Electronic Supporting Information (ESI) for the manuscript:

Photoswitching of the antiferromagnetic coupling in an oxamato-based dicopper(II) anthracenophane

M. Castellano, J. Ferrando-Soria, E. Pardo, M. Julve, F. Lloret,* C. Mathonière, J. Pasán, C. Ruiz-Pérez, L. Cañadillas-Delgado, R. Ruiz-García and J. Cano*

Synthesis and selected data for 1. A 1.0 M methanolic solution of *n*Bu_4NOH (4.0 mL, 4.0 mmol) was added to an aqueous suspension (20 mL) of the H_2Et_2anba proligand (0.41 g, 1.0 mmol) prepared as reported previously.[1] An aqueous solution (25 mL) of $CuCl_2 \cdot 2H_2O$ (0.17 g, 1.0 mmol) was then added dropwise under stirring. The resulting green mixture was filtered to remove the rest of solid particles and then it was extracted with dichloromethane. The organic phase was separated from the mixture and dried over a molecular sieve to give a deep green solution. Solvent was removed under vacuum and the resulting dark green solid was recovered with tetrahydrofuran, collected by filtration, washed with acetone and diethyl eter, and dried under vacuum. Recrystallization from an acetonitrile/methanol mixture (10:1, v/v) afforded X-ray quality crystals of **1** as green tiny prims upon slow vapor diffusion of acetone in a closed flask (0.81 g, 90% yield). Elemental analysis calcd (%) for $C_{100}H_{160}Cu_2N_8O_{12}$: C 66.97, H 8.99, N 6.25; found: C 65.81, H 9.08, N 6.12. IR (KBr): ν = 1684, 1649, 1630, 1605 cm^{-1} (CO). UV-vis (MeCN): λ = 287 nm (ε = 114480 M^{-1} cm^{-1}), 343 (13241), 361 (12746), 389 (11608), 410 (10391), 435sh (4131).

Crystal data for 1: $C_{100}H_{160}Cu_2N_8O_{12}$, M_r = 1793.44, orthorhombic, space group *Pbca*, a = 23.490(5), b = 16.875(3), c = 24.537(5) Å, V = 9726(3) Å^3, T = 293(2) K, Z = 4, ρ_{calcd} = 1.225 g cm^{-3}, μ(Mo-Kα) = 0.500 mm^{-1}, 9873 unique reflections, and 9057 observed with $I > 2\sigma(I)$. Refinement of 577 variables with anisotropic thermal parameters for all non-hydrogen atoms gave R = 0.0641, wR = 0.1804, and GOF = 0.957 (observed data). The X-ray diffraction data of **1** were collected using synchrotron radiation (λ = 0.7293 Å) at the BM16-CRG beamline in the ESRF (Grenoble, France).

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The data were indexed, integrated and scaled using the *HKL2000* program.[2] All calculations for data reduction, structure solution, and refinement were done by standard procedures (*WINGX*).[3] The structure of **1** was solved by direct methods and refined with full-matrix least-squares technique on F^2 using the *SHELXS-97* and *SHELXL-97* programs.[4] The hydrogen atoms from the organic ligands were calculated and refined with isotropic thermal parameters. The final geometrical calculations and the graphical manipulations were carried out with *PARST97* and *CRYSTAL MAKER* programs, respectively.[5] 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–828222. 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].

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). FTIR spectra were recorded on a Nicolet-5700 spectrophotometer as KBr pellets. UV-vis spectra were recorded on an Agilent Technologies-8453 spectrophotometer equipped with a UV-vis Chem Station.

Photomagnetic studies. The irradiation experiments were carried out in a photoreactor equipped with eight UVB lamps (λ in the range of 281–315 nm, λ_{max} centered at 308 nm). Powdered samples of **1** were stored in a sealed Pyrex tube saturated with Ar during the course of the irradiation experiments at room temperature.

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[3] L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837 (*WINGX*).

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Variable-temperature (2.0–300 K) magnetic susceptibility measurements were carried out with a SQUID magnetometer under an applied field of 10 kOe ($T \geq 50$ K) and 100 Oe ($T < 50$ K). The magnetic properties of the irradiated powdered samples of **1** were immediately measured after different irradiation times, and they were then measured after heating *in situ* at 75 ºC for 1 h without irradiation to check for possible thermal relaxation effects. The experimental data were corrected for the diamagnetic contributions of the constituent atoms and the sample holder as well as for the temperature-independent paramagnetism (tip) of the Cu^{II} ion (60×10^{-6} cm^3 mol^{-1}).

Computational details. The molecular geometry of the dinuclear model complex **1** was not optimized, but the bond lengths and interbond angles were taken from the actual structure determined in the solid state by single-crystal X-ray diffraction. The molecular geometry of the dinuclear model complex **2** was optimized in the gas phase using the density functional (DF) methodology. DF calculations were carried out with the hybrid B3LYP method[6] combined with the "broken-symmetry" (BS) approach,[7] as implemented in the Gaussian 09 program.[8] The triple- and double-ζ quality basis sets proposed by Ahlrichs and co-workers were used for the metal and non-metal atoms, respectively.[9] The calculated spin density data were obtained from

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[7] (*a*) E. Ruiz, J. Cano, S. Alvarez and P. Alemany, *J. Comput. Chem.,* 1999, **20**, 1391; (*b*) E. Ruiz, A. Rodriguez-Fortea, J. Cano, S. Alvarez and P. Alemany, *J. Comput. Chem.,* 2003, **24**, 982.

[8] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision A.1*, Gaussian, Inc., Wallingford CT, 2009.

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natural bond orbital (NBO) analysis.[10]

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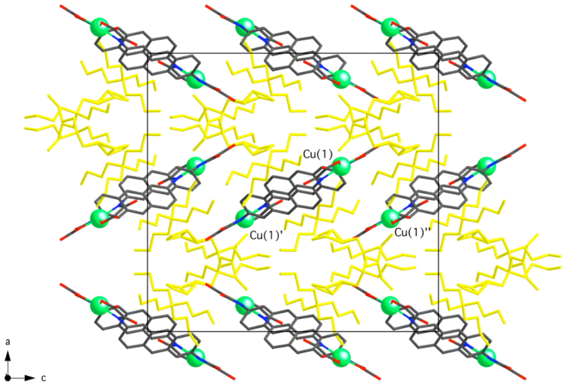

Fig. S1 Crystal packing view of **1** along the *b* axis [symmetry code: (I) = 1 – *x*, 1 – *y*, – *z*; (II) = 1 – *x*, ½ + *y*, ½ – *z*]. The *n*-tetrabutylammonium cations are shown in yellow color (hydrogen atoms have been omitted for clarity).