

Supporting Information

for

Exceptional strong electronic coupling between [Mo₂] units linked by substituted dianionic quinones

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Experimental Section

Materials. All reactions and manipulations were performed under a nitrogen atmosphere, using either drybox or standard Schlenk line techniques. Solvents were purified under argon using a Glass Contour solvent purification system or distilled over appropriate drying agents under nitrogen. The starting materials, Mo₂(DAniF)₃(O₂CCH₃) and the linker precursors 1,5-dihydroxyl-2,4-di(methylamino)benzene ⁱ and 1,4-dihydroxyl-2,5-di(methylamino)benzene ⁱⁱ were prepared according to reported procedures; other commercially available chemicals were used as received.

Physical and Characterization Measurements. Elemental analyses were performed by Robertson Microlit Laboratories, Madison, New Jersey. Electronic spectra were measured on a Shimadzu UV-2501PC spectrometer in CH₂Cl₂ solution. ¹H NMR spectra were recorded on a Mercury 300 spectrometer with chemical shifts (δ) referenced to the CHCl₃ residue in CDCl₃. Cyclic voltammograms and differential pulse voltammograms were recorded on a CH 100 electrochemical analyzer with Pt working and auxiliary electrodes, Ag/AgCl reference electrode, scan rate of 100 mV/sec, and 0.1 M Bu₄NPF₆ as electrolyte. Under the same electrochemical conditions, the $E_{1/2}$ for the

ferrocene/ferrocenium couple (Fc/Fc^+) was measured at 440 mV. The EPR spectra were measured at room temperature in CH_2Cl_2 solutions that had been freshly oxidized in situ with FeCp_2PF_6 . The spectra were collected on a Bruker ESP300 spectrometer and the spectral simulations were performed using the program WIN-EPR SimFonia from Bruker.

Preparation of 1,5-dihydroxyl-2,4-di(methylamino)benzene. Diaminoresorcinol dihydrochloride (0.500 g, 2.35 mmol) was dissolved in 5 mL of water and then an excess of a methylamine solution in water was added. The color changed immediately to purple. This reaction mixture was stirred at room temperature for 30 min and purple crystalline material appeared within 2 h. The product was isolated by filtration and washed with cold water. ^1H NMR in DMSO (ppm): 3.01 (s, 6 H, CH_3), 4.95 (s, 1 H, aromatic), 5.34 (s, 1 H, aromatic), 9.10 (s, 2 H, -NH).

Preparation of 1,4-dihydroxyl-2,5-di(methylamino)benzene. Hydroquinone (2.50 g, 0.0227 mol) was placed in a 250 mL beaker, to which 30 mL of an aqueous CH_3NH_2 solution (40 wt%) was then added. The reaction mixture initially had a clear yellow color that slowly turned to dark red. After about 30 min, dark red crystals were observed at the bottom of the beaker. After 6 h the crystals were collected by filtration and washed with ca. 10 mL portions each of water, ethanol and diethyl ether. ^1H NMR in CDCl_3 (ppm): 2.89 (d, 6 H, $-\text{CH}_3$), 5.28 (s, 2 H, aromatic), 6.59 (s, broad, 2 H, -NH).

Oxidations of 1 and 2. For each compound a sample was placed in an EPR tube and dissolved in CH_2Cl_2 . Then slightly less than one equivalent of FeCp_2PF_6 was added to the

corresponding solution. *Note:* Whenever an small excess of FeCp_2PF_6 was used, a second signal appeared in the EPR spectra that resembled that of $\text{Mo}_2(\text{DAniF})_4^+$.ⁱⁱⁱ If the excess was large, only the second signal appeared indicating that the oxidized species are unstable in CH_2Cl_2 solution in the presence of an excess of FeCp_2PF_6 .

X-ray Structure Determinations. Single crystals suitable for X-ray analyses were obtained by diffusion of ethanol into a THF solution of **1** or a mixture of CH_2Cl_2 and acetone (1:1) for **2**. Each crystal was mounted on the tip of a cryoloop attached to the goniometer head. Data for **1**·5 $\text{C}_4\text{H}_4\text{O}$ and **2**·4 CH_2Cl_2 were collected at $-60\text{ }^\circ\text{C}$ on a BRUKER SMART 1000 CCD area detector system. Cell parameters were determined using the program SMART.^{iv} Data reduction and integration were performed with the software package SAINT^v and absorption corrections were applied by using SADABS.^{vi} Using the program package SHELXTL,^{vii} the structures were solved by direct methods and refined. Occupancies of disordered atoms were refined and soft restraints were used. Non-hydrogen atoms, except for those of disordered units and solvent molecules, were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions. Crystallographic data are presented in Table 1 and selected bond distances and angles are listed in Table 2. In **1**·5 $\text{C}_4\text{H}_4\text{O}$ the THF molecules are disordered and the distances between disordered molecules are not as precise as the intramolecular distances in the metal complex. The intermolecular distances between interstitial disordered THF molecules must be considered as approximations at best. For **2**·4 CH_2Cl_2 , atoms C55 and C56 are found on disordered ligands and the distances stated in the

checkcif report are between partially occupied atoms.

Table 1. X-ray Crystallographic Data for **1** and **2**.

Compound	1 ·5C ₄ H ₈ O	2 ·4CH ₂ Cl ₂
Chemical formula	C ₁₁₈ H ₁₃₈ Mo ₄ N ₁₄ O ₁₉	C ₁₀₂ H ₁₀₆ Cl ₈ Mo ₄ N ₁₄ O ₁₄
Fw	2440.18	2419.37
Space group	<i>P2₁/c</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> (Å)	16.5233(18)	11.345(4)
<i>b</i> (Å)	24.371(3)	16.008(6)
<i>c</i> (Å)	29.569(3)	16.851(6)
α (deg)	90	70.111(7)
β (deg)	106.110(2)	73.723(6)
γ (deg)	90	70.823(6)
<i>V</i> (Å ³)	11440(2)	2668.7(17)
<i>Z</i>	4	1
<i>d</i> _{calcd} (gcm ⁻³)	1.417	1.505
μ (mm ⁻¹)	0.501	0.727
T (K)	213(2)	213(2)
GooF	1.062	1.031
R1, ^a wR2 ^b	0.1030, 0.1835	0.0907, 0.1809
R1, ^a wR2 ^b (I > 2 σ)	0.0599, 0.1387	0.0615, 0.1586

$$^a \text{R1} = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}$$

$$^b \text{wR2} = [\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}, w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP], \text{ where } P = [\max(F_o^2, 0) + 2(F_c^2)]/3.$$

Table 2. Selected Bond Distances (Å) and Angles (°) for **1** and **2**.

	1	2
Mo(1)–Mo(2)	2.0966(7)	2.0902(7)
Mo(3)–Mo(4)	2.0945(7)	
Mo ₂ ···Mo ₂ ^a	8.816	8.832
Mo(1)–N(1)	2.109(5)	2.108(3)
Mo(2)–O(1)	2.075(4)	2.069(3)
Mo(3)–N(8)	2.126(5)	
Mo(4)–O(8)	2.053(4)	
C(1)–C(2)	1.462(8)	1.457(5)
C(2)–C(3)	1.387(8)	1.389(5)
C(3)–C(4)	1.394(8)	
C(4)–C(5)	1.463(8)	
C(5)–C(6)	1.410(8)	
C(6)–C(1)	1.399(8)	
Mo(1)–Mo(2)–O(1)	98.47(11)	99.79(8)
Mo(2)–Mo(1)–N(1)	101.67(14)	100.34(8)
Mo(3)–Mo(4)–O(8)	100.80(11)	
Mo(4)–Mo(3)–N(8)	99.11(13)	

^a distances between midpoints of the [Mo₂] units.

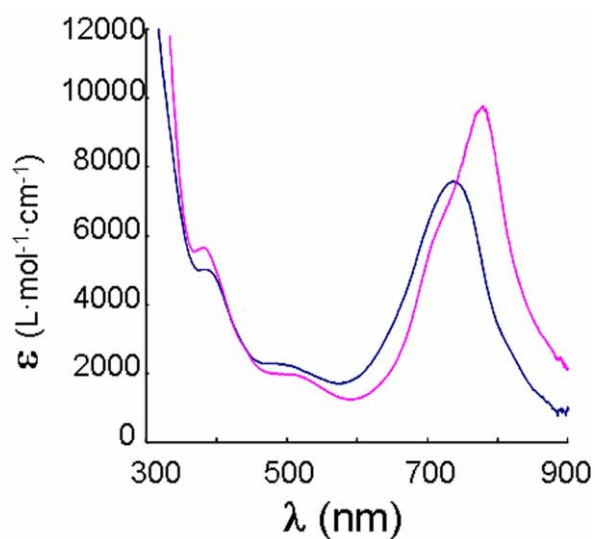


Fig. S1. UV-vis spectra for compound **1** (blue) and **2** (red) in CH₂Cl₂ solutions.

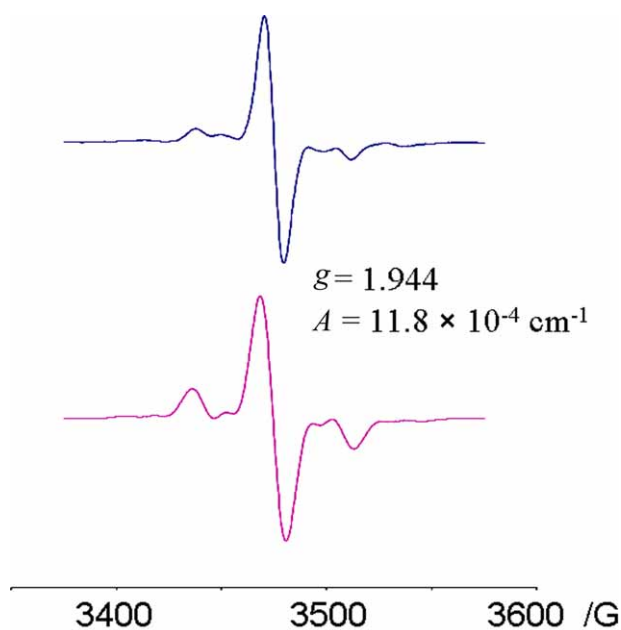


Fig. S2. X-band EPR spectrum for **1**⁺ taken in CH₂Cl₂ solution at room temperature (blue). The simulated spectrum is at the bottom in red. From the simulation $g = 1.944$ and

$$A = 11.8 \times 10^{-4} \text{ cm}^{-1}.$$

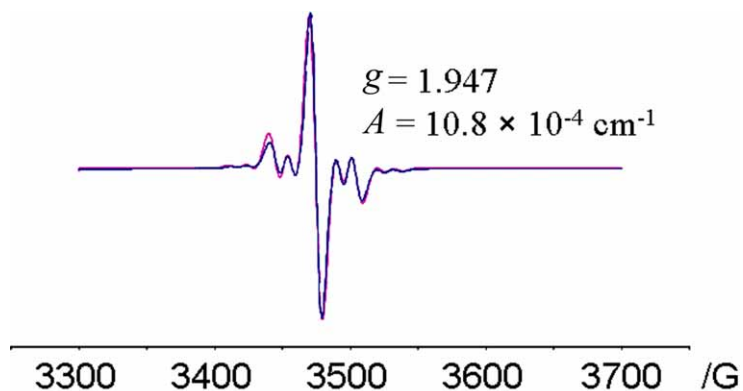


Fig. S3. X-band EPR spectrum for 2^+ in CH_2Cl_2 solution at room temperature (blue). The simulated spectrum is in red.

References

- ⁱ (a) Q. Z. Yang, O. Siri and P. Braunstein, *Chem. Commun.*, 2005, 2660. (b) O. Siri and P. Braunstein, *Chem. Commun.*, 2000, 2223.
- ⁱⁱ R. N. Harger, *J. Am. Chem. Soc.*, 1924, **46**, 2540.
- ⁱⁱⁱ F. A. Cotton, J. P. Donahue, P. L. Huang, C. A. Murillo and D. Villagrán, *Z. Anorg. Allg. Chem.*, 2005, **631**, 2606.
- ^{iv} SMART for Windows NT, Version 5.618: Bruker AXS Inc.: Madison, WI, 2001.
- ^v SAINT, Data reduction Software, version 6.36A; Bruker AXS Inc.: WI, 2001.
- ^{vi} SADABS, Area Detector Absorption and other Corrections Software, version 2.05; Bruker AXS Inc.: Madison, WI, 2000.
- ^{vii} Sheldrick, G. M. *SHELXL*, Version 6.12; Bruker AXS Inc.: Madison, WI, 2002.