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The First Example of Cationic Iron-Coordinated Polyaromatic Ethers and Thioethers with Azo Dye-Functionalized Side Chains

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Recently, there have been a number of articles outlining the unique electrooptic properties that result from the incorporation of azo chromophores into high molecular weight materials.[1] The properties of these materials are related to both the structure of the polymer and the bathochromicity of the dye. These types of polymers often exhibit nonlinear optical properties, which has led to their application in optical storage devices, electrooptic modulators, and second harmonic generators. A recent report has demonstrated the use of azo dye-functionalized polymers as polyelectrolytes and described the property changes that may arise from the trans−cis isomerization of azo chromophores.[2] The UV−vis properties of these azo compounds did not change upon inclusion into the polymers, and they showed promise as ultrathin multilayers and stimuli responsive materials.

Organometallic polymers have received a great deal of attention in recent years due to their interesting electrical, catalytic, physical, and chemical properties.[3] Manners and co-workers have reported the synthesis and liquid crystalline properties of poly(ferrocenylsilanes) incorporating azo chromophores in their side chains.[4] We have recently reported the synthesis of a number of linear and star polymers incorporating cationic cyclopentadienyliron ($CpFe^+$) moieties pendent to their backbones and side chains.[5] Herein, we report the first example of highly colored cyclopentadienyliron-coordinated polyaromatic ethers and thioethers containing azobenzene dyes in their side chains.

It has been established that chloroarenes coordinated to cyclopentadienyliron cations undergo facile nucleophilic aromatic substitution reactions with oxygen- and sulfur-based nucleophiles, resulting in the formation of novel monomeric and polymeric materials.[5] Monomers containing azo dyes in their structures were synthesized via reaction of complex **1**[5c] with dyes **2a**−**c** as described in Scheme 1.[6] Functionalization of the diiron complex **1** with the azo chromophores resulted in orange and red solids (**3a**−**c**) that absorbed at 421, 491, and 452 nm, respectively. These complexes were subsequently reacted with dinucleophiles **4a**−**c** to yield cyclopentadienyliron-coordinated polyaromatic ethers or ether/thioethers containing azo chromophores in their side chains (**5a**−**i**) (Scheme 2).[7] These polymerization reactions occurred under very mild reaction conditions due to the excellent electron-withdrawing capability of the cyclopentadienyliron cations. Polymers **5a**−**i** displayed fair to excellent solubility in polar organic solvents such as DMF, DMSO, and acetonitrile. The molecular weights of the polymers were determined using gel permeation chromatography following cleavage of the cyclopentadienyliron moieties. The weight-average molecular weights of polymers **5a**−**i** were determined to be 13 400−31 600 with polydispersities ranging from 1.2 to 2.6. Reaction of monomer **1** with dinucleophiles **4a**−**c** using the same reaction conditions resulted in the isolation of organoiron-coordinated polymers containing pendent carboxylic acid groups. These polymers could be solubilized in a sodium hydroxide solution and displayed good solubility in DMF and DMSO.

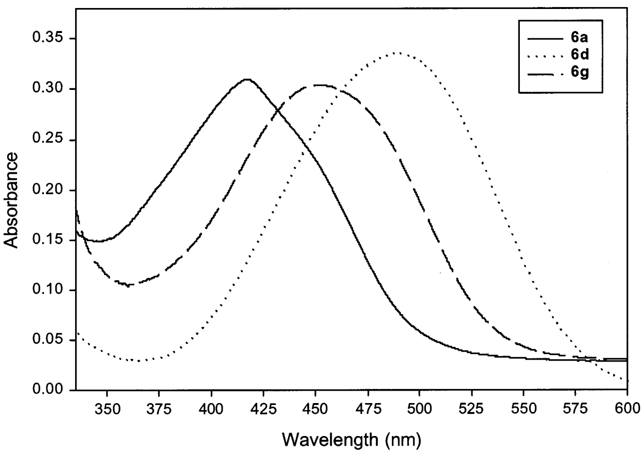

Figure 1. Visible spectra of polymers **6a, 6d**, and **6g** with maxima at 417, 489, and 452 nm, respectively.

The wavelength maxima of organoiron polymers **5a**−**i** were very similar to those of their corresponding monomers. The UV−vis spectra of these polymers obtained in DMF, ethanol, and acidic ethanol show peaks that are characteristic of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of azo dyes.[1] By increasing the electron-withdrawing nature of the R group (H, $COCH_3$, NO_2), these materials exhibited bathochromic shifts, which corresponds to shifts to longer wavelengths.[8] For example, the maxima of **5a**−**c** ranged from 418 to 420 nm, while the maxima of **5d**−**f** and **5g**−**i** ranged from 490 to 491 nm and 451 to 454 nm, respectively, in DMF. Increases in λ_{max} were also observed upon addition of HCl to ethanolic solutions of these polymers. This halochromism is clearly seen by comparing the maxima of **5a** in ethanol (418 nm) and acidic ethanol solutions (520 nm) due to the formation of azonium ions.[8] In contrast to the bright orange and red polymers functionalized with azo dyes (**5a**−**i**), the carboxylic acid-functionalized polymers were pale yellow or beige, and their absorptions occurred between 272 and 274 nm. It was possible to remove the cyclopentadienyliron moieties from the polymer backbones by irradiating the polymers with 300 nm light solutions of dichloromethane/acetonitrile. NMR analysis of these organic polymers (**6a**−**i**) indicated that the organoiron units were no longer present; however, the integrities of the azo-functionalized polymers were retained. Figure 1 shows the visible spectra of polymers **6a**, **6d**, and **6g** prepared via reaction of monomers **3a**−**c** with bisphenol A (**4a**).

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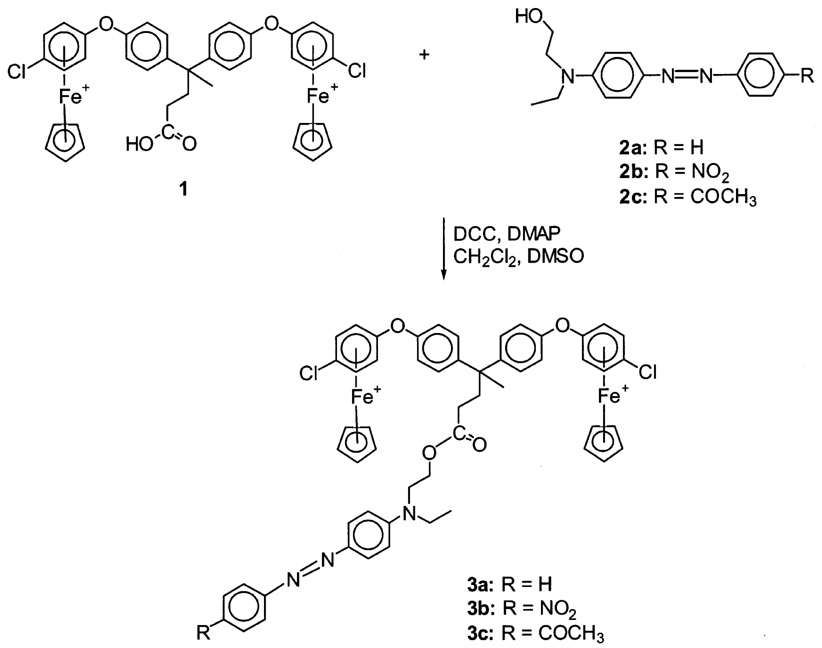
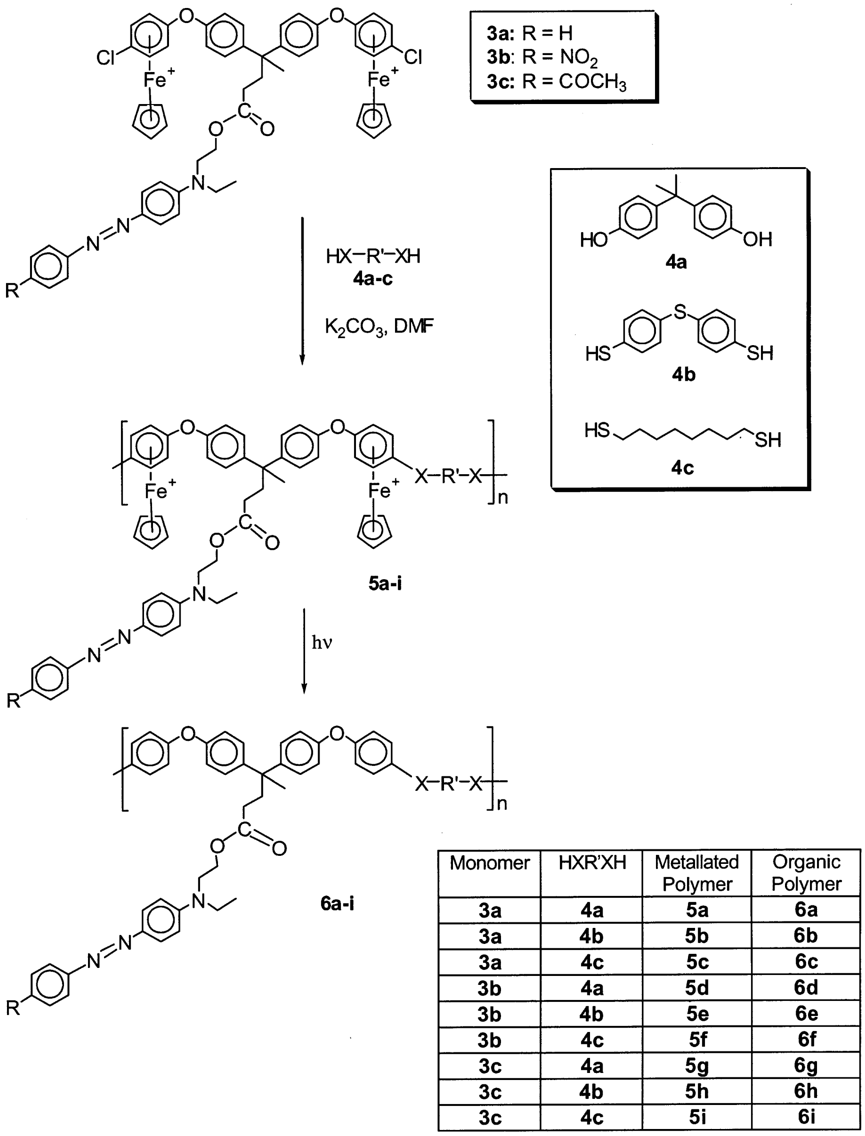
Scheme 1



Scheme 2



Monomer	HXR'XH	Metallated Polymer	Organic Polymer
3a	**4a**	**5a**	**6a**
3a	**4b**	**5b**	**6b**
3a	**4c**	**5c**	**6c**
3b	**4a**	**5d**	**6d**
3b	**4b**	**5e**	**6e**
3b	**4c**	**5f**	**6f**
3c	**4a**	**5g**	**6g**
3c	**4b**	**5h**	**6h**
3c	**4c**	**5i**	**6i**

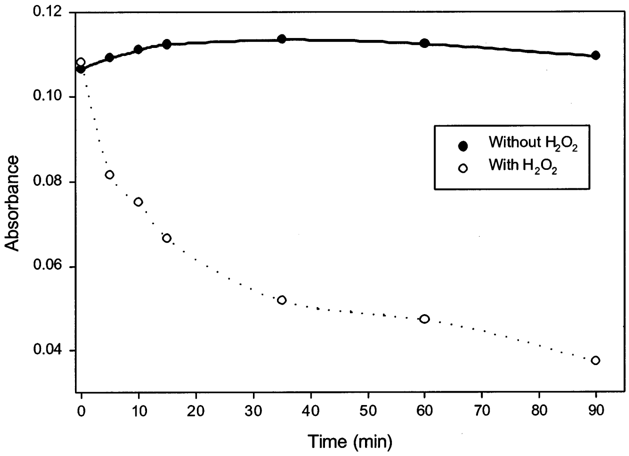


Figure 2. Absorption profile of polymer **6d** in the presence and absence of hydrogen peroxide using a 300 nm light source.

Thermogravimetric analysis of the metalated polymers showed weight losses between 220 and 240 °C, indicative of cleavage of the $CpFe^+$ moieties pendent to their backbones. Following removal of the metallic moieties pendent to the polymer backbones, the TGA of polymers **6a**−**i** no longer showed this weight loss. These results are consistent with our previous studies of polymers containing arenes coordinated to cyclopentadienyliron moieties.[5a] The azo dye-functionalized polymers underwent second weight losses between 250 and 290 °C, which were attributed to decomposition of the azo groups, and a third weight loss around 450 °C, corresponding to polymer decomposition. The carboxylic acid functionalized polymers experienced only the second weight losses starting from 420 to 460 °C, which were attributed to breakdown of the polymer backbones.

The glass transition temperatures (T_g) of the organometallic and organic polymers were measured using differential scanning calorimetry. Because of the presence of the bulky cationic cyclopentadienyliron moieties pendent to the backbones of polymers **5a**−**i**, their T_g's were much higher than those of their organic analogues (**6a**−**i**). For example, the T_g of polymer **5i** occurred at 132 °C, while that of its organic analogue (**6i**) occurred at 64 °C. As well, polymers with flexible aliphatic spacers in their backbones possessed much lower T_g's than polymers incorporating more rigid spacers. The glass transition temperatures of polymers **6c**, **6f**, and **6i** incorporating aliphatic spacers occurred between 34 and 64 °C, while polymers incorporating aryl ether and thioether linkages displayed T_g's between 110 and 122 °C.

Photooxidation of the organic polymers in a 14% CH_3CN aqueous solution was studied in order to determine whether the highly colored polymers could be bleached. The polymer (1 mg) was dissolved in 5 mL of CH_3CN, to which 30 mL of doubly distilled water was added. The UV spectrum of this solution was recorded at time zero, and then 5 mL of 30% H_2O_2 was added, and the tube was tightly capped. Photolysis with 300 nm light was performed for allotted times, after which aliquots were removed and their UV absorbance spectra recorded. The aliquots were returned to the tube, and the solution was placed back in the photoreactor. Figure 2 shows that, upon the addition of H_2O_2, photolysis of polymer **6d** with 300 nm light caused a significant color loss. The absorbance of this polymeric dye at 485 nm decreased quite rapidly, whereas in the absence of H_2O_2, an irradiated solution showed very little change in absorption over time.

In conclusion, a series of cyclopentadienyliron-complexed azo-functionalized polymers were synthesized. The visible spectra of the azo dyes changed upon reaction with organometallic complexes; however, the absorption spectra of the monomers and polymers were very similar. Photolysis of the organoiron polymers allowed for isolation of their organic analogues, which possessed similar visible absorbances. These polymers were subjected to photolysis in the presence of hydrogen peroxide, resulting in bleaching of the azo dye-functionalized polymers.

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(6) Complex **1**[5c] (1.04 g, 1 mmol), **2a**−**c** (1.2 mmol), and DMAP (0.147 g, 1.2 mmol) were combined in 3 mL of DMSO and 10 mL of CH_2Cl_2. The solution was stirred under N_2 for 5 min, and then DCC (0.248 g, 1.2 mmol) was added; the reaction proceeded at room temperature for 16 h. The complex was added to a 10% HCl solution containing NH_4PF_6 (0.326 g, 2 mmol), extracted with CH_2Cl_2, washed with water, and dried over $MgSO_4$. The solution was dried, dissolved in acetone, and filtered into ether, resulting in an orange or red precipitate, which was collected in a crucible and dried. Spectroscopic data of complex **3a** are provided as a representative example. Yield: 90%. IR: 1729 cm^{-1} (C=O). δ_H (acetone-d_6): 1.22 (t, 3H, J = 7.0 Hz, CH_3), 1.68 (s, 3H, CH_3), 2.14 (m, 2H, CH_2), 2.46 (m, 2H, CH_2), 3.58 (q, 2H, J = 7.4 Hz, CH_2), 3.77 (t, 2H, J = 5.5 Hz, CH_2), 4.32 (t, 2H, J = 5.5 Hz, CH_2), 5.33 (s, 10H, Cp), 6.44 (d, 4H, J = 6.6 Hz, complexed Ar), 6.76 (d, 4H, J = 6.6 Hz, complexed Ar), 6.94 (d, 2H, J = 9.4 Hz, Ar), 7.26 (d, 4H, J = 9.0 Hz, Ar), 7.40−7.47 (m, 7H, Ar), 7.76 (d, 2H, J = 7.0 Hz, Ar), 7.82 (d, 2H, J = 9.4 Hz, Ar). δ_C (acetone-d_6): 12.31, 27.76 (CH_3), 30.73, 37.10 (CH_2), 45.42 (C), 46.22, 48.99, 62.42 (CH_2), 77.04 (complexed ArCH), 80.40 (Cp), 87.79 (complexed ArCH), 104.82 (complexed ArC), 112.30, 121.22, 122.77, 125.88, 129.91, 130.29, 130.57 (ArCH), 133.80 (complexed ArC), 143.98, 147.83, 151.73, 152.00, 153.81 (ArC), 173.53 (CO).

(7) Complex **3a**−**c** (0.25 mmol), **4a**−**c** (0.25 mmol), and K_2CO_3 (0.138 g, 1 mmol) were dissolved in 2 mL of DMF and stirred under N_2 at 60 °C overnight. The solution was poured into 10% HCl, to which NH_4PF_6 (0.082 g, 0.5 mmol) was added. The polymer was collected in a crucible, washed with water and ether, and then dried. Spectroscopic data of polymer **5a** are provided as a representative example. Yield: 95%. IR: 1727 cm^{-1} (C═O). δ_H (DMSO-d_6): 1.12 (br s, 3H, CH_3), 1.70 (m, 9H, CH_3), 2.07 (m, 2H, CH_2), 2.38 (m, 2H, CH_2), 3.46 (m, 2H, CH_2), 3.75 (m, 2H, CH_2), 4.21 (m, 2H, CH_2), 5.18 (s, 10H, Cp), 6.21 (s, 8H, complexed Ar), 6.84 (m, 4H, Ar), 7.02 (m, 5H, Ar) 7.20 (m, 8H Ar), 7.42 (m, 4H, Ar), 7.72 (m, 4H, Ar). δ_C (DMSO-d_6): 12.17 (CH_3) 30.11 (CH_2), 30.78 (CH_3), 42.39 (CH_2), 44.68, 44.85 (C), 45.12, 48.13, 61.74 (CH_2), 75.10 (complexed ArCH), 78.05 (Cp), 111.61, 114.98, 117.73, 120.13, 121.90, 125.18, 127.56, 128.94, 129.40 (ArCH), 130.12, 130.34 (complexed ArC), 142.54, 146.04, 147.94, 150.70, 151.47, 152.48, 155.36 (ArC), 172.89 (CO).

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