

Preparation and Characterization of a Bis-Semiquinone: A Bidentate Dianion Biradical

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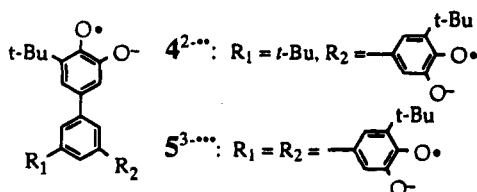
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Introduction

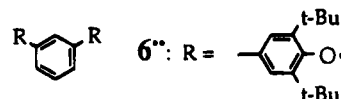
Metal-containing molecular magnetic materials are attractive since metals can serve as both a spin source and their tetrahedral or octahedral coordination spheres can provide a route to three-dimensional structures. Several approaches to metal-containing molecular systems have produced materials showing spontaneous magnetization.^{1,2}

The radical/metal combination offers great potential for preparing molecule-based magnetic materials. We hypothesize that paramagnetic, chelating ligands like 4^{•2-} and 5^{•3-} can be used as effective elements of molecular magnetic materials.³ Herein, we describe the synthesis of **4** and EPR spectra of its two-electron reduction product, 4^{•2-}.



Results and Discussion

Over the past several years chemists have been filling-in the "rule book" for preparation of high-spin molecules.^{1j} An example of a design element that ensures high-spin coupling (in the absence of steric interactions that attenuate coupling)⁴⁻⁶ involves attaching spin-containing functional groups *meta* on a benzene ring. This motif is



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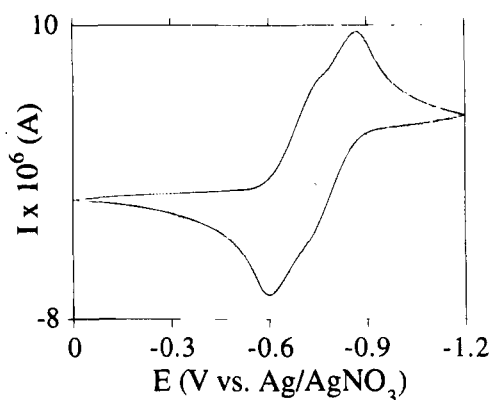
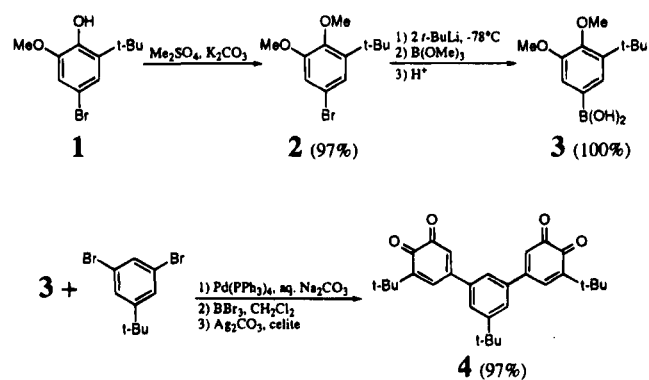


Figure 1. Cyclic voltammogram of **4** in THF (ca. 1mmol) with tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte. Scan rate = 100 mV/s.

Scheme 1



a topological equivalent of *m*-xylylene, a ground state triplet biradical with a singlet-triplet gap of ca. 10 kcal/mol.⁷ Bis-semiquinone 4^{•2-} is based on this design and is akin to the known bis-phenoxyl 6^{••}.⁸

The preparation of **4** is shown in Scheme 1. Compound **2** was prepared by methylation of the known 4-bromo-6-*tert*-butyl-2-methoxyphenol.⁹ Transmetalation of **2**, followed by quenching of the resulting aryllithium with trimethyl borate and subsequent acid hydrolysis yielded the boronic acid **3**. Suzuki coupling¹⁰ of **3** and 5-*tert*-butyl-1,3-dibromobenzene,¹¹ followed by deprotection of the methyl ethers using BBr₃, and oxidation of the resulting catechol derivative using Fetizon's reagent¹² provided **4** in excellent yield.

Cyclic voltammetry of **4** in THF at room temperature with tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte revealed two distinct reduction processes, the first of which is shown in Figure 1. This process is composed of two, reversible, sequential one-electron transfers centered near -0.76 V vs Ag/AgNO₃,

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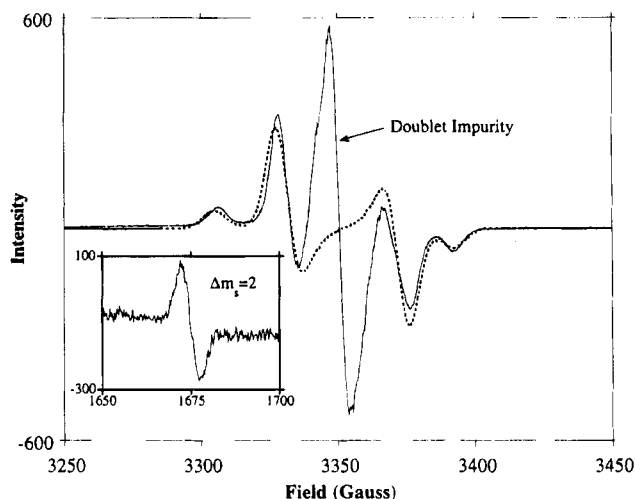


Figure 2. Experimental (—) and simulated (---) EPR spectra of $4^{\bullet\bullet 2-}$. The zero-field splitting parameters, $|D/hc|$ and $|E/hc|$ for $4^{\bullet\bullet 2-}$ were found by simulation¹⁵ to be 0.004112 and 0 cm^{-1} , respectively, with $g_{xx} = g_{yy} = 2.0035$ and $g_{zz} = 2.0055$ ($g_{av} = \frac{1}{3}(g_{xx} + g_{yy} + g_{zz}) = 2.0042$). The experimental spectrum was recorded from a solution of $4^{\bullet\bullet 2-}$ prepared by bulk electrolysis at room temperature of **4** in THF with tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte, and it contains a small amount of doublet impurity. Inset: $\Delta m_s = 2$ transition. The spectra were recorded at 77 K.

and corresponds to two orthoquinone/semiquinone couples.¹³ The first and second reduction potentials are separated by 115 mV, a separation which is common for *m*-phenylene-bridged structures.¹⁴ The second reduction process is chemically irreversible (not shown), occurring near -1.8 V vs Ag/AgNO₃, and corresponds to the semiquinone/catecholate couples.¹³ Exhaustive controlled potential coulometry at -1.2 V vs Ag/AgNO₃ indicated that two electrons were transferred to **4** yielding a dianion-biradical, $4^{\bullet\bullet 2-}$.

The EPR spectrum of a THF solution of $4^{\bullet\bullet 2-}$ obtained by bulk electrolysis was recorded at 77 K and is shown in Figure 2 along with a simulated spectrum. The solution of the dianion is stable for at least one week if kept under inert atmosphere in the absence of light. The spectrum is typical of a randomly oriented triplet ($S = 1$) species¹⁵ containing a small amount of doublet impurity. The intensity of the doublet signal varied from preparation to preparation, while the relative intensities of the four outermost signals did not, supporting the assignment of the central signal as a byproduct of the reduction. Of particular importance is the appearance of a $\Delta m_s = 2$ transition near 1675 G (inset of figure)—the

signature of a high-spin state. The zero-field splitting parameters, $|D/hc|$ and $|E/hc|$ for $4^{\bullet\bullet 2-}$ were found by simulation¹⁶ to be 0.004112 and 0 cm^{-1} , respectively with $g_{xx} = g_{yy} = 2.0035$ and $g_{zz} = 2.0055$ ($g_{av} = \frac{1}{3}(g_{xx} + g_{yy} + g_{zz}) = 2.0042$). These values are similar to those of **6**^{••} ($|D/hc| = 0.00318$ cm^{-1} ; $|E/hc| = 0.00028$ cm^{-1} ; $g_{xx} = 2.0051$; $g_{yy} = 2.0035$; and $g_{zz} = 2.0024$; $g_{av} = 2.0037$),⁸ confirming both the electronic similarity between $4^{\bullet\bullet 2-}$ and **6**^{••} as well as the assignment of $4^{\bullet\bullet 2-}$ as a biradical dianion. Variable temperature EPR experiments are being planned to determine both the ground state multiplicity and the singlet-triplet gap in $4^{\bullet\bullet 2-}$.

Conclusions

We have prepared a new bis-orthoquinone molecule that can undergo a two-electron reduction to a bis-semiquinone, $4^{\bullet\bullet 2-}$. The EPR spectrum of a frozen solution of $4^{\bullet\bullet 2-}$ is typical of an axially symmetric $S = 1$ species. Variable temperature EPR experiments are being planned to determine both the ground state multiplicity and the singlet-triplet gap in $4^{\bullet\bullet 2-}$. Efforts at preparing metal complexes of $4^{\bullet\bullet 2-}$ and similar species are underway.

Experimental Section

Solvent distillations, synthetic procedures, and electrochemistry were carried out under an argon atmosphere. THF was distilled from sodium benzophenone-ketyl prior to use. Methylene chloride was distilled from calcium hydride. Electrochemical experiments were performed with a EG&G PAR Model 273A potentiostat. THF solutions for electrochemistry were 1.5 mM (voltammetry) or 500 μM (coulometry) in substrate and 100 mM in tetra-*n*-butylammonium hexafluorophosphate (TBAH) electrolyte. TBAH was recrystallized three times from 95% ethanol and dried at 125 $^{\circ}\text{C}$ *in vacuo* for 24 h prior to use. Pt disk and Pt wire served as the working and auxiliary electrodes, respectively, and the reference electrode was Ag/AgNO₃ in acetonitrile. All electrochemistry experiments were performed at room temperature under nitrogen. For bulk electrolysis, a standard "H" cell was used with Pt mesh working and counter electrodes and Ag/AgNO₃ in acetonitrile reference electrode. EPR samples were prepared by pipetting a 1 mL aliquot of the bulk electrolysis product into the side arm of a quartz EPR tube attached to a vacuum stopcock. The solution was subjected to four freeze-pump-thaw cycles and closed under vacuum. X-band EPR spectra were recorded on an IBM-Brüker E200SRC spectrometer.

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Supplementary Material Available: Synthetic details and spectral data (2 pages).

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