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## COMMUNICATION

## The first semiquinone-bridged bisdithiazolyl radical conductor: a canted antiferromagnet displaying a spin-flop transition<sup>†</sup>

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The alternating ABABAB  $\pi$ -stacked bis-1,2,3-dithiazolyl radical 2a (2, R<sub>2</sub> = Ph) has a conductivity  $\sigma$  of 3 × 10<sup>-5</sup> S cm<sup>-1</sup> at 300 K, and orders as a spin-canted antiferromagnet ( $T_{\rm N}$  = 4.5 K) which undergoes a spin-flop transition to a field-induced ferromagnetic state saturating (at 2 K) at  $H \sim 20$  kOe.

Interest in the use of thiazyl radicals as building blocks for magnetic and conductive materials is growing rapidly, in part because the heavy heteroatom (sulfur) enhances intermolecular magnetic and electronic interactions.<sup>1</sup> Within this context radicals based on the resonance stabilized, pyridine-bridged bisdithiazolyl framework 1 (Chart 1) are appealing targets, as their solid state structures and transport properties can be finetuned by variations in the size of the exocyclic ligands  $R_1/R_2$ , and/or by replacement of sulfur by its heavier congener selenium.<sup>3,4</sup> The steric bulk of the ligands also helps suppress dimerization, but generally gives rise to herringbone arrays of slipped  $\pi$ -stacks in which orbital overlap along the stacking direction is diminished. In order to avoid the herring-bone mold found for 1 we are now exploring radicals based on the isoelectronic semiquinone-bridged skeleton 2. Herein we report the preparation, structure and transport properties of 2a  $(2, R_2 = Ph)$ , the first example of this new class of radical.



The synthetic sequence to 2a (Scheme 1) begins with a double Herz cyclization of 4-phenyl-2,6-diamino-phenol dihydrochloride  $3^5$  with sulfur monochloride in MeCN at reflux, a process which affords the semiquinone-bridged bis-dithiazolylium chloride [2a][Cl] as a blue-black insoluble solid. Metathesis of this material with silver triflate (AgOTf) in MeCN yields a deep purple solution which, upon solvent removal, leaves metallic green crystals of the triflate salt [2a][OTf]. This material may be recrystallized from MeCN, and its structure has been confirmed by X-ray diffraction.<sup>‡</sup> Reduction of [2a][OTf] with octamethylferrocence (OMFc) yields radical 2a as lustrous black needles.



Cyclic voltammetry on a solution of [2a][OTf] in MeCN (Fig. 1) indicates a reversible +1/0 couple with  $E_{\frac{1}{2}} = 0.108$  V vs. SCE. The second reduction, corresponding to the -1/0 couple, is not reversible, but the cell potential  $E_{cell} = E_{\frac{1}{2}}(ox) - E_{\frac{1}{2}}(red)$  for 2a may nonetheless be estimated in terms of the difference in the two cathodic peak potentials  $E_{pc}$ . The  $E_{cell}$  value (0.60 V) so obtained is substantially smaller than that typically found for 1,<sup>2</sup> which suggests that, in the solid state, semiquinone-bridged radicals 2 will enjoy a lower onsite Mott-Hubbard Coulomb repulsion energy U.<sup>6</sup> The spin distributions of the two systems are, however, quite similar, as indicated by the EPR spectrum of 2a (Fig. 1), which consists of a five-line pattern (g = 2.00093) arising from hyperfine coupling to the two equivalent nitrogens (I(<sup>14</sup>N) = 1) with  $a_N = 0.352$  mT.



**Fig. 1** (a) CV scan of [**2a**][OTf] with Pt electrodes, 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> supporting electrolyte, scan rate 100 mV s<sup>-1</sup>. (b) X-band EPR spectrum of **2a** in toluene at 20 °C.

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**Fig. 2** Unit cell drawing of 2a, viewed perpendicular to the *yz* plane, with intermolecular S3…O' contacts shown with dashed lines.



**Fig. 3** Two views of the alternating ABABAB  $\pi$ -stacks in **2a**, with intrastack S1...S3' contacts d<sub>1</sub> and d<sub>2</sub>.

The crystal structure of **2a** belongs to the non-centric space group  $P2_12_12_1$ , and consists (Fig. 2) of sheets of approximately coplanar radicals laced together by a series of intermolecular S3...O' contacts (2.858 Å). These sheets are packed in layers to produce alternating ABABAB  $\pi$ -stacks in which adjacent radicals are related by the 2-fold screw axis along x (Fig. 3). Nearest neighbors along the  $\pi$ -stacks are separated by S1...S3' contacts d<sub>1</sub> (3.680 Å) and d<sub>2</sub> (3.806 Å), both of which are nominally outside the S...S' van der Waals separation.<sup>7</sup> At a molecular level there are small increases in the S–N and S–S distances in the radical relative to those in the cation that can be related to the occupation of an antibonding SOMO.<sup>2</sup> The C=O distance in the radical (1.225(4) Å) is also slightly longer than in the cation (1.204(2) Å).

The alternating  $\pi$ -stack motif found for **2a**, coupled with the paucity of close intercolumnar S····S' contacts, suggests a relatively one-dimensional electronic structure which might be considered susceptible to a symmetry-lowering, spin-pairing instability, as observed in related radicals with ABABAB  $\pi$ -stacked structures.<sup>8</sup> However, variable temperature (from T = 2-300 K) magnetic susceptibility  $\chi$  measurements (corrected for diamagnetic contributions)<sup>9</sup> establish that this is not the case. For example, a plot of  $\chi T$  (field cooled) *vs*. *T* at a field



**Fig. 4** Plot of  $\chi T vs. T$  for **2a** at H = 1 kOe. Inset shows ZFC-FC plots of  $\chi vs. T$  at H = 100 Oe.

H = 1 kOe (Fig. 4) indicates paramagnetic behavior, with strong local ferromagnetic interactions; a Curie–Weiss fit to the data above 100 K affords C = 0.349 emu K mol<sup>-1</sup> and  $\theta = +32.8$  K. Application of the Baker model<sup>10</sup> for a Heisenberg 1D FM-coupled chain ( $\pi$ -stack) of  $S = \frac{1}{2}$  centers to the data over the range T = 6-30 K yields exchange coupling constants J = 29.5 cm<sup>-1</sup> for interactions along the  $\pi$ -stacks, and zJ' = -2.5 cm<sup>-1</sup> for the cumulative interstack (mean field) interactions.

Additional measurements at lower fields revealed the onset of a slight low temperature discontinuity in  $\chi(T)$  for H < 200 Oe, and a subsequent ZFC-FC experiments at H = 100 Oe (Fig. 4, inset) established a phase transition at 4.5 K. The resulting state may be viewed in terms of spin-canted AFMordering based on the antiparallel alignment of the FM-coupled chains ( $\pi$ -stacks). The degree of canting is, however, very small, as no spontaneous magnetization could be detected. The value of  $T_{\rm N} = 4.5$  K obtained from the ZFC-FC measurements nonetheless compares well with that (6.2 K) estimated using the expression  $kT_{\rm c} \approx 2S^2 (|zJ'| \cdot J^{\frac{1}{2},11}$  which may be derived from mean field theory, with  $S = \frac{1}{2}$  and using values of J and zJ' cm<sup>-1</sup> obtained from the Baker fit to the 1D FM chain model.



**Fig. 5** Plots of M vs. H (left) and dM/dH vs. H (right) for **2a** at T = 2, 5 and 10 K.

Magnetization (*M*) vs. field (*H*) measurements (Fig. 5, left) on **2a** at different temperatures have provided additional insight into its magnetic structure. At T = 2 K, for example, the value of M rises sharply with H, reaching a plateau at 1.00 N $\beta$ , the saturation value expected for a  $S = \frac{1}{2}$  system with a nominal  $g \approx 2$ , just above H = 20 kOe. There is no evidence of hysteresis. At temperatures above  $T_N$ , M rises less steeply, and with decreasing dM/dH, so that saturation does not occur out to H = 50 kOe, the limit of the experiment. These results are broadly consistent with metamagnetic behavior,<sup>12</sup> in which the antiparallel alignment of the FM ordered radical  $\pi$ -stacks is reversed by the field, so that all the chains become aligned in parallel, producing a field-induced FM ordered material. However, a characteristic feature for such systems is an inflexion in the M vs. H plot, with dM/dH reaching a maximum at the field where magnetic realignment occurs. Several nonmetallic radicals and radical ions displaying this behavior have been reported.<sup>13,14</sup> In this case, however, no inflexion is observed in the M vs. H plot, nor is any maximum apparent in the dM/dH vs. H plot (Fig. 5, right) prior to saturation, even at T = 2 K. This result, plus the fact that ZFC-FC measurements establish that AFM ordering collapses above H = 200 Oe, is more consistent with a spin-flop transition.<sup>15–17</sup> The profiles of the *M* vs. *H* curves at  $T > T_N$  are also in keeping with such a process.15



Fig. 6 Log plot of conductivity of 2a vs. inverse temperature.

Variable temperature 4-probe conductivity ( $\sigma$ ) measurements (Fig. 6) on **2a** indicate that  $\sigma(300 \text{ K})$  ( $3 \times 10^{-5} \text{ S cm}^{-1}$ ) is superior to that typically found for the slipped  $\pi$ -stack arrangements of **1**.<sup>2</sup> Moreover, the thermal activation energy  $E_{act} = 0.20 \text{ eV}$ , derived from data collected over T = 160-300 K, is substantially lower than that (0.4–0.5 eV) typically found for **1**.<sup>2</sup> This improved performance, which probably derives from a combination of increased intermolecular overlap afforded by the almost direct superposition of the radicals, and a decreased onsite Coulomb potential *U*, augurs well for the use of semiquinone-bridged radicals **2** in the design of new single-component, molecular electronic and magnetic materials.

The present results also reveal the importance of the lateral  $S \cdots O'$  contacts<sup>18</sup> as supramolecular synthons in the development of sheet-like networks of radicals which are resistive to Peierls-type distortions. The incorporation of the semiquinone unit, as found in **2**, therefore represents a significant structural as well electronic advance over pyridine-bridged radicals **1**. The availability of the carbonyl oxygen for coordination to metals<sup>19</sup> is also a potentially attractive feature.

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## Notes and references

‡ Crystal data at 296(2) K for [**2a**][OTf]:  $C_{13}H_5F_3N_2O_4S_5 M = 470.49$ , monoclinic, a = 8.4534(4), b = 12.9782(6), c = 16.2121(7) Å,  $\beta = 102.762(1)$ , V = 1734.69(14) Å<sup>3</sup>, space group  $P2_1/c$  (#14), Z = 4,  $D_c = 1.802$  g cm<sup>-3</sup>,  $\mu = 0.723$  mm<sup>-1</sup>; 300 parameters were refined using 4183 unique reflections ( $R_{int} = 0.0289$ ) to give R = 0.0366 and  $R_w = 0.0721$  (observed data). Crystal data at 296(2) K for **2a**:  $C_{12}H_5N_2084 M = 321.42$ , orthorhombic, a = 6.8011(7), b = 11.3785(12), c = 15.6525(16) Å, V = 1209.2(2) Å<sup>3</sup>, space group  $P2_{1/21}$  (#19), Z = 4,  $D_c = 1.766$  g cm<sup>-3</sup>,  $\mu = 0.774$  mm<sup>-1</sup>; 174 parameters were refined using 3431 unique reflections ( $R_{int} = 0.0444$ ) to give R = 0.0547 and  $R_w = 0.0739$  (observed data).

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