3}, $\mu = 1.384$ mm^{-1}, Flack parameter = –0.037(17), Measured reflections = 49308, Unique reflections = 3645, Reflections with $I > 2\sigma(I)$ = 3607 [R(int) = 0.0477]. The data collection was carried out in the BM16 beamline at the ESRF (Grenoble, France) and the data were indexed, integrated, and scaled using the HKL2000 program.[2] Empirical absorption correction was performed considering a cylindrical geometry of the crystal, Tmax = 0.8451 and Tmin = 0.8444. All the measured independent reflections were used in the analysis. The structure was solved by direct methods and refined with full-matrix least-squares technique on F^2 using the SHELXS-97 and SHELXL-97 programs.[3] The hydrogen atoms from the organic ligand and the DMF molecules were set on calculated positions and refined with isotropic thermal parameters. Refinement of 238 variables with anisotropic thermal parameters for all non-hydrogen atoms gave R1 (all) = 0.0476, R1 (obs) = 0.0473, wR2 (all) = 0.1304 and wR2 (obs) = 0.1299, with $S = 1.061$. The final Fourier-difference map showed maximum and minimum height peaks of 1.128 and -0.876 e $Å^{-3}$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-720897. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[2] Z. Otwinowski and W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode* Methods in Enzymology, Volume 276: Macromolecular Crystallography, part A, p.307-326, **1997**, C.W. Carter, Jr. & R. M. Sweet, Eds.

[3] Sheldrick, G. M. *SHELX97*, release 97-2; Institüt für Anorganische Chemie der Universität Göttingen: Göttingen, Germany, **1998**.

Optical Measurements. Natural circular dichroism (NCD) curves were recorded using a Jasco model J-810 spectropolarimeter. In a typical experiment, 1 mg of the product and 120 mg of KBr was mixed and pressed as pellets. To enable comparison, the spectra were normalized and corrected for baseline deviation.

Magnetic Measurements. Variable-temperature (2.0-300 K) dc magnetic susceptibility measurements were carried out on polycrystalline samples of **2** with a Quantum Design SQUID magnetometer. The magnetic data were corrected for the diamagnetism of the constituent atoms and the sample holder. Low temperature ac susceptibility measurements were performed using a SQUID magnetometer equipped with a miniature dilution refrigerator developed at the CRTBT-CNRS in Grenoble. In order to ensure good thermal contact at low temperature, vacuum grease was mixed with 0.011 g of **2** and pressed into a small Cu pouch.

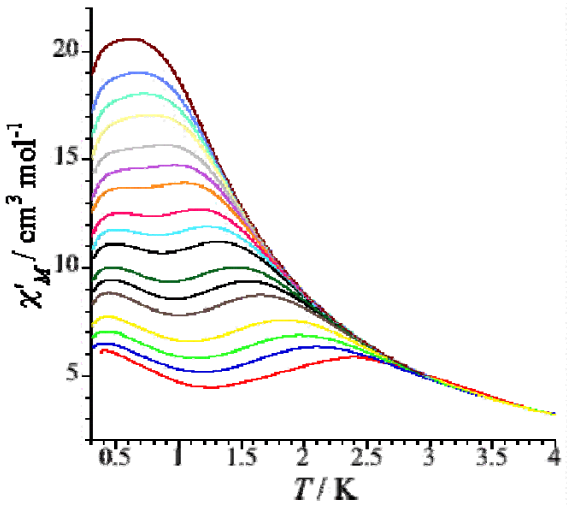

Fig. S1. Temperature dependence of χ_M' of **2** in zero applied static field and under 1 G oscillating field where the frequencies are 0.021, 0.057, 0.11, 0.21, 0.57, 1.11, 2.1, 5.7, 11.1, 21, 57, 111, 211, 570, 1110, 2110 and 5700 Hz.