Electronic Supporting Information

The first semiquinone-bridged bisdithiazolyl radical conductor: a canted antiferromagnet displaying a spin-flop transition

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Section S1 Synthetic procedures and instrumental methods.

General methods and procedures. The solvents acetonitrile (MeCN), acetone, dichloroethane (DCE) and dichloromethane (DCM) were of at least reagent grade. MeCN was dried by distillation from P_2O_5 and/or CaH_2, and both DCE and DCM by distillation from P_2O_5. All reactions were performed under an atmosphere of dry nitrogen. Melting points are uncorrected. Infrared spectra (Nujol mulls, KBr optics) were recorded on a Nicolet Avatar FTIR spectrometer at 2 cm^{-1} resolution. ^{1}H spectra were run on a Bruker Avance 300 MHz NMR spectrometer and low resolution Electro-Spray Ionization (ESI) mass spectra were run on a Micromass Q-TOF Ultima Global LC/MS/MS system. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ 85018.

Preparation of 2,6-dinitro-4-phenylphenol.[1] Concentrated nitric acid (20 mL) was added slowly to a stirred suspension of 4-phenylphenol (20.24 g, 0.119 mol) in glacial acetic acid (100 mL). The reaction mixture was held in an ice/water bath for 45 min, then poured onto 400 mL ice. The product, 2,6-dinitro-4-phenylphenol, a bright yellow solid, was collected by filtration, yield 28.58 g (0.11 mol, 93 %), and recrystallized from acetone. ^{1}H-NMR ($CDCl_3$) δ: 7.58-7.45 (m, 5H, Ar), 8.52 (s, 2H, Ar), 11.40 (s, 1H, OH).

Preparation of 2,6-diamino-4-phenylphenol dihydrochloride 3.[2] Tin powder (9.39 g, 79.1 mmol) was added slowly to a slurry of 2,6-dinitro4-phenylphenol (10.1 g, 38.8 mmol) and $SnCl_2 \cdot 2H_2O$ (10.1 g, 44.7 mmol) in a mixture of ethanol (100 mL) and conc. HCl (30 mL) held at 0 °C in and ice/water bath. After 30 min, the reaction mixture was allowed to warm to room temperature, resulting a light yellow solution. The solution was boiled for 3 h, then concentrated and cooled to room temperature. After 24 h the white solid was filtered off, washed with concentrated HCl and then recrystallized from hot HCl:H_2O (1:1) to afford 2,6-diamino-4-phenylphenol dihydrochloride (7.64 g, 28.0 mmol, 72.0 %). ^{1}H-NMR (DMSO) δ: 7.31 (t, 7.2 Hz, 1H, Ar), 7.42 (t, 7,2 Hz, 2H, Ar),

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[1] G. L. Tullos, J. N. Powers, S. J. Jeskey and L. J. Mathias, *Macromolecules*, 1999, **32**, 3598.

[2] B. K. Chen, Y. J. Tsai and S. Y. Tsay, *Polym. Int.*, 2006, **55**, 93.

7.65 (d, 7.5 Hz, 2H, Ar), 8.30 (s, 1H, Ar). IR (cm^{-1}): 3425 (w, b), 3358 (w, b), 2553 (w, b), 1940 (w, b), 1644 (w), 1577 (w), 1513 (s), 1487 (vs), 1333 (m), 1288 (m), 1235 (m), 1199 (w), 1115 (w), 1074 (w), 1021 (w), 972 (w), 878 (w), 762 (w), 694 (w), 621 (w), 608 (w), 514 (w).

Preparation of [2a][Cl]. A slurry of 2,6-diamino-4-phenylphenol dihydrochloride 3 (5.53 g, 20.3 mmol) and sulfur monochloride (15.2 g, 0.112 mol) in 150 mL MeCN was heated at gentle reflux overnight. The resulting blue/black precipitate of [**2a**][Cl] was filtered off, washed with MeCN, hot DCE and finally CS_2 to remove residual sulfur and sulfur chlorides, and dried in vacuo. Yield 6.13 g (17.2 mmol, 85 %); mp > 250°C. IR (cm^{-1}): 1668 (s), 1401 (vs), 1271 (s), 1103 (w), 824 (w), 784 (w), 734 (m), 688 (w), 551 (w), 514 (w), 487 (m).

Preparation of [2a][OTf]. Silver triflate (5.31 g, 20.7 mmol) was added to a slurry of crude [**2a**][Cl] (6.13 g, 17.2 mmol) in 150 mL MeCN. The resulting deep purple solution was gently heated for 1 hr, then filtered to remove AgCl, and the filtrate flash-distilled to leave crude [**2a**][OTf] as dark purple solid (4.50 g). The product was crystallized from hot MeCN to afford purple shards (3.22 g, 6.8 mmol, 72 %); mp > 250 °C. Anal. Calc. for $C_{13}H_5F_3N_2O_4S_5$: C, 33.19; H, 1.07; N, 5.95. Found: C, 33.02; H, 1.15; N, 5.80. IR (cm^{-1}): 1690 (s), 1414 (vs), 1243 (s), 1222 (m), 1095 (m), 1024 (s), 899 (w), 845 (w), 825 (w), 763 (s), 730 (w), 694 (w), 635 (s), 563 (w), 514 (m), 478 (w).

Preparation of 2a. A solution of [**2a**][OTf] (0.100 g, 0.212 mmol) in 15 mL of degassed (4 freeze-pump-thaw cycles) was allowed to diffuse over a period of 15 h into a solution of octamethylferrocene (0.076 g, 0.27 mmol) in 10 mL of equally degassed MeCN. The lustrous black, needle-shaped crystals of **2a** were collected, washed with MeCN and dried under a flow of nitrogen. Yield 60 mg (0.19 mmol, 88 %); dec 190°C. Anal. Calc. for $C_{12}H_5N_2OS_4$: C, 44.84; H, 1.57; N, 8.71. Found: C, 44.62; H, 1.76; N, 8.46. IR (cm^{-1}): 1608 (s), 1312 (m), 1176 (m), 1070 (w), 1033 (w), 975 (w), 834 (w), 738 (s), 721 (s), 693 (m), 651 (m), 488 (m), 450 (m).

Cyclic Voltammetry. Cyclic voltammetry was performed using a PINE Bipotentiostat, Model AFCClBP1, with scan rates of 50-100 mV s^{-1} on solutions of [**2a**][OTf] in CH_3CN (dried by distillation from P_2O_5 and CaH_2) containing 0.1 M tetra-*n*-butyl-ammonium hexafluorophosphate. Potentials were scanned with respect to the quasi-reference electrode in a single compartment cell fitted with Pt electrodes and referenced to the Fc/Fc^+ couple of ferrocene at 0.38 V *vs* SCE.[3] The E_{pa}-E_{pc} separation of the reversible couples were within 10 % of that of the Fc/Fc^+ couple.

EPR Spectroscopy. The X-Band EPR spectrum of **2a** was recorded at ambient temperature using a Bruker EMX-200 spectrometer; samples of the radicals were dissolved in degassed toluene. Hyperfine coupling constants were obtained by spectral simulation using Simfonia[4] and WinSim.

X-ray Measurements. Needles of [**2a**][OTf] and **2a** were glued to glass fibers with epoxy. X-ray data were collected using omega scans with a Bruker APEX I CCD detector on a D8 3-circle goniometer and Mo K_α ($\lambda = 0.71073$ Å) radiation. The data were scanned using Bruker's SMART program and integrated using Bruker's SAINT software.[5] The structures were solved by direct methods using SHELXS-90[6] and refined by least-squares methods on F^2 using SHELXL-97[7] incorporated in the SHELXTL[8] suite of programs.

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[3] R. T. Boeré, K. H. Moock and M. Parvez, *Z. Anorg. Allg. Chem.*, 1994, **620**, 1589.

[4] WinEPR Simfonia, version 1.25; Bruker Instruments, Inc., Billerica, MA, 1996.

[5] SAINT, version 6.22 Bruker Advanced X-ray Solutions, Inc., Madison, WI, 2001.

[6] Sheldrick, G. M. SHELXS-90. *Acta Crystallogr. A* 1990, **46**, 467.

[7] Sheldrick, G. M. SHELXL-97. Program for the Refinement of Crystal Structures, University of Gottingen, Gottingen, Germany, 1997.

[8] SHELXTL, VERSION 6.12 Program Library for Structure Solution and Molecular Graphics, Bruker Advanced X-ray Solutions, Inc., Madison, WI, 2001.

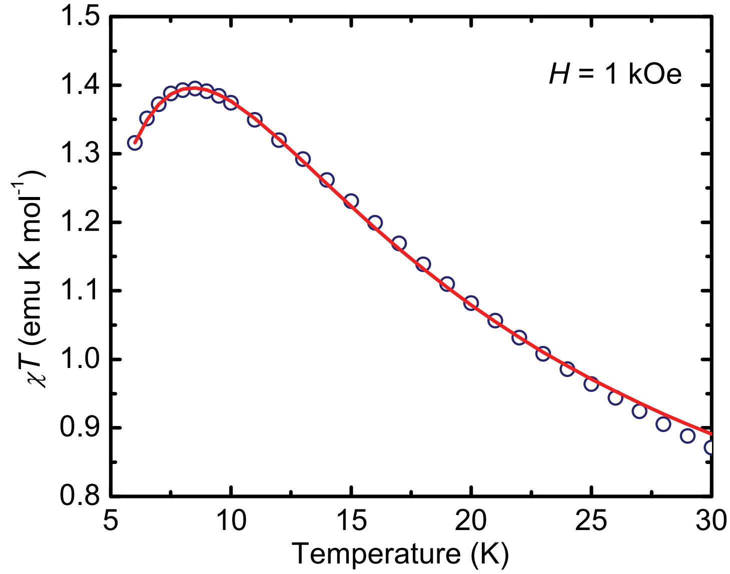
Section S2. Fitting of the magnetic data for **2a**.

The low temperature (T = 6-30 K) magnetic susceptibility of **2a** was fitted (Equation 1) to the Baker 1D S = ½ FM chain model[9] modified to include a molecular field parameter (zJ') to account for interchain interactions (Equation 2). Contributions from Temperature Independent Paramagnetism (TIP) and Curie-Weiss impurities (α) were also included (Equation 3).

$$\chi_{1D} = \frac{Ng^2\beta^2}{4k(T-\theta)}\left[\frac{1.0+5.7979916X+16.902653X^2+29.376885X^3+29.832959X^4+14.036918X^5}{1.0+2.7979916X+7.0086780X^2+8.653644X^3+4.5743114X^4}\right]^{2/3} \quad \text{(Eqn 1)}$$

$$where\ X = \frac{|J|}{2kT}$$

$$\chi_{2D} = \frac{\chi_{1D}}{1-\dfrac{2(zJ')\chi_{1D}}{Ng^2\beta^2}} \quad \text{(Eqn 2)} \qquad \chi_{calc} = \left\{\frac{\alpha\left[Ng^2\beta^2 S(S+1)\right]}{3kT} + TIP + \left[1-\alpha\right]\chi_{2D}\right\} \quad \text{(Eqn 3)}$$



Baker Fit to data from T = 6-30 K:

$\boldsymbol{J}$ = +29.5 cm^{-1}
$z\boldsymbol{J'}$ = −2.5 cm^{-1}
g = 2.009
θ = 6.6 K
α = 0.009
TIP = 0.000 emu mol^{-1}
$R^2(\chi)$* = 8.2 × 10^{-6}

*$R^2(\chi) = [\Sigma(\chi_{obs} - \chi_{calc})^2/\Sigma(\chi_{obs})^2]^{1/2}$

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[9] G. A. Baker, G. S. Rushbrooke and H. E. Gilbert, *Phys. Rev.*, 1964, **135**, A1272.