

Supporting Information For:

Trinuclear Mn(II) Complex With Paramagnetic Bridging 1,2,3-Dithiazolyl Ligands

David J. Sullivan,^a Rodolphe Clérac,^{b,c} Michael Jennings,^d Alan J. Lough^e and Kathryn E. Preuss^{a*}

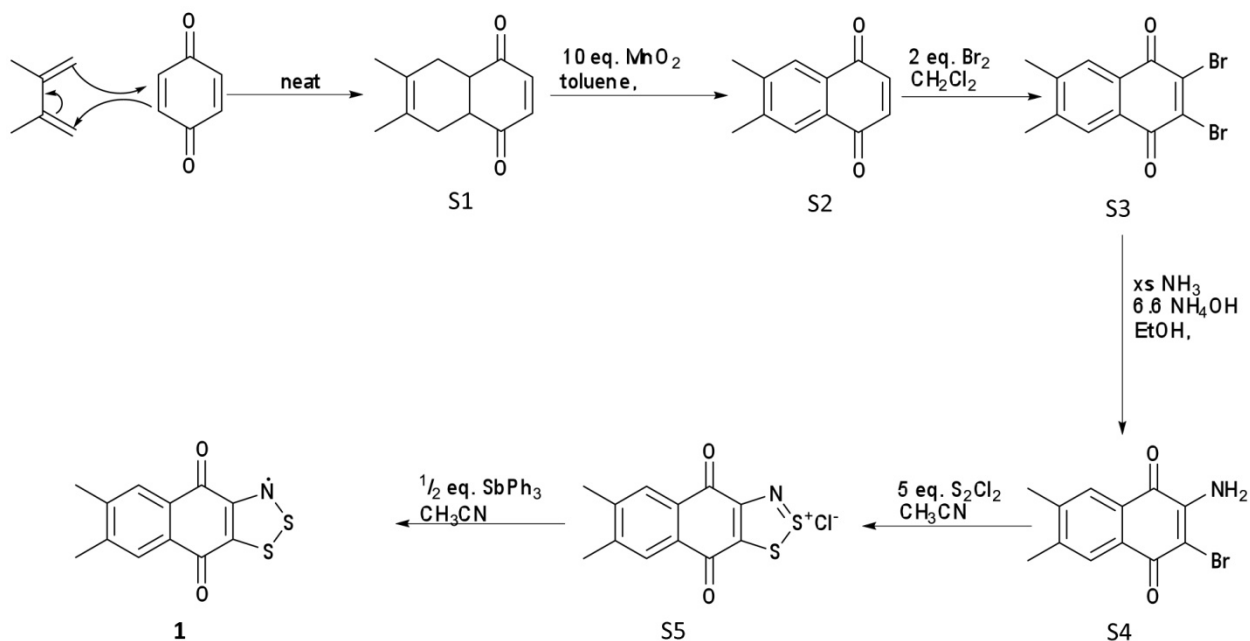
^a Department of Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

^b CNRS, CRPP, UPR 8641, F-33600 Pessac, France

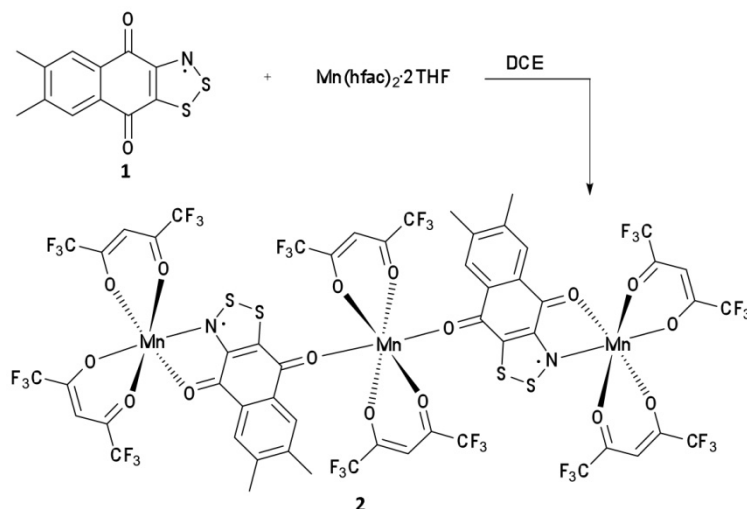
^c Univ. Bordeaux, CRPP, UPR 8641, F-33600 Pessac, France

^d 185 Chelsea Ave., London, ON, N6J 3J5

^e Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 3H6.



Scheme S1. Synthetic route for radical ligand **1**.



Scheme S2. Synthetic route for coordination complex 2.

Experimental Section

General Considerations. Where indicated, reactions performed under $\text{Ar}_{(\text{g})}$ atmosphere were achieved using standard Schlenk and glove box techniques. Solvents were dried on a SP-1 Stand Alone Solvent Purification System from LC Technology Solutions Inc, using molecular sieves. All commercial reagents were used as received, with the exception of manganese oxide which was activated¹ by heating to 100 °C for a minimum of 24 h prior to use, and triphenyl antimony which was recrystallized from acetonitrile; 2,3-dimethylbutadiene and p-benzoquinone from Acros Organics; MnO_2 , $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, SbPh_3 , and S_2Cl_2 from Sigma Aldrich; Hhfac from Alfa Aesar. 6,7-Dimethyl-5,8,9,10-tetrahydronaphthoquinone² (**S1**), 2,3-dibromo-6,7-dimethyl-1,4-naphtho-quinone³ (**S3**) and $\text{Mn}(\text{hfac})_2(\text{THF})_2$ ⁴ were prepared according to literature methods. IR (KBr pressed pellet) spectra were recorded on a Nicolet 4700 FT-IR spectrometer at 4 cm^{-1} resolution. NMR spectra were recorded on a Bruker Avance-400 spectrometer at 298 K. Elemental analyses were performed by MHW Labs, Phoenix, AZ, USA. Crystal data on **1** and **2** were collected by Dr. Alan Lough at the University of Toronto on a Nonius Kappa-CCD system and solved by Dr. Michael Jennings. Crystal data on **S4** were collected by Dr. Dmitriy Soldatov at the University of Guelph on a SuperNova Dual with Atlas CCD system and solved by David J. Sullivan.

6,7-Dimethyl-1,4-naphthoquinone (S2). A modification of the procedure reported by Mashraqui and Keehn⁵ was used. Dry toluene (185 mL) was added to a solid mixture of **1** (4.9625 g, 26.085 mmol) and activated MnO₂ (23.01 g, 301.5 mmol) under Ar_(g) atmosphere. The resulting solution was refluxed for 3h, then filtered hot through Celite. The filtrate was collected and the solids on the Celite plug were washed with anhydrous ethanol, which was then added to the filtrate. Evaporation of the solvent from the filtrate afforded the crude product **S2**, which was recrystallized from anhydrous ethanol to give a yellow crystalline product. Yield: 3.2242 g (17.312 mmol, 66%). mp: 113-116 °C. **IR(KBr)** $\bar{\nu}/\text{cm}^{-1}$: 2952 (w), 2918 (w), 2849 (w), 1666 (s), 1599 (s), 1560 (w), 1508 (w), 1449 (m), 1392 (m), 1360 (w), 1341 (m), 1328 (s), 1309 (s), 1262 (w), 1220 (w), 1202 (w), 1143 (m), 1099(w), 1072 (w), 1057 (s), 1019 (m), 995 (w), 971(w), 902 (w), 837 (s), 805 (w), 768 (w), 712 (w), 626 (w), 512 (m), 499 (m), 471 (w), 450 (m), 426 (m), 412 (w). **¹H NMR:** (400 Mhz, CDCl₃, 25 °C, ppm) δ 2.39 (6 H, s, CH₃), δ 6.88 (2 H, s, CH), δ 7.81 (2 H, s, CH).

2-Amino-3-bromo-6,7-dimethyl-1,4-naphthoquinone (S4). A modification of the procedure reported by Hoover and Day⁶ was used for this preparation. A suspension of **S3** (3.3563 g, 97.567 mmol) was heated to reflux in anhydrous ethanol (200 mL) under Ar_(g) atmosphere. Concentrated (28%) NH₄OH_(aq) (4.50 mL) was added and the mixture was refluxed under ammonia atmosphere (sealed system with a balloon of NH_{3(g)}) for 8 h. The solution was cooled in an ice bath and the resulting orange precipitate was recovered by filtration and washed with deionized water. The product, **S4**, was dried *in vacuo* overnight. Yield: 2.7128 g (96.826 mmol, 99%). mp: 226-228 °C. **IR(KBr)** $\bar{\nu}/\text{cm}^{-1}$: 3528 (m), 3461 (m), 3423 (m), 3322(s), 3073 (w), 2973 (w), 2946 (w), 2919 (w), 1831 (w), 1794 (w), 1682 (s), 1631 (s), 1606 (s), 1588 (s), 1566(s), 1448 (m), 1405 (m), 1386 (m), 1367 (s), 1330 (s), 1297 (s), 1240 (w), 1201 (w), 1178 (w), 1064 (w), 1023 (w), 1000 (w), 964 (m), 916 (w), 899 (w), 801 (m), 760 (w), 744 (s), 688 (w), 676 (w), 622 (m), 577 (m), 549 (m), 499 (m), 446 (w), 426 (m). **¹H NMR:** (400 Mhz, CDCl₃, 25 °C, ppm) δ 2.35 (3 H, s, CH₃), δ 2.37 (3 H, s, CH₃), δ 7.78 (1 H, s, CH), δ 7.88 (1 H, s, CH). Crystals of the hemi-hydrate **S4·0.5H₂O** suitable for single crystal X-ray analysis were grown from EtOH at 10 °C. These desolvated rapidly when removed from the mother liquor. **Crystal data:** SuperNova Dual Atlas-CCD radiation source CuK α , wavelength = 1.5418 Å at University of Guelph; *T* = 150(2) K; monoclinic; *C*₂/*c*; *a* = 7.72070(7), *b* = 13.73969(16), *c* =

21.1400(2) Å; $\beta = 94.0880(10)^\circ$; $V = 2236.83(4) \text{ \AA}^3$; $Z = 8$; Total Refls. = 18184; Ind. Refls. = 2345; $R(\text{int}) = 3.44$; $R_1(I > 2\sigma) = 3.29\%$; $wR_2(\text{all data}) = 8.17\%$.

6,7-Dimethyl-1,4-dioxo-naphtho[1,2-*d*][1,2,3]dithiazol-2-ium chloride (S5). Excess S_2Cl_2 (6.00 mL, 74.8 mmol) was added to a solution of **S4** (4.1079g, 14.665mmol) in dry CH_3CN (45 mL) under $\text{Ar}_{(\text{g})}$ atmosphere. The reaction mixture was refluxed for 3 h, effecting a Herz-like⁷⁻¹¹ ring closure. The resulting orange slurry was filtered warm to isolate a fine precipitate, which was washed with dry CH_3CN (6 mL). The product, **S5**, was an orange powder which was dried *in vacuo*. Crude yield: 3.8674 g (12.987 mmol, 89%). **IR(KBr)** $\bar{\nu}/\text{cm}^{-1}$: 3035 (w), 3014 (w), 2953 (w), 2921 (w), 1686 (s), 1671 (s), 1593 (s), 1558 (w), 1452 (m), 1407 (w), 1396 (m), 1374 (m), 1292 (s), 1226 (w), 1194 (s), 1172 (w), 1094 (s), 1032 (s), 994 (m), 938 (w), 918 (s), 906 (m), 852 (s), 819 (w), 804 (w), 774 (w), 748 (w), 729 (s), 691 (m), 643 (m), 603 (w), 583 (w), 539 (m), 503 (m), 466 (w), 439 (m), 424 (m).

6,7-Dimethyl-1,4-dioxo-naphtho[2,3-*d*][1,2,3]dithiazolyl (1). Triphenyl antimony (0.6130 g, 1.7365 mmol) was added to a suspension of **S5** (1.0336g, 3.4710mmol) in dry CH_3CN (20 mL) under $\text{Ar}_{(\text{g})}$ resulting in an instant color change from orange to purple. The slurry was stirred for 0.5 h at RT and then the purple precipitate isolated from the green solution by filtration. The fine purple solid **1** was washed with dry CH_3CN (10 mL) and dried *in vacuo*. Crude yield: 0.8370 g (3.1906 mmol, 92%). A portion of the crude product (0.1453 g, 0.5539 mmol) was purified by sublimation under dynamic vacuum (10^{-5} Torr) using a 4 stage gradient tube furnace (175, 95, 70, 30 °C) to generate purple crystals of **1**. Sublimation yield: 0.0930 g (0.355 mmol, 64%). **IR(KBr)** $\bar{\nu}/\text{cm}^{-1}$: 3326 (w), 3049 (w), 2969 (w), 2944 (w), 2916 (w), 1670 (s), 1602 (m), 1593 (w), 1574 (s), 1550 (m), 1535 (m), 1500 (w), 1458 (w), 1448 (w), 1421 (s), 1401 (w), 1380 (w), 1375 (w), 1350 (s), 1305 (w), 1282 (s), 1259 (s), 1193 (s), 1178 (m), 1078 (m), 1034 (m), 995 (m), 940 (w), 892 (m), 815 (s), 760 (m), 740 (m), 723 (m), 693 (m), 683 (m), 639 (m), 594 (w), 574 (m), 530 (w), 506 (w), 482 (w), 454 (w), 438 (w), 417 (m). **Crystal data:** Nonius Kappa CCD using graphite monochromatized Mo-K α radiation wavelength = 0.71073 Å at University of Toronto; $T = 150(2) \text{ K}$; monoclinic; $P2_1/c$; $a = 11.055(2)$, $b = 7.9789(16)$, $c = 13.222(3) \text{ \AA}$; $\beta = 113.03(3)^\circ$; $V = 1073.32 \text{ \AA}^3$; $Z = 4$; Total Refls. = 8545; Ind. Refls. = 1893; $R(\text{int}) = 7.38$; $R_1(I > 2\sigma) = 4.28\%$; $wR_2(\text{all data}) = 11.30\%$. **Elemental Anal.** Calc. for $\text{C}_{12}\text{H}_8\text{NO}_2\text{S}_2$: C, 54.94; H, 3.07; N, 5.34%. Found: C, 54.77; H, 3.01; N, 5.33%.

Mn(hfac)₂-Rad-Mn(hfac)₂-Rad-Mn(hfac)₂ (2). Dry 1,2-dichloroethane (300 mL) was added to a solid mixture of Mn(hfac)₂(THF)₂ (0.4740 g, 0.773 mmol) and **1** (0.1997 g, 0.762 mmol), under inert atmosphere, generating dark green slurry. After 1 h of gentle heating and stirring, an olive green solution, free of precipitates, was obtained. The solvent was removed *in vacuo* resulting in a dark green powder of **2**. Crude yield: 0.5509 g, 98% of total mass was recovered. A portion of the crude product (0.2533 g) was purified by sublimation under dynamic vacuum (10⁻⁵ Torr) using a 4 stage gradient tube furnace. The best yields were obtained by quickly ramping the furnace up to the ideal temperature gradient (130, 90, 60, 40 °C). Dynamic vacuum sublimation afforded dark emerald green crystals of **2**. Sublimation yield: 0.0955 g (0.0494 mmol, 41%). **IR(KBr)** $\bar{\nu}/\text{cm}^{-1}$: 1645 (s), 1576 (m), 1561 (w), 1534 (w), 1479 (m), 1407 (m), 1307 (m), 1255 (s), 1200 (s), 1147(s), 1094 (m), 1041 (w), 906 (w), 836 (w), 806 (s), 800 (s), 767 (w), 742 (w), 734 (w), 665 (s), 648 (w), 585 (s), 527 (w), 511 (w), 499 (w), 485 (w), 472 (w), 459 (w), 441 (w), 428 (w), 415 (w), 411 (w). **Crystal data:** Nonius Kappa CCD using graphite monochromatized Mo-K α radiation wavelength = 0.71073 Å at University of Toronto; *T* = 150(2) K; monoclinic; *P*-1; *a* = 12.178(2), *b* = 12.716(16), *c* = 12.809(3) Å; α = 69.55(3)°, β = 113.03(3)°, γ = 68.97(3)°; *V* = 1721.95 Å³; *Z* = 1; Total Refls. = 28760; Ind. Refls. = 6083; *R*(int) = 9.03; *R*₁ (*I*>2 σ) = 4.89%; *wR*₂(all data) = 11.42%. **Elemental Anal.** Calc. for C₅₄H₂₂F₃₆Mn₃N₂O₁₂S₄: C, 33.57; H, 1.15; N, 1.45%. Found: C, 33.36; H, 1.32; N, 1.42%.

Cyclic Voltammetry (CV). Cyclic voltammetry data were collected using a BASi Epsilon-EC Bioanalytical Systems, Inc. Version 2.10.73_USB, 2009 instrument. Cells were prepared in a glovebox using dry, degassed solvent. Experiments were performed using Pt wire working, counter and reference electrodes, 0.05 M (*n*-Bu₄)NPF₆ and 2.0 mM of analyte **1**, at a scan rate of 100 mV/s. The ferrocene/ferrocenium (fc/fc⁺) redox couple was used as an internal reference ($E_{1/2}^{(\text{fc}/\text{fc}^+)} = +0.40$ V vs. SCE in CH₃CN; $E_{1/2}^{(\text{fc}/\text{fc}^+)} = +0.46$ V vs. SCE in CH₂Cl₂).¹² In acetonitrile, there are two reversible redox processes at $E_{1/2}^{(0/1^+)} = 0.81$ V ($\Delta E_{\text{pp}} = 96$ mV) and $E_{1/2}^{(1^-/0)} = -0.41$ V ($\Delta E_{\text{pp}} = 111$ mV) corresponding to oxidation to the closed shell cation and reduction to the closed shell anion respectively. These reversible processes are observed in methylene chloride at $E_{1/2}^{(0/1^+)} = 0.86$ V ($\Delta E_{\text{pp}} = 86$ mV) and $E_{1/2}^{(1^-/0)} = -0.32$ V ($\Delta E_{\text{pp}} = 108$ mV).

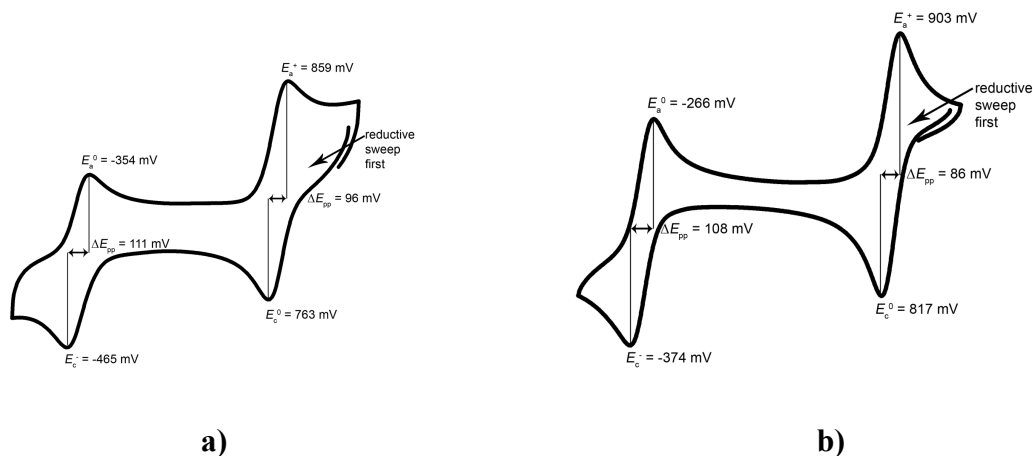


Fig. S1 CV of **1** in a) CH_3CN and b) CH_2Cl_2 .

Computational analysis. Geometry optimization of **1** was performed using uB3LYP/6-31g(d,p) as found in the Gaussian 09 EM64-G09RevA.02 software package.¹³ This particular DFT method was selected because it is commonly used for thiazyl radical species and therefore generates data that is comparable to that found in the literature for other similar species. The B3LYP functional has been optimized for 6-31g, hence the selection of this particular basis set. To accommodate the sulfur and hydrogen atoms, the 6-31g(d,p) basis set specifically has been selected. The output data for the isotropic Fermi contact couplings, Mulliken spin densities and charges for all atoms are listed in Table S1.

Magnetic measurements. Magnetic susceptibility measurements were obtained using a Quantum Design MPMS-XL SQUID magnetometer. The measurements were performed on polycrystalline samples of **1** (8.3 mg) and **2** (17.8 mg) introduced in a sealed polyethylene bag ($3 \times 0.5 \times 0.02 \text{ cm}$; 28.6 and 29.8 mg respectively) under argon in a glovebox. The *dc* measurements were conducted from 300 to 1.8 K and between -7 T and 7 T applied *dc* fields. An *M* vs *H* measurement was performed at 100 K to confirm the absence of ferromagnetic impurities in these samples. Experimental data were corrected for the sample holder and for the diamagnetic contribution of the sample.

X-Band EPR Spectroscopy. X-band EPR spectra were recorded on a Bruker EMX spectrometer.

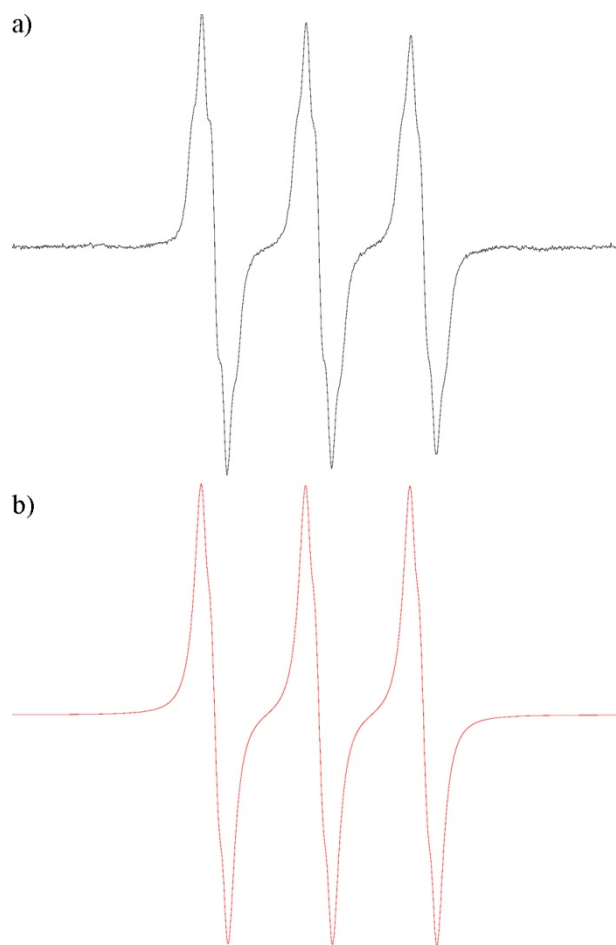


Fig. S2 a) X-band EPR spectrum of a dilute solution of ligand **1** at ambient temperature in CH_2Cl_2 . b) Simulation¹⁴ using $a_{\text{N}} = 4.46$, $a_{\text{H}} = 0.32$, $a_{\text{H}'} = 0.53$ G; $g = 2.0095$; line width = 0.38 G.

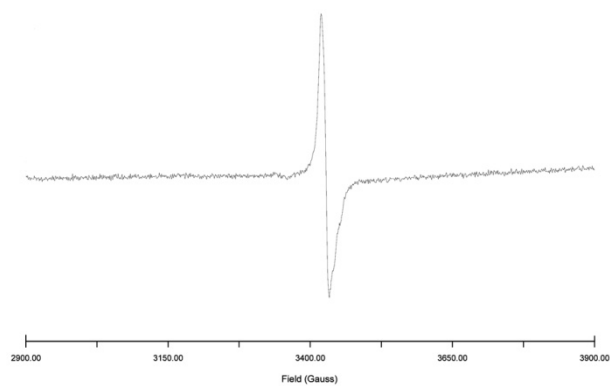
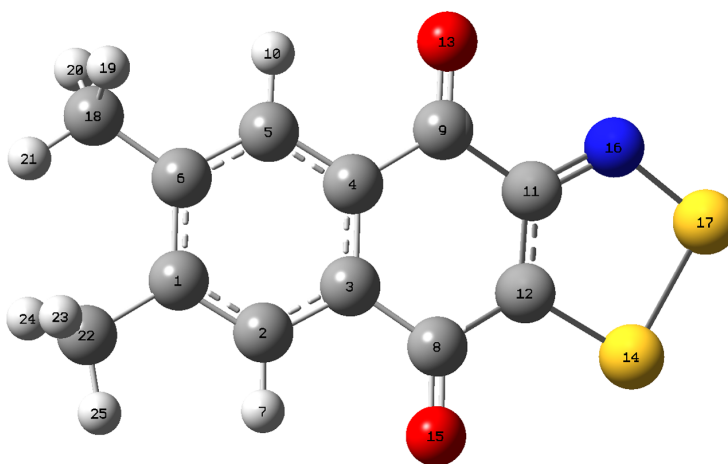


Fig. S3 X-band EPR spectrum of solid **1** at low temperature (ca. 200 K).

Table S1 Relevant computational output from the geometry optimization of radical **1** using uB3LYP/6-31g(d,p). Computational numbering scheme illustrated below.

<i>Atom name (computational)*</i>	<i>Atom name (crystallographic)</i>	<i>Isotropic Fermi Contact Coupling (Gauss)</i>	<i>Mulliken Atomic Spin Densities</i>	<i>Mulliken Atomic Charges</i>
1 C(13)	C6	-0.35887	-0.005421	0.100885
2 C(13)	C7	0.30221	0.011073	-0.157735
3 C(13)	C8	-0.94035	-0.006235	0.041581
4 C(13)	C3	0.63525	0.012262	0.017424
5 C(13)	C4	-0.50446	-0.009391	-0.146033
6 C(13)	C5	0.73340	0.016566	0.084369
7 H(1)	H7a	-0.24952	-0.000745	0.118698
8 C(13)	C9	-3.70369	-0.017998	0.406646
9 C(13)	C2	1.04764	0.013580	0.398574
10 H(1)	H4a	0.16534	0.000372	0.117530
11 C(13)	C1	-9.30828	-0.142530	0.249519
12 C(13)	C10	15.68330	0.333024	-0.267504
13 O(17)	O1	0.59614	-0.022879	-0.447133
14 S(33)	S1	3.19129	0.230414	0.166239
15 O(17)	O2	-3.60040	0.131354	-0.496212
16 N(14)	N1	4.85551	0.254334	-0.491748
17 S(33)	S2	2.58978	0.202050	0.313187
18 C(13)	C11	-0.17962	-0.001217	-0.384340
19 H(1)	H11b	0.59823	0.000729	0.134435
20 H(1)	H11a	0.59962	0.000730	0.134457
21 H(1)	H11c	0.01484	0.000028	0.114576
22 C(13)	C12	0.02934	0.000316	-0.389792
23 H(1)	H12c	-0.13749	-0.000194	0.130208
24 H(1)	H12b	-0.13747	-0.000195	0.130205
25 H(1)	H12a	-0.01646	-0.000028	0.121965

*Isotope considered for the Fermi contact coupling is given in brackets.



References

- (1) Fatiadi, A. J. *Synthesis* **1976**, *133*, 65.
- (2) Mandelbaum, A.; Cais, M. *J. Org. Chem.* **1962**, *27*, 2243.
- (3) Buckle, D. R.; Smith, H.; Spicer, B. A.; Tedder, J. M. *J. Med. Chem.* **1983**, *26*, 714.
- (4) Britten, J.; Hearn, N. G. R.; Preuss, K. E.; Richardson, J. F.; Bin-Salamon, S. *Inorg. Chem.* **2007**, *46*, 3934.
- (5) Mashraqui, S.; Keehn, P. *Synth. Commun.* **1982**, *12*, 637.
- (6) Hoover, J. R. E.; Day, A. R. *J. Am. Chem. Soc.* **1954**, *76*, 4148.
- (7) Herz, R.; Leopold Cassella & Co.: German, 1922.
- (8) Warburton, W. K. *Chem. Rev.* **1957**, *57*, 1011.
- (9) Huestis, L. D.; Walsh, M. L.; Hahn, N. *J. Org. Chem.* **1965**, *30*, 2763.
- (10) Hope, P.; Wiles, L. A. *Chem. Ind.* **1966**, 32.
- (11) Hope, P.; Wiles, L. A. *J. Chem. Soc. C* **1967**, 1642.
- (12) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.
- (13) 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; O. Farkas; J. B. Foresman; J. V. Ortiz; J. Cioslowski; Fox, D. J. *Gaussian 09, Revision A.02*, Gaussian Inc., 2009.
- (14) O'Brien, D. A.; Duling, D. R.; Fann, Y. C. *WinSim Public EPR Software Tools*, MS-Windows 9x, NT Version 0.98, National Institute of Environmental Health Sciences, 2002.