

SUPPORTING INFORMATION

Isolated Single-Molecule Magnets on native gold

L. Zobbi, M. Mannini, M. Pacchioni, G. Chastanet, D. Bonacchi, C. Zanardi, R. Biagi, U. Del Pennino, D. Gatteschi, A. Cornia, R. Sessoli

Synthesis. A slurry of complex **1** (204 mg, 0.0990 mmol) in anhydrous toluene (10 mL) was treated with 4-(methylthio)benzoic acid (333 mg, 1.98 mmol). The mixture was concentrated at reduced pressure to remove acetic acid as the toluene azeotrope. When almost all the toluene had been removed more toluene (10 mL) was added and removed by evaporation, and the process was repeated 3 times. After the final evaporation the resulting black solid was dissolved in CHCl₃ (10 mL) and layered with *n*-hexane to afford black needles in two weeks. The crystals were redissolved in CHCl₃ and the solution was allowed to slowly evaporate at room temperature. The large blocks of 2·8CHCl₃ obtained in two weeks were collected on a glass frit and dried in vacuum (0.1–0.2 mmHg, 75 min). Yield 220 mg, (62 %).

FT-IR (KBr pellet): 1593 (ν_{AS}(OCO)), 1407 (ν_S(OCO)), 1185, 1089, 768 cm⁻¹.

MALDI-ToF (1,8-dihydroxy-9(10H)-anthracenone) *m/z* = 3385 [(M-L)CO]⁺, 3218 [(M-2L)CO]⁺, 3049 [(M-3L)CO]⁺, with M=[Mn₁₂O₁₂(L)₁₆] (*m/z* = 3524).

X-ray analysis

Selected bond lengths [Å] and angles [deg]: Mn1–O1 1.911(4), Mn1–O1^a 1.915(5), Mn1–O1^c 1.923(5), Mn1–O2^c 1.890(5), Mn1–O3 1.858(5), Mn1–O4 1.902(4), Mn2–O3 1.903(5), Mn2–O2^c 1.903(6), Mn2–O8 1.946(5), Mn2–O10 1.955(5), Mn2–O6 2.177(5), Mn2–O5 2.230(5), Mn3–O3 1.880(5), Mn3–O2 1.891(5), Mn3–O11^a 1.953(5), Mn3–O9 1.965(5), Mn3–O7^a 2.098(6), Mn3–O12 2.268(6), O3–Mn1–O2^c 84.82(18), O3–Mn1–O4 91.7(2), O2^c–Mn1–O4 93.7(2), O3–Mn1–O1 89.8(2), O2^c–Mn1–O1 92.2(2), O4–Mn1–O1 174.0(2), O3–Mn1–O1^a 97.3(2), O2^c–Mn1–O1^a 175.7(2), O4–Mn1–O1^a 90.0(2), O1–Mn1–O1^a 84.1(2), O3–Mn1–O1^c 173.4(2), O2^c–Mn1–O1^c 97.1(2), O4–Mn1–O1^c 94.4(2), O1–Mn1–O1^c 83.9(2), O1^a–Mn1–O1^c 80.39(19), O3–Mn2–O2^c 83.24(17), O3–Mn2–O8 94.7(2), O2^c–Mn2–O8 177.8(2), O3–Mn2–O10 173.1(2), O2^c–Mn2–O10 95.7(2), O8–Mn2–O10 86.5(2), O3–Mn2–O6 94.6(2), O2^c–Mn2–O6 93.3(2), O8–Mn2–O6 86.1(2), O10–Mn2–O6 92.3(3), O3–Mn2–O5 84.0(2), O2^c–Mn2–O5 89.6(2), O8–Mn2–O5 91.0(2), O10–Mn2–O5 89.2(2), O6–Mn2–O5 176.7(2), O3–Mn3–O2 95.11(18), O3–Mn3–O11^a 172.6(2), O2–Mn3–O11^a 90.9(2), O3–Mn3–O9 90.7(2), O2–Mn3–O9 171.2(2), O11^a–Mn3–O9 82.8(2), O3–Mn3–O7^a 93.2(2), O2–Mn3–O7^a 97.9(2), O11^a–Mn3–O7^a 90.1(3), O9–Mn3–O7^a 88.3(3), O3–Mn3–O12 89.8(2), O2–Mn3–O12 86.8(2), O11^a–Mn3–O12 86.3(3), O9–Mn3–O12 86.6(3), O7^a–Mn3–O12 174.1(3), Mn1–O1–Mn1^c 95.3(2), Mn1–O1–Mn1^a 95.1(2), Mn1^c–O1–Mn1^a 99.59(18), Mn1^a–O2–Mn3 130.8(3), Mn1^a–O2–Mn2^a 94.4(2), Mn3–O2–Mn2^a 122.7(3), Mn1–O3–Mn3 131.9(3), Mn1–O3–Mn2 95.5(2), Mn3–O3–Mn2 131.3(3).

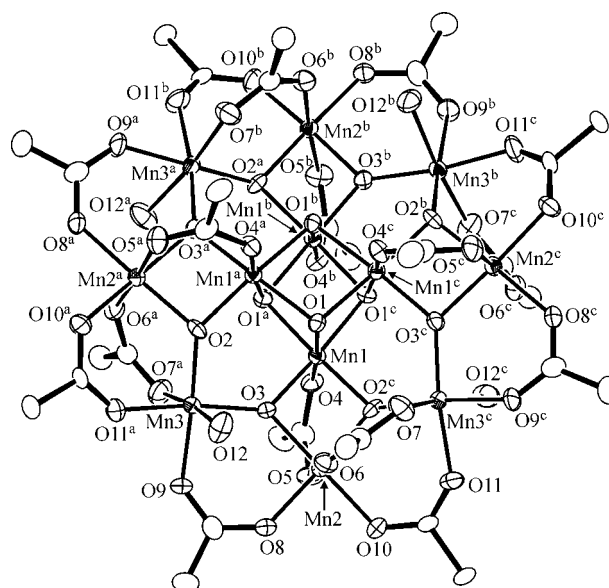


Figure S1. Structure of the Mn/O core of **2**, with the carboxylate and α -C atoms and the atom labelling scheme. Thermal ellipsoids are shown at 50% probability level. Hydrogen atoms omitted for clarity.

CCDC-XXXXXX (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

¹H-NMR (200 MHz, CD₂Cl₂, 25°C, TMS): δ = 12.6 (8H; CH (*m*, ax. III–III)), 10.8 (8H; CH (*o*, ax. III–IV)), 9.3 (8H; CH (*m*, ax. III–IV)), 7.6 (8H; CH (*o*, ax. III–III)), 5.5 (16H; CH (*m*, eq.)), 4.1 (24H; CH₃ (eq.)), 3.4 (12H; CH₃ (ax., III–IV)), 2.9 (12H; CH₃ (ax. III–III)), 1.6 ppm (16H; CH (*o*, eq.)).

For reference spectra see: Aubin, S.M.J. *et al. Inorg.Chem.* **2001**, *40*, 2127.

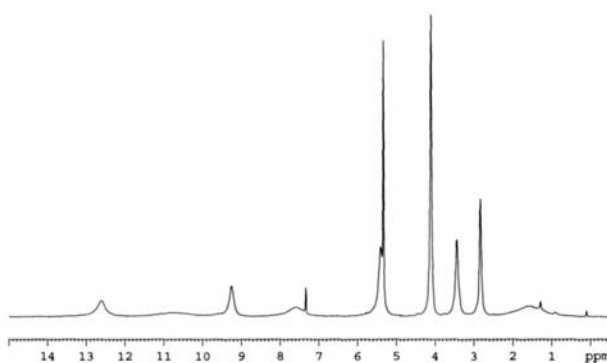


Figure S2. ¹H-NMR spectrum of **2** in CD₂Cl₂.

Electrochemical data (CV and DPV, CH₂Cl₂+TBAPF₆ 0.1 M, 25°C, Pt-disk working, GC auxiliary, SCE reference electrode) E1/2 vs. Fe/Fe+: 0.77 (1st oxidn), 0.07 (1st redn), -0.39 V (2nd redn).

For a reference CV see: Eppley, H.J. *et al. J.Am.Chem.Soc.* **1995**, *117*, 301.

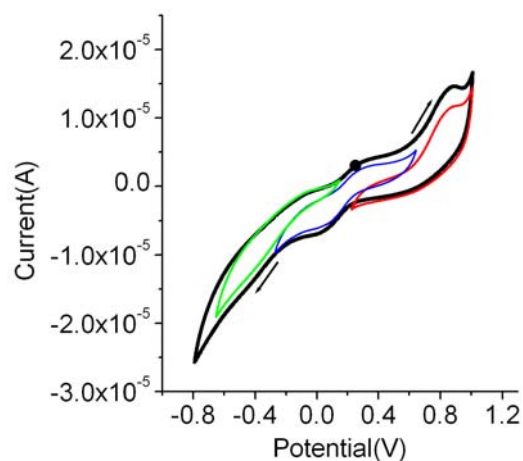


Figure S3. Cyclic voltammogram of 1 mM **2** in CH₂Cl₂ + 0.1 M TBAPF₆, $v=0.05$ V/s.

ToF-SIMS spectra

ToF-SIMS analysis was carried out with a TRIFT III time-of-flight secondary ion mass spectrometer (Physical Electronics, Eden Prairie, MN, USA) equipped with a ⁶⁹Ga⁺ liquid-metal primary ion source. Positive and negative ion spectra were acquired with a pulsed, bunched 15 keV primary ion beam at 600 pA by rastering the ion beam over a 100 μ m x 100 μ m sample area. The primary ion dose was kept below 10¹³ ions/cm² to maintain static SIMS conditions.

Table S1. Characteristic peaks in the positive and negative ion ToF-SIMS spectra of **2** SAMs on Au.

Peak (m/z)	Molecular Formula	Ion description
<i>Positive ion mode</i>		
47	CH ₃ S ⁺	Ligand fragment
55	Mn ⁺	
91	C ₇ H ₇ ⁺	Ligand fragment
151	C ₈ H ₇ OS ⁺	CH ₃ SC ₆ H ₄ CO ⁺
256	C ₈ H ₉ O ₄ SMn ⁺	CH ₃ SC ₆ H ₄ COOMn(OH) ₂ ⁺
<i>Negative ion mode</i>		
32	S ⁻	
47	CH ₃ S ⁻	Ligand fragment
87	MnO ₂ ⁻	
108	C ₆ H ₄ S ⁻	Ligand fragment
123	C ₇ H ₇ S ⁻	Ligand fragment
167	C ₈ H ₇ O ₂ S ⁻	Intact ligand molecule - H
269	C ₈ H ₆ O ₅ SMn ⁻	CH ₃ SC ₆ H ₄ COOMnO ₃ ⁻

Profile analysis and statistics on STM images

Further investigations on the organization of **2** on the Au(111) surface are shown here. The profile section evidences the size of **2** (calculated from the point of maximum slope of each profile) as well as the distance between two nearest-neighbor particles. The particle-size distribution has been evaluated from a set of 6 images obtained independently but in identical conditions. The software for data fitting is Origin (version 7.5, 2003) supplied by OriginLab Corp.

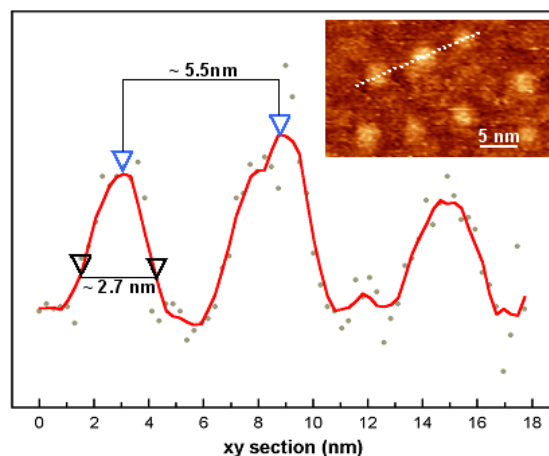


Figure S4. Profile section of Constant-current STM drawn along the line represented in the inset.

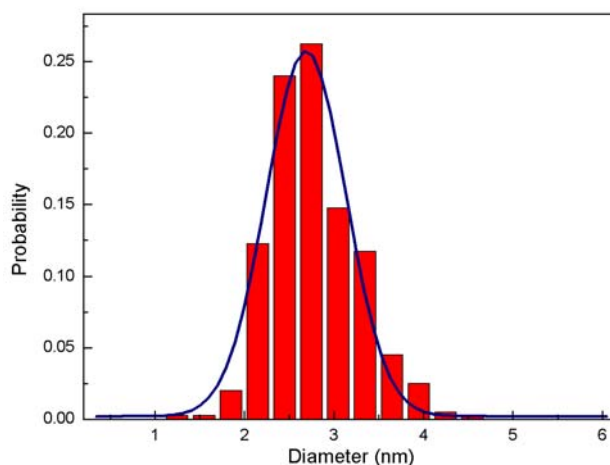


Figure S5. Size distribution of **2** calculated from ca. 400 measurements. The best-fit gaussian distribution is shown as a blue curve ($R^2=0.97$, $x_c = 2.7$ nm, $\sigma = 0.5$ nm).