Electronic Supporting Information (ESI) for the manuscript:

Multielectron transfer in a dicopper(II) anthraquinophane

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Materials

All chemicals were of reagent grade quality. They were purchased from commercial sources and used as received, except those for electrochemical measurements. The *n*Bu_4NPF_6 salt was recrystallized twice from ethyl acetate/diethyl ether, dried at 80 °C under vacuum, and kept in an oven at 110 °C. Acetonitrile and dichloromethane were purified by distillation from calcium hydride on activated 3 Å molecular sieves and stored under argon. Elemental analyses (C, H, N) were performed at the Servicio Central de Soporte a la Investigación (SCSIE) at the Universitat de València (Spain).

Preparations

***N,N′*-1,4-bis(oxamic acid ethyl ester)-9,10-anthraquinone (Et_2H_2-1,4-quanba):** Ethyl oxalyl chloride ester (2.8 mL, 24 mmol) was poured into a solution of 1,4-diamino-9,10-anthraquinone (2.9 g, 12 mmol) and triethylamine (3.4 mL, 24 mmol) in THF (150 mL) under vigorous stirring at 0 °C on an ice-bath. The reaction mixture was then refluxed for 1 h. The deep orange solid was collected by filtration after cooling, washed thoroughly with water to remove the white precipitate of Et_3NHCl and then with diethyl eter, and dried under vacuum (4.5 g, 85% yield). Anal.: calcd for $C_{22}H_{18}N_2O_8$ (438.2 g mol^{-1}): C, 60.27; H, 4.15; N, 6.39%. Found: C, 59.18; H, 4.28; N, 5.69%; ^{1}H NMR ($CDCl_3$): δ = 1.50 (t, 6 H, 2 CH_3), 4.52 (q, 4 H, 2 CH_2O), 7.86 (dd, 2 H, H^6 and H^7 of $C_{14}H_6O_2$), 8.38 (dd, 2 H, H^5 and H^8 of $C_{14}H_6O_2$), 9.27 (s, 2 H, H^2 and H^3 of $C_{14}H_6O_2$), 13.91 (s, 2 H, 2 NH); IR (KBr): ν = 3125 (N–H), 1721, 1642 cm^{-1} (C=O).

(*n*$Bu_4N)_4[Cu_2$(1,4-quanba)$_2$] · 2MeCN · 2Et_2O (1): A 1.0 M methanolic solution of *n*Bu_4NOH (8.0 mL, 8.0 mmol) was added to a suspension of Et_2H_2-1,4-quanba (0.88 g, 2.0 mmol) in 20 mL of methanol under gentle warming. $Cu(ClO_4)_2 \cdot 6H_2O$ (0.75 g, 2.0

mmol) dissolved in methanol (10 mL) was then added dropwise under stirring. The resulting deep purple solution was filtered to separate the small amount of solid particles and the solvent was removed under vacuum. The solid was recovered with THF, collected by filtration, washed thoroughly with THF to remove the precipitate of $n\mathrm{Bu_4NClO_4}$, and air dried. Recrystallization from an acetonitrile/methanol solution solution (4:1 v/v) gave X-ray quality dark purple tiny prisms of **1** upon slow vapor difussion of diethyl ether (1.3 g, 70% yield). Anal.: calcd for $C_{112}H_{176}Cu_2N_{10}O_{18}$ (2077.7 g mol^{-1}): C, 64.74; H, 8.54; N, 6.74%. Found: C, 64.24; H, 8.60; N, 6.76%; IR (KBr): ν = 3432 (O–H), 1648, 1607 cm^{-1} (C=O).

Physical techniques

^{1}H NMR spectra were recorded at room temperature on a Bruker AC 200 (200.1 MHz) spectrometer. Chemical shifts are reported in δ (ppm) *vs*. TMS. $CDCl_3$ was used as solvent and internal standard (δ = 7.27 ppm). FTIR spectra were recorded on a Nicolet-5700 spectrophotometer as KBr pellets.

X-ray crystallographic data collection and structure 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$_\alpha$ radiation at T = 100 K. Due to the poor crystal quality, a lower $\theta_{\max}$ of diffraction was obtained even if all possible steps were undertaken to ensure that the experiment has been able to extract the best diffracting power from the sample. Low temperature measurements were also used in order to enhance the reflection intensities and the extent of the "observed" data. Unfortunately, all our attempts to grow single crystals of better quality were unsuccessful. All calculations for data reduction, structure solution, and refinement were done through the SAINT[1] and SADABS[2] programs.

The structure of **1** was solved by Patterson method and subsequently completed by Fourier recycling using the SHELXTL software package.[3] The final geometrical calculations and the graphical manipulations were carried out with WinGX and CRYSTAL MAKER programs, respectively.[4,5] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were set in calculated positions and refined as riding atoms. However, it was not possible to find a reasonable model for the highly disordered acetonitrile and diethyl ether molecules of crystallization in the refinement of the structure of **1**. The contribution to the diffraction pattern from the crystallization solvent molecules, which are located in the channels of the lattice (17.2% percentage void volume of the unit cell), were subtracted from the observed data by using the "SQUEEZE" method, as implemented in PLATON.[6] In fact, the SQUEEZE-Bypass method described therein is widely used in the crystallographic analysis of compounds containing substantial amounts of disordered solvent and/or counterions that cannot be located accurately from diffraction data. So, the values of the residual agreement factors for the reflections with $I > 2\sigma(I)$ of **1** were $R_1 = 0.1085$ and $wR_2 = 0.3058$ before SQUEEZE, or $R_1 = 0.0553$ and $wR_2 = 0.1656$ after SQUEEZE. The final formulation of the compound is in agreement with the residual electron density and cell volume.

Crystal data for **1**: $C_{112}H_{176}Cu_2N_{10}O_{18}$, $M = 2077.71$, tetragonal, space group $P4_2/m$, $a = 14.842(1)$, $c = 25.816(2)$ Å, $V = 5686.9(7)$ Å^3, $T = 100(2)$ K, $Z = 2$, $\rho_{\text{calcd}} = 1.213$ g cm^{-3}, μ(Mo-Kα) = 0.441 mm^{-1}, 3281 unique reflections, and 2959 observed with $I > 2\sigma(I)$.

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[1] *SAINT*, version 6.45, Bruker Analytical X-ray Systems, Madison, WI, 2003.

[2] G.M. Sheldrick, *SADABS Program for Absorption Correction*, version 2.10, Analytical X-ray Systems, Madison, WI, 2003.

[3] *SHELXTL*, Bruker Analytical X-ray Instruments, Madison, WI, 1998.

[4] L.J. Farrugia, *J. Appl. Cryst.*, 1999, **32**, 837.

[5] D. Palmer, *CRYSTAL MAKER,* Cambridge University Technical Services, Cambridge, 1996.

[6] (*a*) A. L. Spek, *Acta Cryst.*, 1990, **A46***,* C34; (*b*) P. Van der Sluis and A. L. Spek, *Acta Cryst.*, 1990, **A46***,* 194.

Refinement of 290 variables with anisotropic thermal parameters for all non-hydrogen atoms gave R_1 = 0.0553, wR_2 = 0.1656, and GOF = 1.229 (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–919043. 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).

Magnetic measurements

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 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}).

Electrochemical measurements

The electrochemical studies were performed using a PAR 273A scanning potentiostat operating at a scan rate of 10–1000 mV s^{-1}. Cyclic voltammograms were carried out using 0.1 M nBu$_4$NPF$_6$ as supporting electrolyte and 1.0 mM of the Et$_2$H$_2$-1,4-quanba proligand and complex **1** in dichloromethane and acetonitrile, respectively. The working electrode was a glassy carbon disk (0.32 cm^2) that was polished with 1.0 μm diamond powder, sonicated, washed with absolute ethanol and acetone, and air dried. The reference electrode was $AgClO_4$/Ag separated from the test solution by a salt bridge containing the solvent/supporting electrolyte, with platinum as auxiliary electrode. All experiments were performed in standard electrochemical cells at 25 °C under argon. The investigated potential range was in the range of –2.00 to +1.80 V *vs*. SCE. The formal potentials were measured at a scan rate of 100 mV s^{-1} and were referred to the saturated calomel electrode (SCE). Ferrocene (Fc) was added as internal standard at the end of the measurements. The measured formal potential values of ferrocene are $E(Fc^+/Fc)$ = +0.46 (CH_2Cl_2, 0.1 M *n*Bu_4NPF_6, 25 °C) and +0.40 V *vs*. SCE (CH_3CN, 0.1 M *n*Bu_4NPF_6, 25 °C).[7] The values of the anodic to cathodic peaks separation of ferrocene are $\Delta E_p(Fc^+/Fc)$ = 100 (CH_2Cl_2, 0.1 M *n*Bu_4NPF_6, 25 °C) and 70 mV (CH_3CN, 0.1 M *n*Bu_4NPF_6, 25 °C)].

Chemical oxidation procedures and spectroscopic measurements

The monooxidized species was obtained by addition of a 0.01 M acetonitrile solution of bromine (0.1 mL) to a 1.0 mM acetonitrile solution of **1** (0.1 mL) at –40 °C. X-band EPR spectra ($\nu = 9.47$ GHz) of frozen-matrix acetonitrile solutions were recorded under non-saturating conditions on a Bruker ER 200 D spectrometer equipped with a helium cryostat.

Computational details

Density functional (DF) calculations were carried out on the actual crystal structure of **1** in acetonitrile solution with the hybrid B3LYP method[8] combined with the "broken-symmetry" approach,[9] as implemented in the Gaussian 09 program.[10] The triple- and double-ζ quality basis sets proposed by Ahlrichs and co-workers[11] were

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[7] N. G. Connelly and W. E. Geiger, *Chem. Rev.,* 1996, **96**, 877.

[8] A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 5648.

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

[10] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, 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, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03, Revision C.02* Gaussian, Inc., Wallingford CT, 2004.

[11] (*a*) A. Schaefer, H. Horn and R. Ahlrichs, *J. Chem. Phys.,* 1992, **97**, 2571; (*b*) A. Schaefer, C. Huber and R. Ahlrichs, *J. Chem. Phys.,* 1994, **100**, 5829.

used for the metal and non-metal atoms, respectively. Solvation effects were introduced using a polarizable continuum model (PCM), where the cavity is created via a series of overlapping spheres.[12]

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[12] (*a*) M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comp. Chem.,* 2003, **24**, 669; (*b*) J. Tomasi, B. Mennucci and E. Cances, *J. Mol. Struct.-Theochem.,* 1999, **464**, 211.

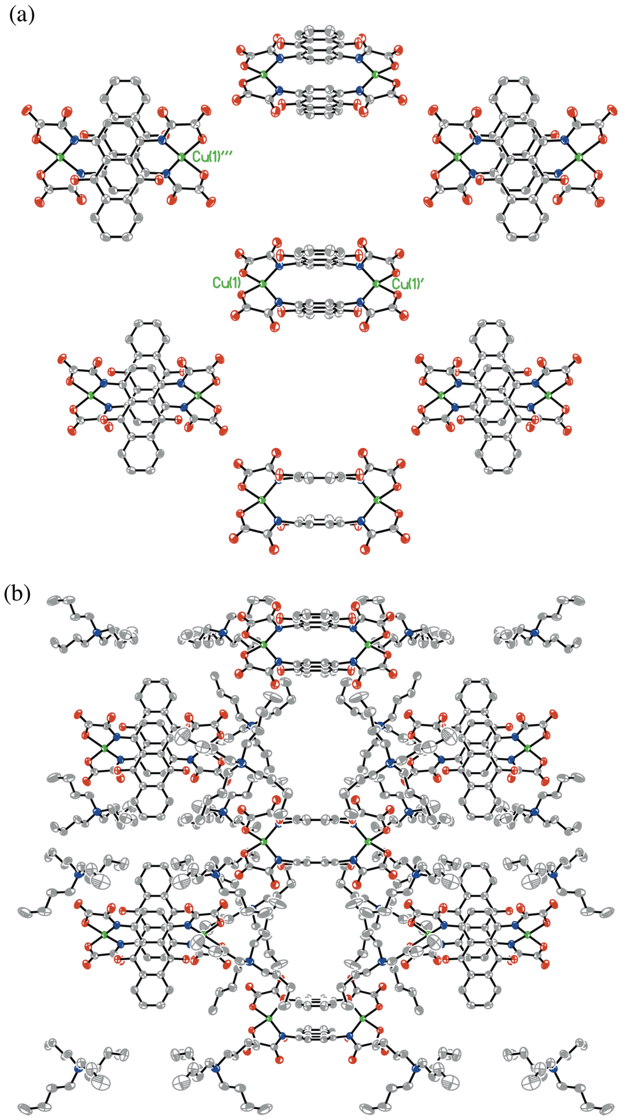

Fig. S1 (a) ORTEP drawing of the discrete anionic dicopper units of **1** along the crystallographic *b* axis [symmetry code: (I) = *x*, *y*, – *z*; (III) = –1 + *y*, – *x*, ½ – *z*]. The thermal ellipsoids are drawn at the 50% probalility level. (b) Crystal packing view of **1** along the crystallographic *b* axis.

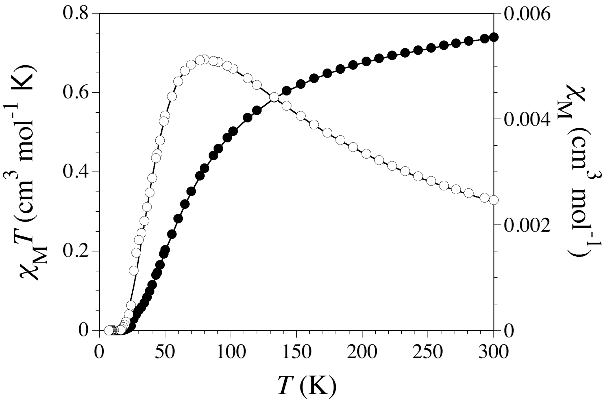

Fig. S2 Temperature dependence of χ_M (○) and $\chi_M T$ (●) for **1**. The solid lines correspond to the best-fit curves (see text).

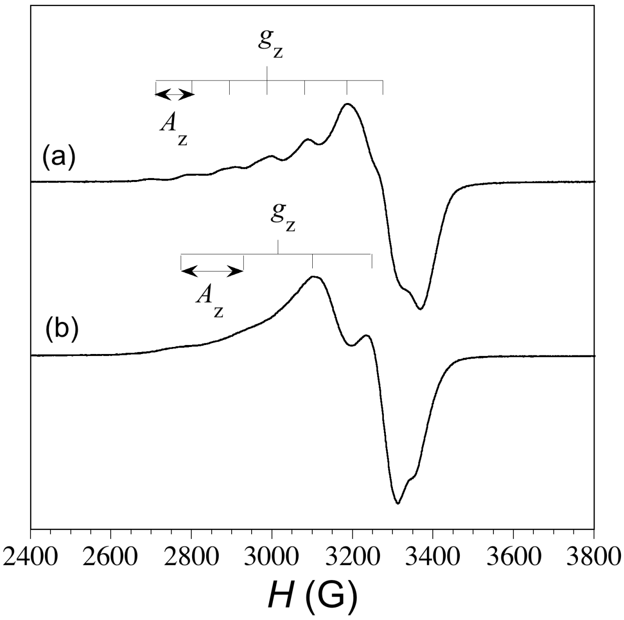

Fig. S3 X-band EPR spectra of **1** (a) and the monoxidized species (b) in acetonitrile at 77 K and 4 K, respectively.