

## Preparation and Characterization of a Bis-galvinoxyl-disulfide

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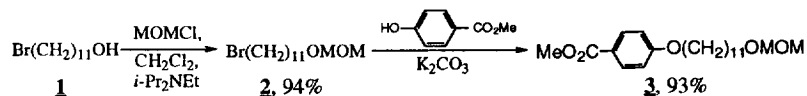
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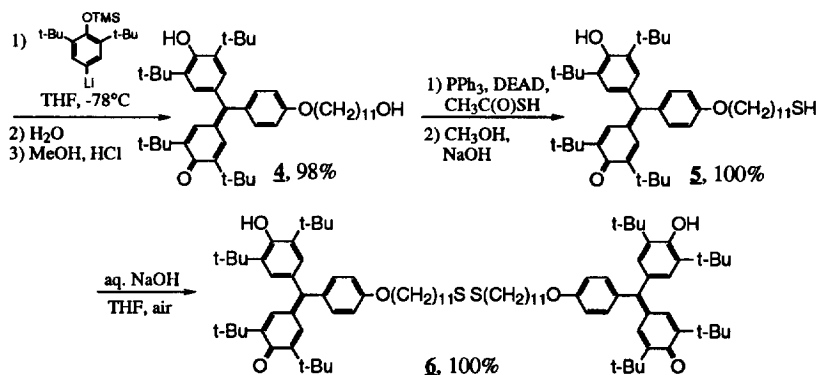
**Abstract:** The synthesis of a biradical disulfide is described. This biradical exhibits an EPR spectrum consistent with  $|J| \gg a$ . Cyclic voltammetry of monolayers of this biradical shows that the radical monolayer exhibits less pH-dependence than its phenol counterpart. Copyright © 1996 Elsevier Science Ltd

Multilayers are uniquely suited to serve as molecular magnets<sup>1</sup> since they provide a direct link between surfaces and magnetic properties, that is, magnetic information storage.<sup>2,3</sup> An important design element of our multilayer scheme is the use of paramagnetic ligands. With this approach we can take advantage of large paramagnetic-ligand to metal antiferromagnetic exchange couplings to yield high- $T_c$  ferrimagnetic materials.

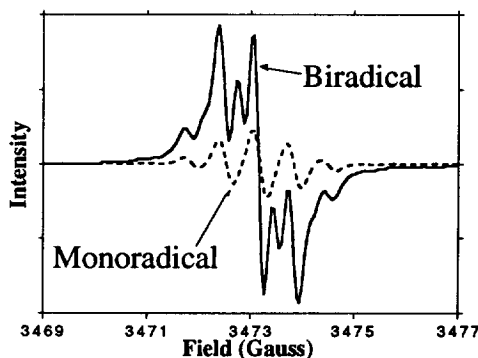
Since the basal monolayer is the stage upon which the multilayer is formed, success of our multilayer approach depends on an understanding of the gross structure of the basal monolayer as well as the formulation of a working model of the spin-spin interactions within the monolayer. Consequently, our goal is to prepare and characterize stable, free-radical-substituted alkanethiol self-assembled monolayers (SAMs) as models of the basal region of molecular magnetic materials prepared via a multilayer approach. We recently reported the electrochemistry of a galvinoxyl alkanethiol attached to a polycrystalline gold electrode.<sup>4</sup> Herein, we report the preparation and EPR spectrum of a disulfide biradical, **6**<sup>••</sup>. This molecule can be used to prepare paramagnetic monolayers.

The synthesis of **6** follows our previously reported procedure<sup>4</sup> and is outlined below. Commercially available 11-bromoundecanol was protected using methoxymethyl chloride, and then used as an alkylating agent for methyl 4-hydroxybenzoate. Ester **3** was transformed into galvinoxyl **4** by first using the modified procedure<sup>5</sup> of Kurreck for galvinoxyl formation,<sup>6</sup> and then standard deprotection protocol. Compound **4** was converted to thiol **5** using Mitsunobu conditions<sup>7</sup> to prepare a thioester, followed by alkaline hydrolysis. When **2** was dissolved in aqueous base/THF and exposed to air, **6** was formed quantitatively.



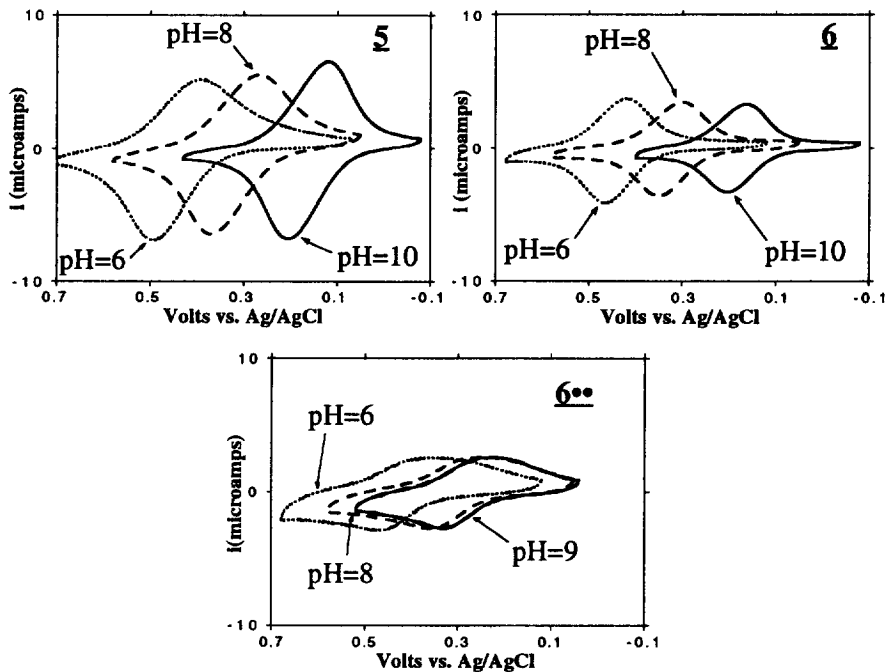


The oxidation of **6** to the biradical, **6\*\***, can be followed by EPR spectroscopy as shown below. Surprisingly, the spectrum recorded after several hours is consistent with a biradical in which the absolute value of the exchange interaction,  $|J|$ , is greater than the hyperfine interaction,  $a$ .<sup>8,9,10</sup> The  $|J| \gg a$  spectral type is evidenced by the appearance of additional hyperfine lines of the biradical that grow between the original five lines of the monoradical. This spectral type is somewhat unexpected considering the length of the chains connecting the paramagnetic centers.<sup>11</sup>



Biradical **6\*\*** was isolated and characterized by mass spectrometry and IR spectroscopy. IR spectra of disulfide **6** and biradical disulfide **6\*\*** differ by two dramatic spectral features: **6\*\*** lacks the sharp OH stretch of **6** at  $3650 \text{ cm}^{-1}$ ; and **6\*\*** shows a shift and splitting of stretches in the  $1600 \text{ cm}^{-1}$  region.

Cyclic voltammograms for monolayers consisting of **5**, **6**, and **6\*\*** are shown below.<sup>12</sup> These initial results are quite interesting. Disulfide **6** apparently gives monolayers with slightly lower surface coverage, however its electrochemistry is more reversible than that observed for monolayers formed from **5**. Biradical **6\*\*** gives slightly lower surface coverage than **6**. The lower surface coverage with **6\*\***, lower reversibility, and response to pH are currently under investigation, and we will report our findings in the near future.



### EXPERIMENTAL SECTION

$^1\text{H}$  NMR spectra were obtained from a General Electric GN 300 Omega 300 MHz spectrometer. Mass spectra were obtained at the Mass Spectrometry Laboratory for Biotechnology with a JEOL HX110HF mass spectrometer. Electrochemical experiments were performed with a EG&G PAR Model 273 potentiostat. Coated, gold films served as working electrodes and Pt wire served as the auxiliary electrode, while the reference electrode was Ag/AgCl. Commercial phosphate buffers used to control pH were prepared by dissolving in deionized water. All electrochemical experiments were performed in air.

### ACKNOWLEDGMENTS

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### REFERENCES

1. For references concerning molecule-based magnetism, see the following: (a) Iwamura, H. *Pure & Appl. Chem.* **1986**, *58*, 187; (b) Iwamura, H. *Pure Appl. Chem.* **1987**, *59*, 1595; (c) Iwamura, H. *Adv.*

*Phys. Org. Chem.* **1990**, *26*, 179; (d) Buchachenko, A.A. *Russ. Chem. Rev.* **1990**, *59*, 307; (e) Gatteschi, D.; Kahn, O.; Miller, J.S.; Palacio, F. *Adv. Mater.* **1991**, *3*, 161; (f) Iwamura, H.; Koga, N. *Acc. Chem. Res.* **1993**, *26*, 346; (g) Day, P. *Science* **1993**, *261*, 431; (h) Rajca, A. *Chem. Rev.* **1994**, *94*, 871; (i) Gatteschi, D. *Adv. Mater.* **1994**, *6*, 635; (j) Clément, R.; Lacroix, P.G.; O'Hare, D.; Evans, J. *Adv. Mater.* **1994**, *6*, 794; (k) Miller, J.S.; Epstein, A.J. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 385; (l) Miller, J.S. *Adv. Mater.* **1994**, *6*, 322; (m) Veciana, J.; Cirujeda, J.; Rovira, C.; Vidal-Gancedo, J. *Adv. Mater.* **1995**, *7*, 221; (n) "Proceedings of the Symposium on Ferromagnetic and High Spin Based Materials," Miller, J.S.; Dougherty, D.A. *Mol. Cryst. Liq. Cryst.* **1989**, *176*; (o) "Proceedings of the Conference on Chemistry and Physics of Molecular Based Magnetic Materials," Iwamura, H.; Miller, J.S. *Mol. Cryst. Liq. Cryst.* **1993**, *180*; (p) "Proceedings of the Fourth International Conference on Molecule-Based Magnets," Miller, J.S.; Epstein, A.J. *Mol. Cryst. Liq. Cryst.* **1995**, *271-274*; (q) Gatteschi, D. *Molecular Magnetic Materials*; Kluwer Academic Publishers: Amsterdam, 1991; (r) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993; (s) O'Connor, C.J. *Research Frontiers in Magnetochemistry*; World Scientific: Singapore, 1993.

2. Biricik, V.W. *Appl. Opt.* **1989**, *28*, 1501.

3. Visnovsky, S.; Kielar, P.; Nyvlt, M.; Parizek, V.; Flevaris, N.K.; Krishnan, R. *IEEE Transactions on Magnetism* **1993**, *29*, 3373.

4. Shultz, D.A.; Tew, G., N. *J. Org. Chem.* **1994**, *59*, 6159.

5. Kirste, B.; Grimm, M.; Kurreck, H. *J. Am. Chem. Soc.* **1989**, *111*, 108.

6. Harrer, W.; Kurreck, H.; Reusch, J.; Gierke, W. *Tetrahedron* **1975**, *31*, 625.

7. Volante, R.P. *Tetrahedron Lett.* **1981**, *22*, 3119.

8. Atherton, N.M. *Principles of Electron Spin Resonance*; Ellis Horwood PTR Prentice Hall: New York, 1993.

9. Wertz, J.E.; Bolton, J.R. *Electron Spin Resonance*; Chapman and Hall: New York, 1986.

10. The EPR spectra of  $\dot{\text{G}}^{\bullet\bullet}$  are inconsistent with the formation of Yang's biradical by decomposition. Yang's biradical gives an S=1 spectrum at 77K (see: Mukai, D.; Ishizu, K. *J. Chem. Phys.* **1977**, *66*, 1680), while  $\dot{\text{G}}^{\bullet\bullet}$  gives a narrow doublet spectrum. The appearance of the EPR spectrum of  $\dot{\text{G}}^{\bullet\bullet}$  is also concentration independent, suggesting a lack of intermolecular interactions influencing the spectral shape.

11. Experiments are underway to determine if this molecule exhibits temperature dependence of J-coupling. This "J-modulation" has been observed in transient biradicals, see: Forbes, M.D.E.; Schulz, G.R. *J. Am. Chem. Soc.* **1994**, *116*, 10174.

12. Monolayers were prepared as described in ref. 4.

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