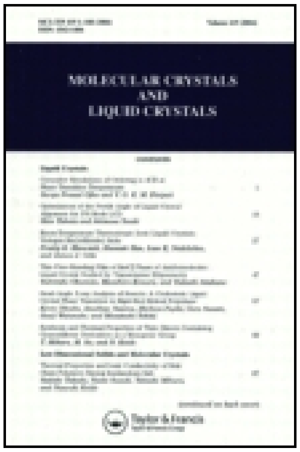

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Preparation of Paramagnetic Ligands for Coordination-Complexes and Networks with Interesting Magnetic Properties

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PREPARATION OF PARAMAGNETIC LIGANDS FOR COORDINATION-COMPLEXES AND NETWORKS WITH INTERESTING MAGNETIC PROPERTIES

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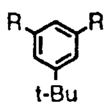
Abstract We hypothesize that paramagnetic, multidentate, chelating ligands can be used to create molecular magnetic materials with high ordering temperatures. The ligands proposed for such materials are di-, tri-, and oligosemiquinone molecules. This paper will discuss the synthesis and characterization of these semiquinone ligands.

INTRODUCTION

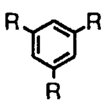
Metal-containing molecular magnetic materials are attractive since metals can serve as a spin source and their coordination spheres can provide a rational approach to extended networks. Different approaches to metal-containing molecular systems have produced materials showing spontaneous magnetization, including: charge-transfer complexes prepared by Miller and coworkers,[1] ferrimagnetic chains by Kahn et al,[2-5] metal-radical complexes by Caneschi, Gatteschi, and coworkers[6, 7] and Iwamura and coworkers,[8-10] mixed-metal assemblies by Matsumoto and Okawa,[11-14] and metal oxalate networks by Decurtins and coworkers.[15, 16]

We feel that the radical/metal approach offers considerable potential for preparing molecule-based magnetic materials. We hypothesize that paramagnetic, chelating ligands like those shown below, can be used to create metal complex networks with high ordering-temperatures. Our contention is based on several design elements: the proposed ligands form octahedral metal complexes favoring three-dimensionality — a prerequisite for bulk magnetism; semiquinone ligands are chelating and therefore their complexes have more built-in order than those of monodentate ligands; semiquinones are paramagnetic, thus the total spin angular momentum of the building blocks can be augmented; our design can take advantage of large ligand-metal antiferromagnetic exchange couplings to yield ferrimagnetic materials.

Over the past several years organic chemists have begun filling-in the "rule book" for preparing high-spin molecules, and the synthesis of paramagnetic ligands can be based on this growing body of knowledge. Factors to consider include topology, conjugation, steric interactions, and substituent effects. Semiquinones and **6sq**$_2$ and **7sq**$_3$ are expected to exhibit high-spin ground states based on the findings of a related nitroxide molecule studied by Iwamura.[17] Confidence in the assignment of a high-spin ground state to **10sq**$_2$, a trimethylenemethane-type system, is less straightforward owing to steric interactions of the semiquinone rings with the adamantane bridgehead protons. Elucidation of the ground spin-state of **10sq**$_2$ will be reported elsewhere in the near future. Herein, we describe the synthesis and 77K EPR spectra of **6sq**$_2$, **7sq**$_3$, **10sq**$_2$, as well as the preparation of **poly[16bq]**.[18]

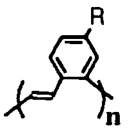


6sq$_2$



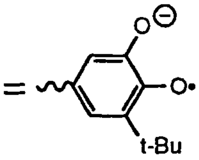
7sq$_3$

10sq$_2$



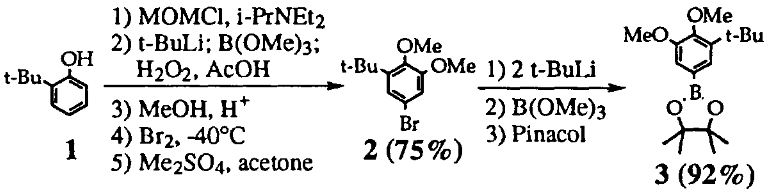
poly[16sq]

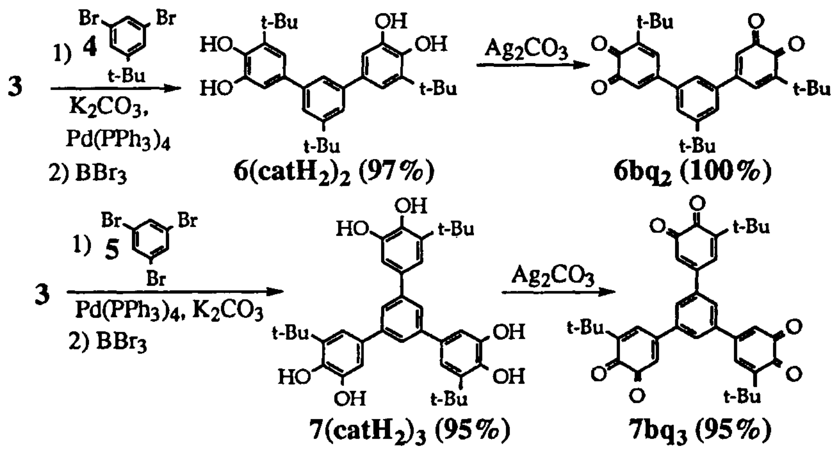
R =



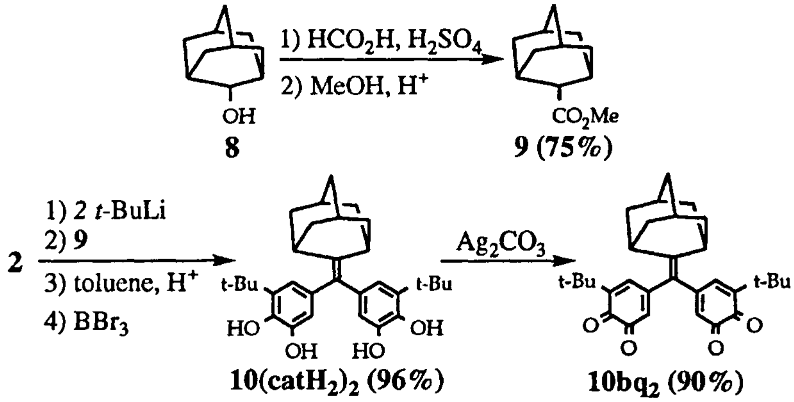
RESULTS AND DISCUSSION

Compound **2** was prepared by ortho-metallation of methoxymethyl protected 2-*t*-butylphenol, reaction of the aryllithium with trimethylborate, oxidation using H_2O_2/AcOH, removal of the methoxymethyl group, bromination, and methylation. Transmetallation of **2**, followed by quenching of the resulting aryllithium with trimethylborate and subsequent reaction with pinacol yielded the boronic ester **3**. Suzuki coupling[19] of **3** with **4**[20] and commercially available **5**, followed by deprotection of the methyl ethers using BBr_3, gave catechols **6(catH**$_2$**)**$_2$ and **7(catH**$_2$**)**$_3$, respectively. Oxidation of the catechol derivatives using Fetizon's reagent[21] provided **6bq**$_2$ and **7bq**$_3$ in excellent yield. All compounds gave satisfactory IR, NMR (^{1}H and ^{13}C) and HRMS.

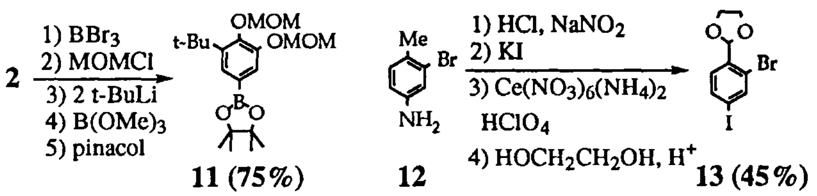


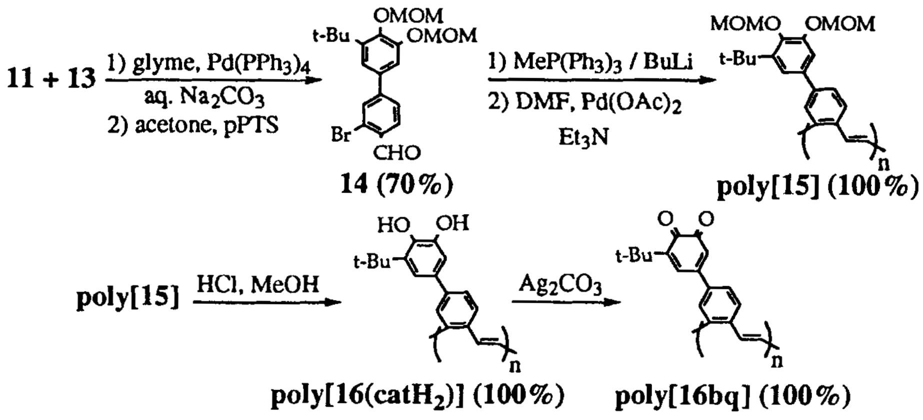


Methyleneadamantane-bisquinone, **10bq$_2$**, was prepared starting with adamantane-2-ol. Use of the Koch-Haaf[22] reaction and esterification provided ester **9** in high yield. Reaction of **9** with the lithium reagent derived from bromide **2**, followed by dehydration and deprotection gave **10(catH$_2$)$_2$** in excellent yield. Oxidation afforded the corresponding bisquinone, **10bq$_2$**.



The synthesis of a polymeric quinone is shown below. The key step involves a Heck polymerization[23-25] of a bromo-styrene derivative.





The degree of polymerization of **poly[15]** vs. polystyrene is 4-8. The intense fluorescence of **poly[15]**, characteristic of polyphenylenevinylenes, is centered near 450 nm. Fluorescence in **poly[16bq]** is dramatically diminished, consistent with the presence of the carbonyl-containing orthoquinone moiety. The IR spectrum of of **poly[16bq]** displays the characteristic stretches for the orthoquinone group at 1621 cm^{-1}, 1658 cm^{-1}, and 1684 cm^{-1}.

Cyclic voltammograms of quinones **$6bq_2$**, **$7bq_3$**, and **$10bq_2$** are shown in Figure 1. The voltammograms show two, three, and two reversible, sequential

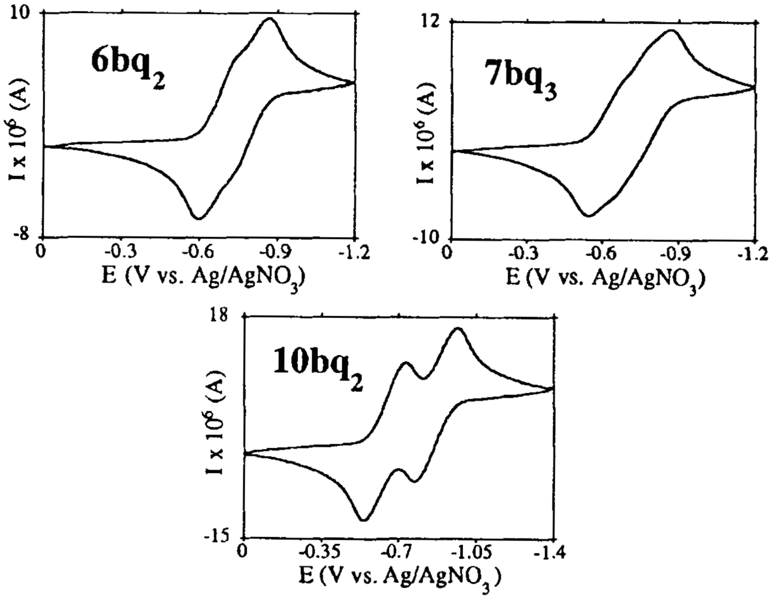


FIGURE 1 Cyclic Voltammograms of orthoquinones **$6bq_2$**, **$7bq_3$**, and **$10bq_2$** as solutions in tetrahydrofuran. Scan rate = 100 mV/s.

one-electron transfers for **6bq$_2$**, **7bq$_3$**, and **10bq$_2$**, respectively, near -0.8 V vs. Ag/AgNO$_3$, corresponding to the quinone/semiquinone couple(s)[26]. These data are consistent with the formation of a biradical dianion, a triradical trianion, and a biradical dianion by reduction of **6bq$_2$**, **7bq$_3$**, and **10bq$_2$**, respectively. The chemical reversibility of the reductions is demonstrated by equivalent amounts of charge passed for the forward and reverse reactions, i.e. $i_{p,c}/i_{p,a} \approx 1$. At more negative potentials the semiquinones are reduced to the corresponding catecholates, a process that is known to be irreversible in all but scrupulously anhydrous solvents.[26]

Controlled-potential coulometry at -1.2 V vs. Ag/AgNO$_3$ of **6bq$_2$**, **7bq$_3$**, and **10bq$_2$**, resulted in two-, three- and two-electron reductions, respectively. EPR spectra of **6sq$_2$**, **7sq$_3$**, and **10sq$_2$** were recorded at 77K and are shown in Figures 2 and 3.[27] The spectrum of **6sq$_2$** is consistent with a randomly oriented triplet species[28] along with a small amount of doublet monoradical impurity. Zero field splitting parameters are shown in Figure 2. In addition, a $\Delta m_s = 2$ transition appeared near half-field. The spectrum of **7sq$_3$** is typical of a randomly oriented, axially symmetric quartet (S = 3/2) species.[28] As expected, there are five transitions in the $\Delta m_s = 1$ region ($g \approx 2$) of the spectrum. The zero-field splitting parameters are given in Figure 2. Triradical **7sq$_3$** also has a $\Delta m_s = 2$ absorption with shoulders on either side of the transition maximum. The $\Delta m_s = 1$ region of the spectrum of **7sq$_3$** is also consistent with a triplet biradical containing doublet impurity. However, the g = 2 signal, in part, could be due to thermally-populated doublet states. The observation of a $\Delta m_s = 3$ transition would distinguish between the possibilities, unfortuneately, none was

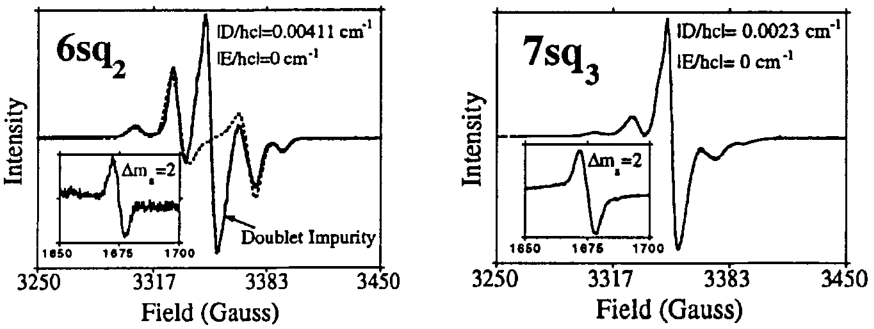
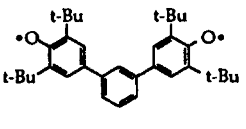


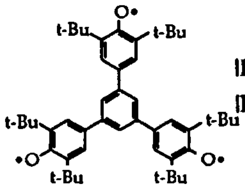
FIGURE 2 EPR spectra recorded at 77K of quinones **6sq$_2$** and **7sq$_3$** as solutions in tetrahydrofuran. The dotted line spectrum for **6sq$_2$** is a simulation using $g_{xx} = g_{yy} = 2.0035$, $g_{zz} = 2.0055$, $|D/hc| = 0.004112 cm^{-1}$, $|E/hc| = 0 cm^{-1}$.

observed at the X-band frequency. Efforts are underway to prove the existence of the S = 3/2 state for **7sq$_3$**.

The frozen solution spectra for **6sq$_2$** and **7sq$_3$** are similar to those for the corresponding phenoxy radicals,[29, 30] shown below, illustrating the electronic similarity between the pairs of radicals.

|D/hcl| = 0.00318 cm^{-1}
|E/hcl| = 0.00028 cm^{-1}





|D/hcl| = 0.0021 cm^{-1}
|E/hcl| = 0 cm^{-1}

The EPR spectrum and zfs parameters of **10bq$_2$** is shown below. As with **6bq$_2$** and **7sq$_3$**, a $\Delta m_s = 2$ transition is observed near half field. The intensity of the peak near 3275 G varies from preparation to preparation, and might be associated with dissolved oxygen present during electrolysis.

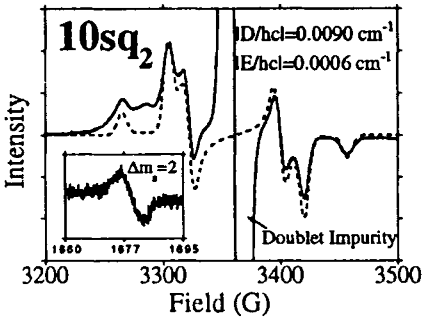


FIGURE 3 EPR spectrum recorded at 77K of **10sq$_2$** as a solution in tetrahydrofuran. The dotted line spectrum is a simulation using $g_{xx} = g_{yy} = 2.0065$, $g_{zz} = 2.0055$, |D/hc| = 0.0090 cm^{-1}, |E/hc| = 0.0006 cm^{-1}.

CONCLUSIONS

We have prepared several semiquinone ligands to be used for preparation of coordination polymer networks. Electrochemical results and EPR spectra of these semiquinones are consistent with the structure of the molecules. Unequivocal assignment of an S = 3/2 state to **7sq$_3$** was not possible due to the absence of a $\Delta m_s = 3$ transition in the EPR spectrum. Spectroscopic results for **poly[16bq]** are also consistent with the proposed structure. This polymer should complement the nitroxide polymers of Nishide and Tsuchida, et al[23, 31] in that high-spin coupling along the mainchain should be supplemented by strong metal complex-imposed interchain coupling. Assignment of ground spin-states for **6sq$_2$**, **7sq$_3$**, and **10sq$_2$** awaits variable-temperature EPR and magnetometry experiments. In addition, efforts are underway toward preparation of molecular metal complexes of these ligands to assist in determining the spin-spin coupling within the ligands.

EXPERIMENTAL

Solvent distillations, synthetic procedures, electrochemistry, and EPR sample preparation were carried out under an argon or nitrogen atmosphere. Reported yields are unoptimized. Electrochemical experiments were performed with a EG&G PAR Model 273A potentiostat. THF (anhydrous) solutions for electrochemistry were 1.5 mM (voltammetry) or 200 μM (coulometry) in substrate and 100 mM in tetra-*n*-butylammonium hexafluorophosphate electrolyte. Pt disk and Pt wire served as the working and auxiliary electrodes, respectively, and the reference electrode was Ag/AgNO$_3$ in acetonitrile. Bulk electrolyses were performed using a standard "H" cell equipped with Pt mesh working and counter electrodes and Ag/AgNO$_3$ in acetonitrile reference electrode. X-band EPR spectra were recorded on an IBM-Brüker E200SRC spectrometer.

ACKNOWLEDGMENTS

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