

Supporting Information (SI) concerning the manuscript:

**Very Long-Distance Magnetic Coupling in a Dicopper(II) Metallacyclophane
with Extended π -Conjugated Diphenylethyne Bridges**

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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. 4,4'-Diphenylethyne diamine was prepared by the Pd/Cu catalyzed, Sonogashira-type cross-coupling reaction of *para*-ethynylaniline and *para*-iodoaniline, as reported in the literature.¹

Et₂H₂dpeba: Ethyl oxalyl chloride ester (0.5 mL, 4.0 mmol) was added to a solution of 4,4'-diphenylethyne diamine (0.42 g, 2.0 mmol) in THF (75 mL) under vigorous stirring at room temperature. The reaction mixture was then charged with triethylamine (0.6 mL, 4.0 mmol) and it was further stirred for 1h at room temperature. The white solid was collected by filtration, washed thoroughly with water to remove the precipitate of Et₃NHCl, and then with acetone and diethyl ether, and dried under vacuum (0.7 g, 85% yield). Anal. Calcd for C₂₂H₂₀N₂O₆ (408): C, 64.70; H, 4.94; N, 6.86. Found: C, 64.77; H, 4.97; N, 6.82. ¹H NMR (C₂D₆SO): δ 1.32 (t, 6 H, 2 CH₃), 4.31 (q, 4 H, 2 CH₂O), 7.54 (dd, 4 H, 3-H, 5-H, 3'-H, and 5'-H), 7.82 (dd, 4 H, 2-H, 6-H, 2'-H, and 6'-H), 10.96 (s, 2 H, 2 NH). IR (KBr): 3335 (NH), 1729, 1706 cm⁻¹ (CO).

(*n*Bu₄N)₄[Cu₂(dpeba)₂] · 4MeOH · 2Et₂O (1): A 1.0 M methanolic solution of *n*Bu₄NOH (4.0 mL, 4.0 mmol) was added to a suspension of Et₂H₂dpeba (0.41 g, 1.0 mmol) in 20 mL of methanol under gentle warming. A methanol solution (10 mL) of Cu(ClO₄)₂ · 6H₂O (0.37 g, 1.0 mmol) was then added dropwise under stirring. The resulting mixture was filtered to eliminate the small amount of solid particles and the solvent was removed under vacuum. The solid was recuperated with THF, collected by filtration, washed thoroughly with THF to remove the precipitate of *n*Bu₄NClO₄, and air dried. Recrystallization from a methanol solution gave brown prisms of **1** suitable for single-crystal X-ray diffraction upon layering of diethyl ether (0.72 g,

70% yield). Anal.: calcd for $C_{112}H_{196}Cu_2N_8O_{18}$: C, 64.99; H, 9.54; N, 5.41. Found: C, 65.31; H, 9.38; N, 5.22. IR (KBr) 1683, 1649, 1619 cm^{-1} (CO).

(Ph₄P)₄[Cu₂(dpeba)₂] · 4H₂O (2): An aqueous solution (10 mL) of Ph₄PCl (0.38 g, 1.0 mmol) was added to a solution of **1** (0.52 g, 0.25 mmol) in 15 mL of water. The brown solid that appeared was collected by filtration and dried under vacuum (0.40 g, 70% yield). Anal.: calcd for $C_{132}H_{104}Cu_2N_4O_{16}P_4$: C, 70.36; H, 4.65; N, 2.49. Found: C, 70.15; H, 4.32, N 2.52. IR (KBr, cm^{-1}) 1680, 1651, 1615 cm^{-1} (CO).

Physical Techniques. Elemental analyses (C, H, N) were performed at the Servicio Central de Soporte a la Investigación (SCSIE) at the Universitat de València (Spain). ¹H NMR spectra were recorded at room temperature on a Bruker AC 200 (200.1 MHz) spectrometer. C₂D₆SO was used as solvent and internal standard (δ = 2.50 ppm). FTIR spectra were recorded on a Nicolet-5700 spectrophotometer as KBr pellets.

Magnetic measurements. Variable-temperature (2.0–300 K) magnetic susceptibility measurements under different magnetic dc fields were carried out on powdered samples of **1** and in methanol solution (0.015 g of **1** in 0.25 mL of MeOH) with a SQUID magnetometer. Variable-field (H = 0.1–50 kOe) magnetic susceptibility measurements at low temperatures (T < 25 K) were also performed on powdered samples of **1** and **2**. We measured the diamagnetism of the 0.25 mL of methanol and the experimental susceptibility data of the methanolic solution of complex **1** was corrected for. This correction is equivalent to $-2.4 \times 10^{-2} cm^3 mol^{-1}$ per mol of dicopper(II) complex.

The procedure used for the magnetic measurements in solution with the SQUID device was as follows: two quartz tubes of suprasil quality (8 cm height \times 5 mm outer diameter with 0.5 mm

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wall thickness) were placed together in vertical position, the top tube containing the sample in methanol (8 mm is the height of the solution) and the bottom one being open on both sides. The two tubes fit perfectly in the plastic straw normally used in the SQUID devices. Placing the two tubes one on the top of the other in a vertical manner minimizes their magnetic contribution. At that respect, it is very illustrative that the two empty tubes placed in the plastic straw under an applied dc magnetic field of 1 T gave a signal less than 5.0×10^{-6} emu, that is a magnetic contribution clearly negligible.

Crystal Structure Data Collection and Refinement. Single-crystal X-ray diffraction data of **1** were collected on a Bruker-Nonius X8APEXII CCD area detector diffractometer using graphite-monochromated Mo-K α radiation. All calculations for data reduction, structure solution, and refinement were done through the SAINT² and SADABS³ programs.

The structure of **1** was solved by direct methods and subsequently completed by Fourier recycling using the SHELXTL software package.⁴ All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were set in calculated positions and refined as riding atoms. The final geometrical calculations and the graphical manipulations were carried out with PARST97⁵ and CRYSTAL MAKER programs, respectively.⁶

Crystal data for **1**: C₁₁₂H₁₉₆Cu₂N₈O₁₈, $M = 2069.85$, monoclinic, space group $P2_1/c$, $a = 15.261(2)$, $b = 25.691(4)$, $c = 17.279(3)$ Å, $\beta = 116.180(6)$, $V = 6079.4(16)$ Å³, $T = 100(2)$ K, $Z = 2$, $\rho_{\text{calcd}} = 1.131$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.412$ mm⁻¹, 10675 unique reflections, and 9467 observed

2000, 309, 109.

(2) SAINT, version 6.45; Bruker Analytical X-ray Systems: Madison, WI, 2003.

(3) Sheldrick G.M. SADABS Program for Absorption Correction, version 2.10; Analytical X-ray Systems: Madison, WI, 2003.

(4) SHELXTL; Bruker Analytical X-ray Instruments: Madison, WI, 1998.

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(6) Palmer, D. CRYSTAL MAKER, Cambridge University Technical Services, Cambridge, 1996.

with $I > 2\sigma(I)$. Refinement of 645 variables with anisotropic thermal parameters for all non-hydrogen atoms gave $R = 0.0740$, $wR = 0.2073$, and $\text{GOF} = 1.175$ (observed data). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-831325. 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).

Computational Details. Density functional (DF) calculations were carried out on the broken-symmetry (BS) singlet and triplet spin states of **1** with the hybrid B3LYP method⁷ combined with the “broken-symmetry” approach,⁸ as implemented in the Gaussian 09 program.⁹ The triple- and double- ζ quality basis sets proposed by Ahlrichs and co-workers¹⁰ were used for the metal and non-metal atoms, respectively. The calculated spin density data were obtained from Natural Bond Orbital (NBO) analysis.¹¹

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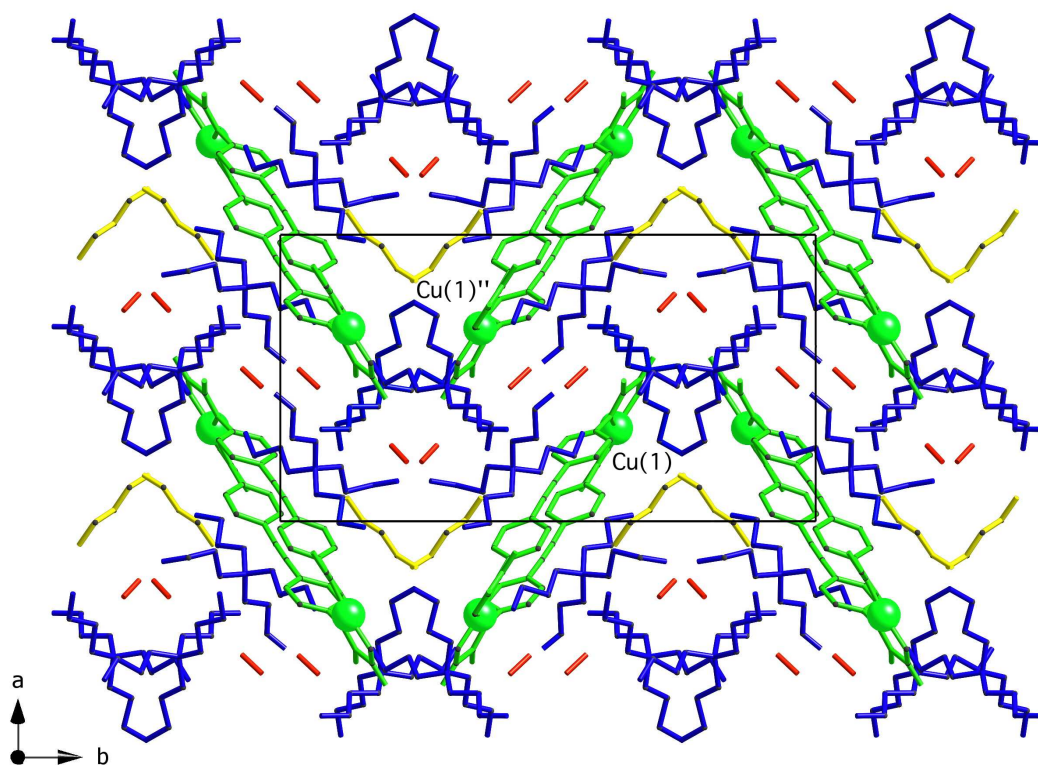


Figure S1. Crystal packing view of **1** along the *c* axis [symmetry code: (II) = $1 - x, 1 - y, 1 - z$]. The dicopper anions and the tetrabutylammonium cations are shown in green and blue colors, respectively, while the methanol and diethyl ether molecules are shown in red and yellow colors, respectively (hydrogen atoms have been omitted for clarity).

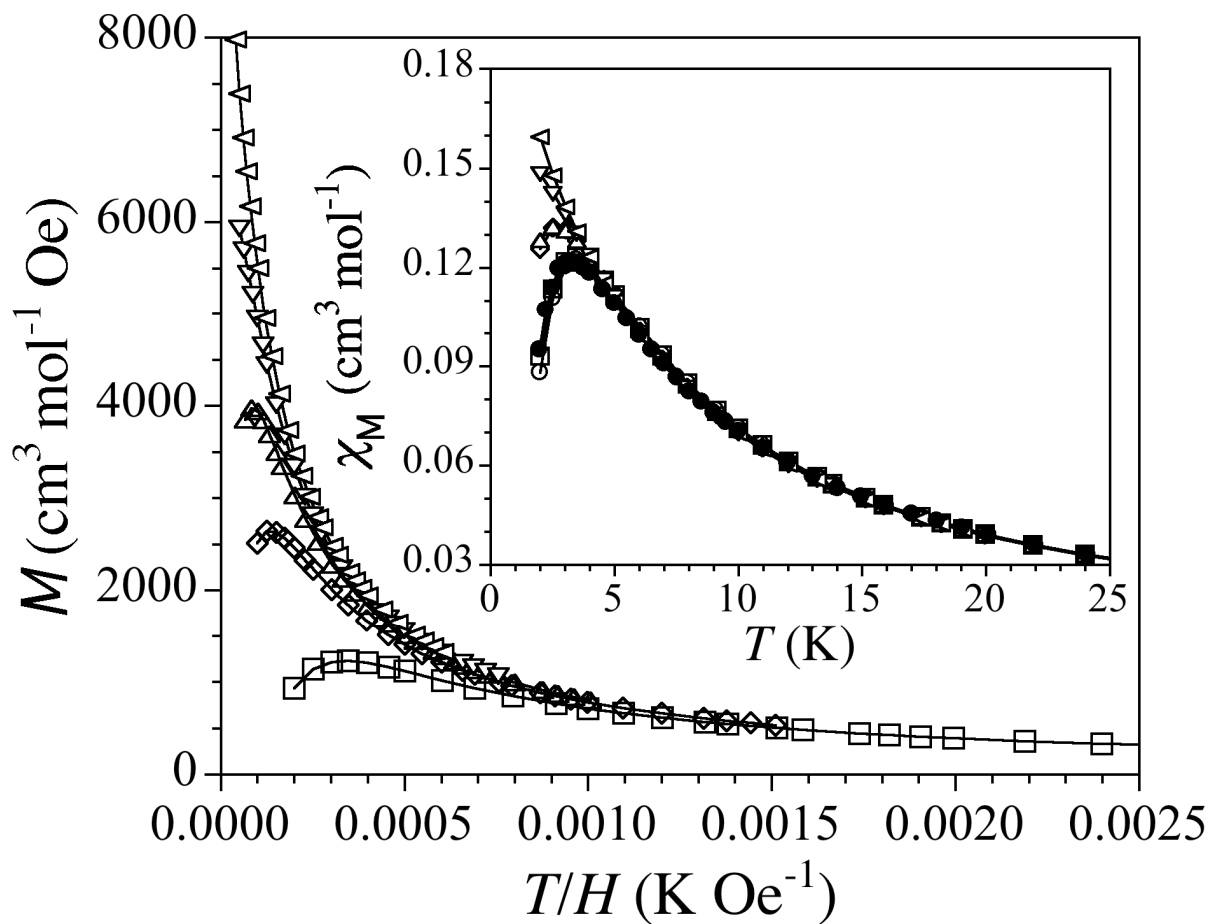


Figure S2. M vs. T/H plots for **1** at $H = 10$ (\square), 20 (\diamond), 30 (\triangle), 40 (∇), and 50 kOe (\triangleleft). The inset shows the χ_M vs. T plots at $H = 0.1$ (\bullet), 1 (\circ), 10 (\square), 20 (\diamond), 30 (\triangle), 40 (∇), and 50 kOe (\triangleleft). The solid lines are the best-fit curves (see text).

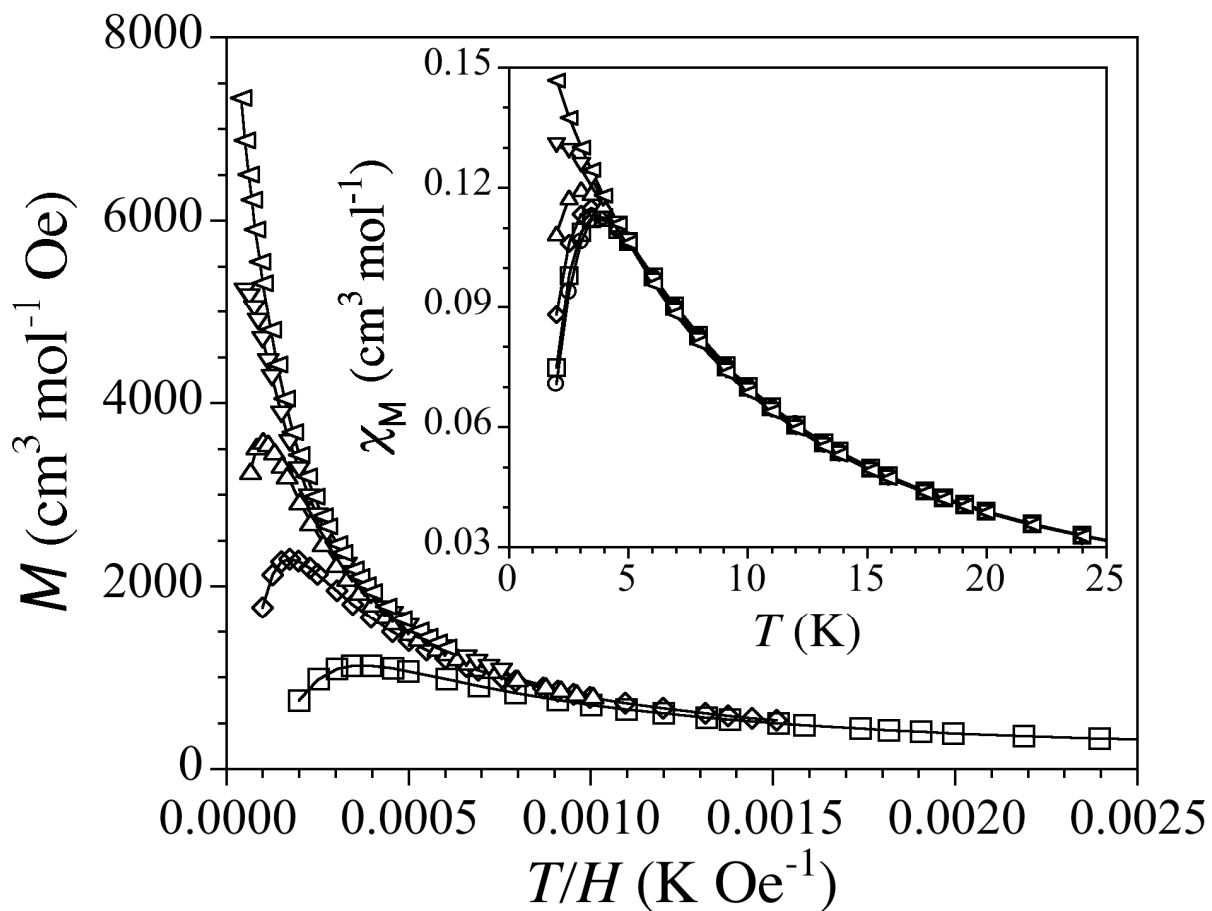


Figure S3. M vs. T/H plots for **2** at $H = 10$ (\square), 20 (\diamond), 30 (\triangle), 40 (∇), and 50 kOe (\triangleleft). The inset shows the χ_M vs. T plots at $H = 1$ (\circ), 10 (\square), 20 (\diamond), 30 (\triangle), 40 (∇), and 50 kOe (\triangleleft). The solid lines are the best-fit curves (see footnote 12).