

**Appendix II: Towards the Development of a High-spin
Organic Polymer**

II.1 Introduction

The development of pure organic materials with ferromagnetic properties is of long standing theoretical and experimental interest. To obtain high-spin organic materials, it is necessary to control spin-spin interactions of organic radicals. Spin control in organic radicals can be divided into intermolecular control and intramolecular control. Chapter 7 and Appendix III deal with controlling intermolecular interactions using crystal engineering, and here we discuss control of intramolecular interactions using organic polymers.

The model shown in Figure II.1 describes the simplest high-spin organic polymer (Dougherty, 1991). This system can be broken down into two pieces: a spin containing unit and a ferromagnetic coupling unit. For development of organic ferromagnets, organic radicals serve as spin containing units. The ferromagnetic coupling unit is responsible for ensuring that adjacent spins align parallel with respect to each other.

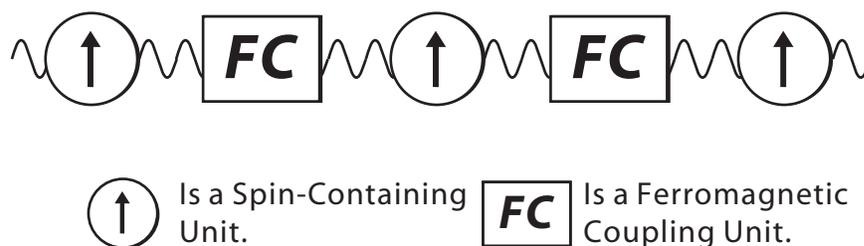


Figure II.1: Schematic for a one-dimensional ferromagnetic polymer.

Previous work from our group has identified three ferromagnetic coupling units, *meta*-phenylene, 1,1-ethylene, and substituted 1,3-cyclobutanediyls (Jacobs et al., 1993). Of these, the most robust ferromagnetic coupling unit is *meta*-phenylene, with a singlet-triplet gap of around 10 kcal/mol. The work described here will utilize the *meta*-phenylene coupling unit with two different spin containing units.

The smallest spin containing units for organic magnetic materials are charged or uncharged monoradicals. Although some monoradicals are stable, typically simple organic radicals are only stable at very low temperatures in solid matrices. Results from conducting polymers have shown that polarons, delocalized radical cations or radical anions, can be easily generated and are relatively stable at room temperature. For this reason, this work and previous work has employed polarons as the spin containing units for the development of ferromagnetic organic polymers.

Traditionally, work in our group has focused on the use of oxidatively doped radical cations as spin containing units (Murray et al., 1994). Figure II.2 shows a series of polymers that have been oxidatively doped to produce radical cations. All of these polymers showed spin values greater than one half at very low spin concentrations, suggesting parallel alignment between adjacent radicals. However, at high-spin concentrations, above one percent, typically the spin values observed were well below one, which is most likely indicative of bipolaron (spinless dication) formation and/or decomposition of the material. In these systems it was thus impossible to generate the large number of aligned spins needed to achieve long-range magnetic behavior.

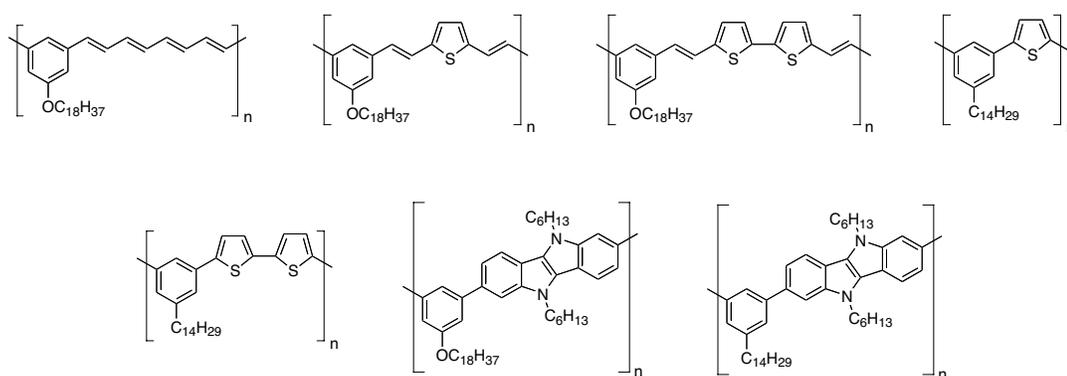
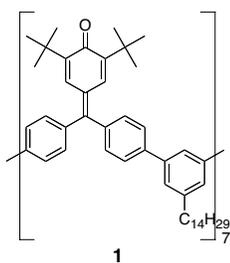


Figure II.2: Model one-dimensional oxidatively doped polaronic ferromagnets.

Many of the problems associated with the early prototypical oxidatively doped radical cation systems were resolved by introduction of a reductively doped radical anion spin containing unit (Anderson and Dougherty, 1998). 2,6-di-*tert*-butylfuchsonone was chosen, since its radical anion is readily generated electrochemically in solution and the second reduction potential is sufficiently removed (~ 400 mV) to prevent formation of large amounts of bipolarons. Using this spin containing unit, polymer **1** was produced.



Polymer **1** showed improved magnetic properties upon electrochemical reduction between -1.0 V and -1.4 V versus Ag(s)/AgCl(s). With this material a spin value of 2.0 at a spin concentration of 58% was achieved. Additionally, analysis of the susceptibility

temperature product as a function of temperature showed a ferromagnetic transition at around 40 K followed by an antiferromagnetic transition around 3 K. Presumably the observed antiferromagnetic transition arises from weak antiferromagnetic intermolecular interactions.

Despite significantly improved magnetic behavior, reductive doping of polymer **1** remained problematic. For solubility reasons, electrochemistry of **1** had to be carried out in tetrahydrofuran. Tetrahydrofuran is a poor solvent for electrochemistry since it requires high electrolyte concentrations to achieve usable electrochemical cell resistances. As a result during bulk electrolysis decomposition of the electrolyte solution in the counter cell was observed along with corrosion of the Ag(s)/AgCl(s) working electrode. Here we describe modification of polymer **1** to increase its solubility in good electrochemical solvents, such as acetonitrile. It was hoped that such a polymer might increase the efficiency of the electrochemical reduction, thus giving high-spin values and higher spin concentrations.

In addition to modifying the solubility of polymer **1**, it was hoped that analogous polymers could be produced in which ferromagnetic behavior was observed at higher temperatures. Theoretically, the ferromagnetic critical temperature is simply a consequence of the singlet-triplet gap for the coupling unit and the spin density of the spin containing unit at the connection point. Since *meta*-phenylene already has the largest singlet-triplet gap of the identified ferromagnetic coupling units, modulation of ferromagnetic critical temperature was attempted by modulation of the spin density at the connection point.

Figure II.3 shows the spin density at the central carbon of 2,6-di-*tert*-butylfuchstone and the spin density at the connection point between 2,6-di-*tert*-butylfuchstone and *meta*-phenylene in polymer **1**. The calculated spin densities shown are from Huckel calculations, and the experimental spin density is from EPR measurements. The theoretical coupling strength for polymer **1** can be calculated by scaling the singlet triplet gap for *meta*-xylene (10 kcal/mol) by the square of the spin density at the connection point (0.066 or 0.09). A resulting coupling strength of 40-90 cal/mol is obtained, which corresponds to ferromagnetic critical temperature between 20 and 45 K. The predicted ferromagnetic critical temperature is in good agreement with observed critical temperature for polymer **1**.

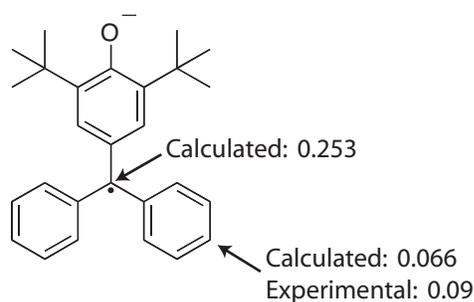
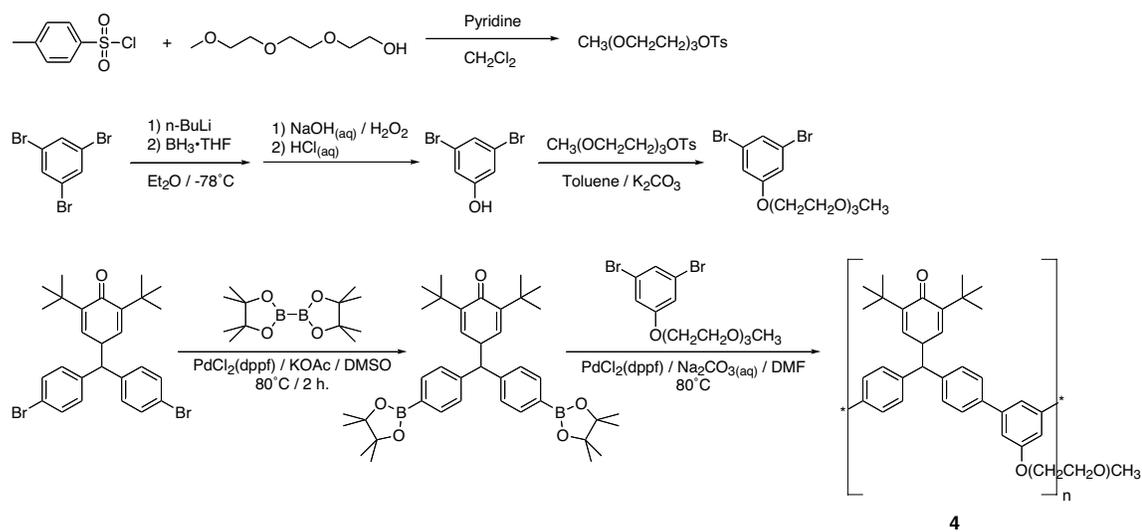


Figure II.3: Selected spin densities are shown from the 2,6-di-*tert*-butylfuchstone radical anion.

Based on these considerations polymers **2** and **3** were designed to have increased spin density at the connection point between the spin containing unit and the ferromagnetic coupling unit. Calculating the theoretical coupling strength as above, polymers **2** and **3** have coupling strength of 170 cal/mol and 640 cal/mol respectively. These correspond to

pure THF. Figure II.4 shows a comparison of the results of obtained from cyclic voltammetry on polymer **4**.



Scheme II.1: Synthesis of polymer **4**.

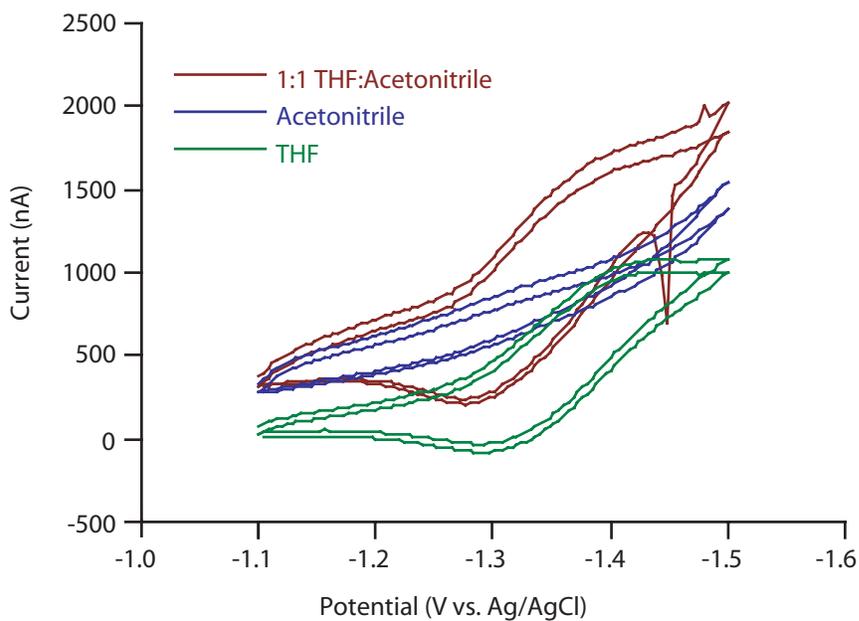


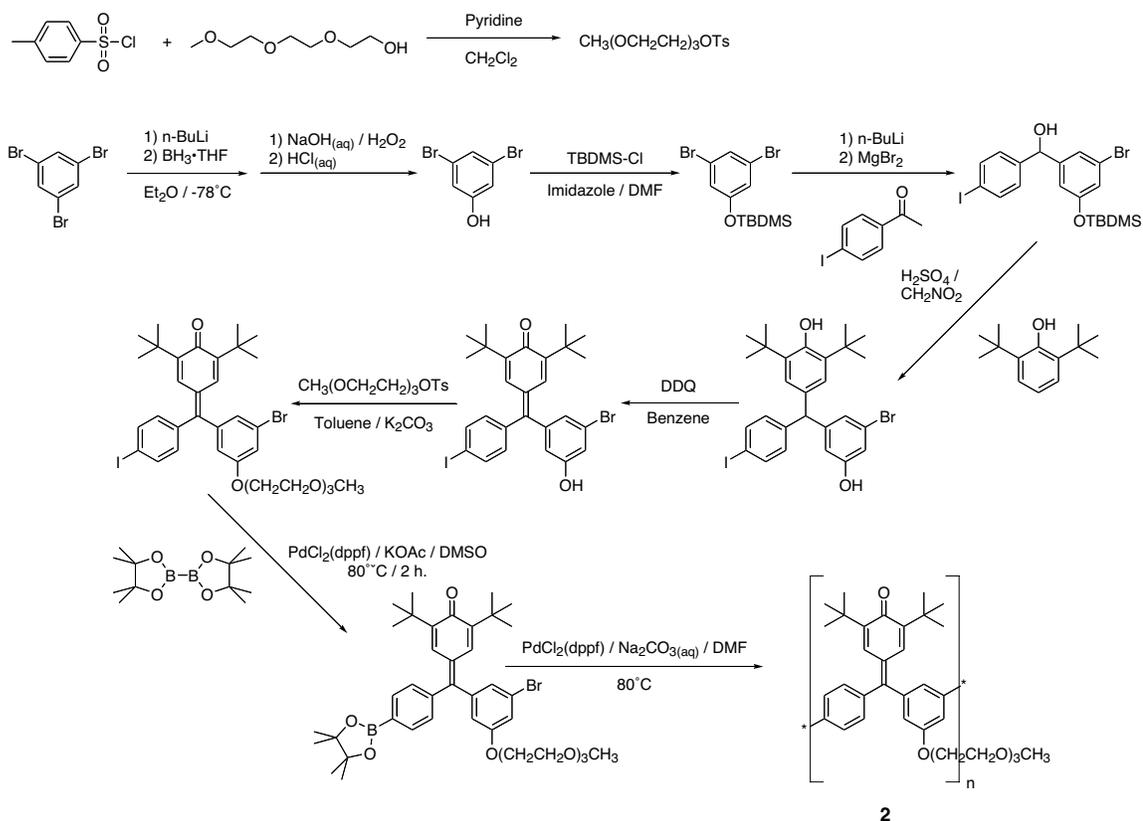
Figure II.4: Cyclic voltammograms for polymer **3** in THF, acetonitrile, and 1:1 THF:acetonitrile.

The cyclic voltammograms obtained in acetonitrile were essentially shapeless, due to the poor solubility of polymer **4** in acetonitrile. The curves obtained for cyclic voltammetry in THF and 1:1 acetonitrile:THF were qualitatively similar to each other. Additionally, the cyclic voltammogram for polymer **4** was qualitatively similar to that of polymer **1**.

Since in principle 1:1 acetonitrile:THF is a better solvent mixture for electrochemistry than THF, bulk electrolysis of polymer **4** was attempted in 1:1 acetonitrile:THF using 0.3 M tetrabutyl ammonium perchlorate as electrolyte. Over the course of the electrical reduction, rapid degradation of the solid Ag/AgCl reference electrode was observed at the potentials necessary for reduction of the polymer **4**. Solid Ag/AgCl reference electrodes are also known to lack stability in other good electrochemistry solvents (such as DMF or DMSO). To resolve this problem a different reference electrode is needed, such as a solution Ag/AgCl electrode, a saturated calomel electrode, or a dropping mercury electrode. However, it is not obvious that the gains from electrochemistry in a higher dielectric solvent would be significant to merit further investigation.

II.2.2 Synthesis and Electrochemical Characterization of Polymer 2

The synthesis of polymer **2** was carried out as described in Scheme II.2. This synthetic strategy takes advantage of the selectivity of the diboron reaction for iodide over bromide when installing the boric ester necessary for the final polymerization. Additionally, since the poly(ethyleneglycol) tail is installed towards the end of the synthesis, variation of polymer solubility, by variation of this tail, should be straight forward.

Scheme II.2: Synthesis of polymer **2**.

Gel permeation chromatography of polymer **2** was carried out in methylene chloride. Polymer **2** showed an apparent molecular weight of 21,708 g/mol and a polydispersity index of 1.9. This corresponds to an approximate oligomerization state of 41 monomers per polymer unit.

A cyclic voltammogram of polymer **2** was obtained in THF (Figure II.5). As expected the general shape of the voltammogram was similar to that polymers for **1** and **4**. The first reduction potential for the fuschone was observed around -1.3 V versus silver/silver chloride.

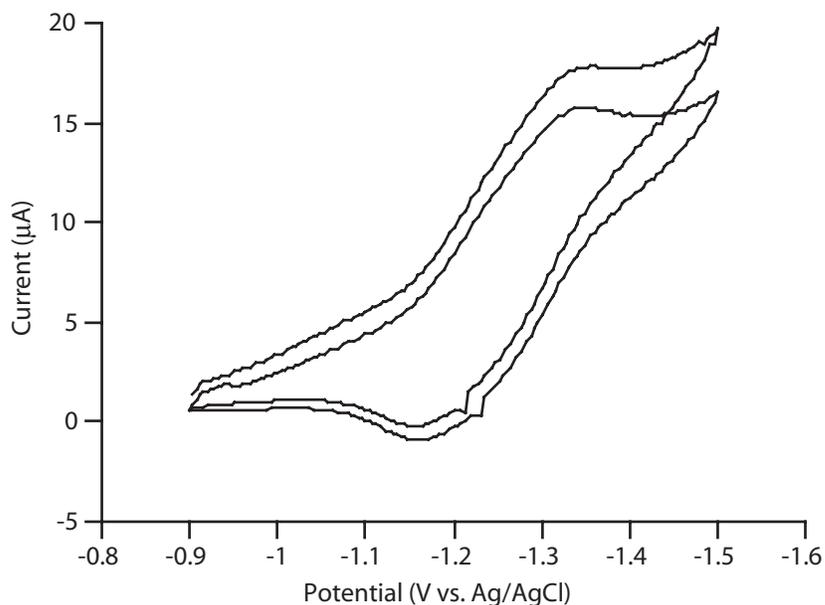


Figure II.5: Cyclic voltammogram for polymer **2** in THF.

Bulk electrolysis of polymer **2** at -1.3V versus silver/silver chloride was attempted in THF with tetrabutyl ammonium electrolyte. The resulting product showed no paramagnetic species by SQUID magnetometry. The lack of fuschone radical formation may be due to problems encountered during the bulk electrolysis or may be due to issues of sample handling. The electrochemical reduction of polymer **2** merits further investigation as it may be possible to achieve good electrochemistry, using a more ideal electrochemical setup than the one employed here.

II.3 Literature Cited.

Anderson, K. K., and Dougherty, D. A. (1998). An improved model for one-dimensional polaronic ferromagnetism: Electrochemically doped poly(m-phenylene-fuchson). *Advanced Materials* *10*, 688-692.

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