

# Synthesis and Multistage Redox Properties of 9,10-Bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene Derivatives Functionalized with Ferrocenyl and Tetrathiafulvalenyl Units

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There is considerable current interest in the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene system as an electron donor moiety for the formation of novel organic conductors. The parent compound **1**,<sup>1</sup> derivatives bearing substituents on the 1,3-dithiole rings,<sup>2</sup> and heterocyclic analogues containing 1,3-selenathiol-2-ylidene,<sup>1c,2b</sup> 1,2,5-thiadiazole,<sup>3</sup> 1,2,5-selenadiazole,<sup>3</sup> and quinoxaline rings<sup>4</sup> have been studied in this context.<sup>5</sup> Important features of system **1** are (i) its high electron donor ability, which is characterized by a single two-electron wave to yield a thermodynamically stable dication at  $E_{1^{ox}} = ca. +0.3$  V (vs Ag/AgCl) in the cyclic voltammogram;<sup>1c,6</sup> (ii) the unusual saddle shaped structure of the molecule, as revealed by single crystal X-ray analysis, enforced by the boat conformation of the central anthracenediylidene ring, which, in turn, results from steric crowding of the sulfur atoms and the *peri* hydrogens.<sup>2a</sup> Taken together, these properties suggest that this framework has considerable potential as a building block in supramolecular redox systems.<sup>7</sup> From this viewpoint we now report the covalent attachment to system **1**, via ester linkages, of other electron donor moieties, specifically tetrathiafulvalenyl and ferrocenyl groups, to yield triad assemblies **8** and **9**, of general structure D<sup>1</sup>- $\sigma$ -D<sup>2</sup>- $\sigma$ -D<sup>1</sup>, along with a study of their redox behavior.<sup>8</sup>

Compound **6** was targeted since 2,6-dihydroxyanthraquinone (**3**) is commercially-available, and the hydroxy substituents of **6** should provide a suitable 'handle' for further reactions. Methylthio-substituted 1,3-dithiole rings were chosen for three reasons: (i) the Horner-Wittig reagent **7** is readily available from cheap starting

materials;<sup>9</sup> (ii) the methylthio substituents have the benefit of slightly raising the oxidation potential of the anthracenediylidene system relative to derivative **1**, thereby increasing the air-stability of the compounds;<sup>9</sup> and (iii) the solubility of such systems is improved by the presence of methylthio groups. 2,6-Dihydroxyanthraquinone (**3**) was protected as the bis-silylated derivative **4** by reaction with *tert*-butylchlorodiphenylsilane in the presence of imidazole (61% yield). Two-fold reaction of quinone **4** with the phosphorus-stabilized carbanion generated from reagent **7**<sup>9a</sup> (*n*-butyllithium, THF, 20 °C) gave derivative **5** (59% yield) which was deprotected (tetrabutylammonium fluoride, THF) to give diol **6** (*ca.* 70% yield). Compound **6** was only sparingly soluble in common organic solvents which hindered purification and precluded its use in further reactions. Nonetheless, derivatives of **6** were prepared from the soluble silylated derivative **5** in a one-pot procedure, without isolation of diol **6**. Accordingly, a solution of **5** in THF was treated with fluoride ion in the presence of ferrocenylcarbonyl chloride<sup>10</sup> or tetrathiafulvalenylcarbonyl chloride<sup>11</sup> and triethylamine, to afford compounds **8** (55% yield) and **9** (30% yield), respectively, as shelf-stable solids which are soluble in organic solvents, e.g. halocarbons.

The solution electrochemistry of compounds **8** and **9** has been studied by cyclic voltammetry; the data are collated in Table 1 along with data for model compounds and the cyclic voltammograms are shown in Figure 1. For compound **8** oxidation of the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene moiety occurs as a single, two-electron, quasireversible wave ( $E_{1^{ox}} = +0.61$  V,  $E_{1^{red}} = +0.32$  V) to yield the dication species. The assignment of this wave as a two-electron process is based upon literature precedent for this donor framework.<sup>6</sup> Simultaneous oxidation of the two ferrocene units gives the ferrocene/ferrocinium redox couple, observed as a cleanly reversible wave at  $E^{1/2} = +0.75$  V, to afford a system bearing four positive charges. The cyclic voltammogram of compound **9** reveals that the two-electron oxidation of the anthracenediylidene and the first oxidation of the two TTF units (neutral TTF  $\rightarrow$  TTF<sup>•+</sup>) are not resolved and occur as a single, broad peak at  $E_{1^{ox}} = +0.50$  V. The second oxidation of the TTF units (TTF<sup>•+</sup>  $\rightarrow$  TTF<sup>2+</sup>) occurs as a quasireversible couple ( $E_{2^{ox}} = +0.94$  V,  $E_{3^{red}} = +0.82$  V) to generate a system bearing six positive charges.<sup>12</sup> The reduction of the TTF radical cations to neutral TTF and the two-electron reduction of the anthracenediylidene moiety are just resolved, occurring at  $E_{2^{red}} = +0.42$  V and  $E_{1^{red}} = +0.36$  V, respectively.

From these data for both compounds **8** and **9** there appears to be some inter- or intramolecular interactions between the different redox moieties in the system which

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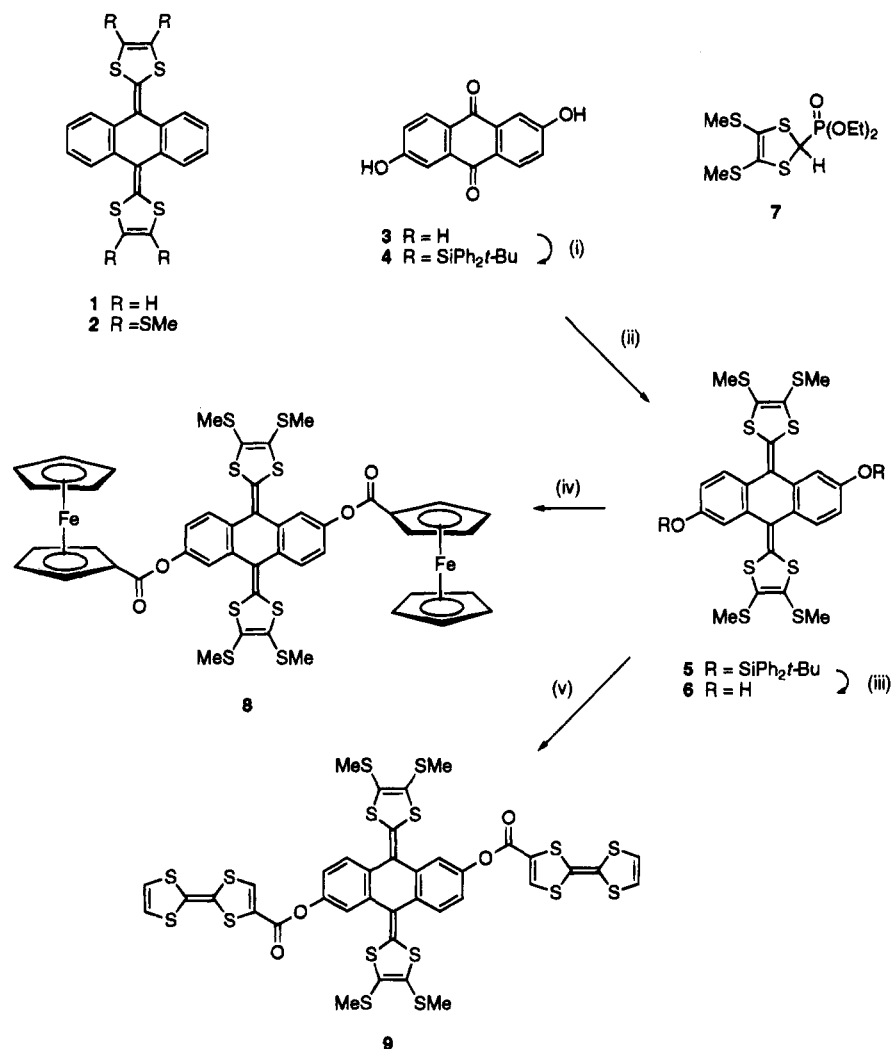
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Scheme 1<sup>a</sup>

<sup>a</sup> Reagent and Conditions: (i) *tert*-butyldiphenylchlorosilane, imidazole, DMF, 20 °C; (ii) reagent 7, *n*-butyllithium, THF, 20 °C; (iii) tetrabutylammonium fluoride, THF, 20 °C; (iv) ferrocenecarbonyl chloride, triethylamine, tetrabutylammonium fluoride, THF, 20 °C; (v) tetrathiafulvalenecarbonyl chloride, triethylamine, tetrabutylammonium fluoride, THF, 20 °C.

Table 1. Cyclic Voltammetric Data<sup>a</sup>

donor	$E_{1}^{ox}/V$	$E_{2}^{ox}/V$	$E_{1}^{red}/V$	$E_{2}^{red}/V$	$E_{3}^{red}/V$
8	+0.61	+0.78	+0.32	+0.73	
9	+0.50	+0.94	+0.36	+0.42	+0.82
TTF-CO <sub>2</sub> Me	+0.48	+0.87	+0.41	+0.80	
Fc-CO <sub>2</sub> Me	+0.65		+0.58		
2	+0.60		+0.31		

<sup>a</sup> Data were obtained at 20 °C versus Ag/AgCl, in dry dichloromethane under argon using a platinum button electrode and a platinum wire counter electrode, *ca.*  $5 \times 10^{-4}$  M compound, 0.1 M tetrabutylammonium hexafluorophosphate, scan rate 100 mV s<sup>-1</sup>, using a BAS 100 electrochemical analyzer.

are electronically isolated from each other by the ester spacer groups. The irreversibility of the anthracenediylidene oxidation process arises jointly from a change in conformation and aromatic stabilization. At the dication redox stage there is a gain in aromaticity of the newly-formed anthracene system and the  $6\pi$ , 1,3-dithiolium cation rings. The marked conformational change that must occur on reduction (planar anthracene  $\rightarrow$  buckled anthraquinodimethane)<sup>2a</sup> is the other factor accounting for the observed redox behavior in this system. It is notable that the anodic peak potential ascribed to the anthracenediylidene moiety in 8 is different from that in 9, and the TTF units in 9 do not show

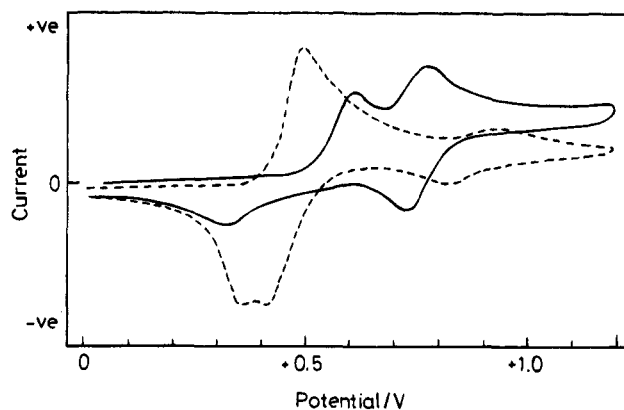


Figure 1. Cyclic voltammograms of compound 8 (—) and compound 9 (---).

a cleanly reversible second redox wave, in contrast to most TTF derivatives, e.g. TTF-CO<sub>2</sub>Me (Table 1).

In summary, we have established that ferrocene and TTF units can be conveniently attached to the 9,10-bis-(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene framework to produce D<sup>1</sup>- $\sigma$ -D<sup>2</sup>- $\sigma$ -D<sup>1</sup> triad systems which display well-defined electrochemical properties. The study of highly-

functionalized redox assemblies of this type is relevant to the development of molecular materials with potential future applications in the arena of molecular electronics<sup>7b</sup> and nanotechnology.<sup>13</sup>

### Experimental Section

**General Details.** Details of instrumentation have been reported recently.<sup>14</sup>

**2,6-Bis[(*tert*-butyl-diphenylsilyl)oxy]anthraquinone (4).** To a solution of 2,6-dihydroxyanthraquinone (5.00 g, 20.8 mmol) in DMF (250 mL) was added *tert*-butylchlorodiphenylsilane (13.75 g, 50.0 mmol) followed by imidazole (14.17 g, 208 mmol) and the reaction stirred under nitrogen at 20 °C for 16 h. DMF was removed *in vacuo*, the residue dissolved in dichloromethane, washed with water, and dried (MgSO<sub>4</sub>), and solvent removed *in vacuo*. Chromatography of the residue on silica gel, eluent hexane/dichloromethane (2:1 v/v) afforded compound **4** (9.05 g, 61%) as a yellow solid, mp 226–228 °C. Anal. Calcd for C<sub>46</sub>H<sub>44</sub>O<sub>4</sub>Si<sub>2</sub>: C, 77.0; H, 6.2. Found: C, 77.0; H, 6.2%. *m/z* (DCI) 717 (M<sup>+</sup> + 1); δ<sub>H</sub>(CDCl<sub>3</sub>) 7.95, 7.63, and 6.94 (2 × AMX each 3H, *J*<sub>AX</sub> = 8.4, *J*<sub>MX</sub> = 2.7 and *J*<sub>AM</sub> < 1 Hz), 7.70 (8H, m), 7.40 (12H, m), 1.13 (18H, s); ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 3070, 2931, 2857, 1672, 1587, 1313, 904, 701.

**2,6-Bis[(*tert*-butyldiphenylsilyl)oxy]-9,10-bis[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-9,10-dihydroanthracene (5).** To a solution of Horner–Wittig reagent **7**<sup>9</sup> (4.65 g, 14.0 mmol) and compound **4** (4.01 g, 5.60 mmol) in dry THF (150 mL) at 20 °C, was added *n*-butyllithium (1.6 M, 9.63 mL, 15.4 mmol) dropwise with stirring under nitrogen over 10 min. Stirring was continued for 16 h after which time chromatography of the crude reaction mixture on silica gel, eluent hexane/dichloromethane (2:1 v/v), afforded compound **5** (3.52 g, 59%) as a yellow solid: mp 242–244 °C. Anal. Calcd for C<sub>56</sub>H<sub>56</sub>O<sub>2</sub>S<sub>8</sub>Si<sub>2</sub>: C, 62.6; H, 5.3. Found: C, 62.9; H, 5.4%. *m/z* (DCI) 1073 (M<sup>+</sup> + 1); δ<sub>H</sub>(CDCl<sub>3</sub>) 7.74 (8H, m), 7.39 (12H, m),

7.19, 6.93, and 6.66 (2 × AMX each 3H, *J*<sub>AX</sub> = 8.6, *J*<sub>MX</sub> = 2.6 and *J*<sub>AM</sub> < 1 Hz), 2.34 (6H, s), 2.27 (6H, s), 1.11 (18H, s); ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 3070, 2928, 2856, 1465, 1312, 1226, 1110, 705.

**2,6-Bis[(Ferrocenylcarbonyl)oxy]-9,10-bis[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-9,10-dihydroanthracene (8).** To a solution of compound **5** (250 mg, 0.23 mmol) in dry THF (60 mL) at 20 °C was added ferrocenecarbonyl chloride<sup>10</sup> (140 mg, 0.56 mmol) followed by dry triethylamine (0.08 mL, 0.58 mmol). Tetrabutylammonium fluoride (1 M in THF, 0.93 mL, 0.93 mmol) was added dropwise over 10 min and stirring continued under nitrogen at 20 °C for 16 h. Chromatography of the crude reaction mixture on silica gel, eluent dichloromethane followed by recrystallization from dichloromethane/hexane, afforded compound **8** (130 mg, 55%) as a yellow solid: mp > 200 °C dec. Anal. Calcd for C<sub>46</sub>H<sub>36</sub>Fe<sub>2</sub>O<sub>4</sub>S<sub>8</sub>: C, 54.1; H, 3.6. Found: C, 53.9; H, 3.5%. *m/z* (DCI: impinging gas NH<sub>3</sub>) 1021 (M<sup>+</sup> + 1); δ<sub>H</sub>(CDCl<sub>3</sub>) 7.60, 7.40, and 7.16 (2 × AMX each 3H, *J*<sub>AX</sub> = 8.3, *J*<sub>MX</sub> = 1.7, and *J*<sub>AM</sub> < 1 Hz), 5.00 (4H, broad s), 4.53 (4H, broad s), 4.34 (10H, s), 2.41 (6H, s), 2.38 (6H, s); ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 2920, 1735, 1450, 1262, 1193, 1152, 1110, 1088.

**2,6-Bis[(tetrathiafulvalenylcarbonyl)oxy]-9,10-bis[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-9,10-dihydroanthracene (9).** To a solution of compound **5** (340 mg, 0.32 mmol) in dry THF (60 mL) at 20 °C was added tetrathiafulvalenecarbonyl chloride<sup>11</sup> (200 mg, 0.75 mmol) followed by dry triethylamine (0.11 mL, 0.79 mmol). Tetrabutylammonium fluoride (1.1 M in THF, 1.15 mL, 1.26 mmol) was added dropwise over 10 min and stirring continued under nitrogen at 20 °C for 16 h. Chromatography of the crude reaction mixture on silica gel, eluent dichloromethane, afforded compound **9** (100 mg, 30%) as an orange solid: mp 178–180 °C. Anal. Calcd for C<sub>38</sub>H<sub>24</sub>O<sub>4</sub>S<sub>16</sub>: C, 43.2; H, 2.3. Found: C, 43.5; H, 2.4%. *m/z* (PDMS) 1057.6 (M<sup>+</sup>) calcd for C<sub>38</sub>H<sub>24</sub>O<sub>4</sub>S<sub>16</sub> 1057.6; δ<sub>H</sub>[(CD<sub>3</sub>)<sub>2</sub>SO] 8.15 (2H, s), 7.57 (2H, m), 7.38 (2H, m), 7.28 (2H, m), 6.79 (4H, s), 2.40 (12H, s); ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 3066, 2916, 1720, 1534, 1461, 1256, 1223, 1186.

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