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Poly(3,3′-dihexyl-4,4′-dimethyl-1,1′-ferrocenylene-1,4-phenylene) and Poly(3,3′-dihexyl-4,4′-dimethyl-1,1′-ferrocenylene-2,5-thienylene)

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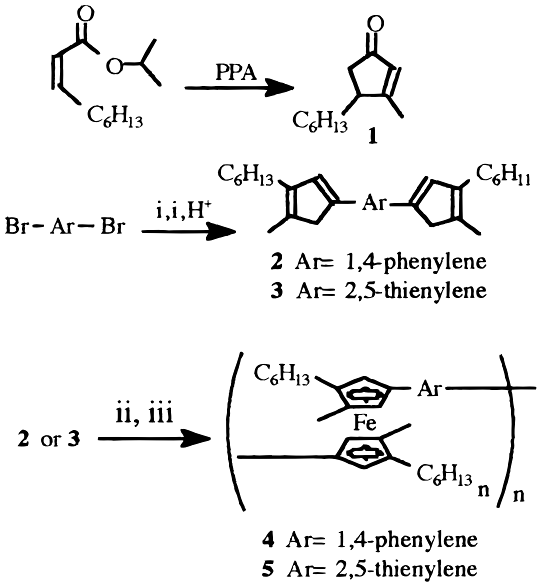
Summary: Bis(3-hexyl-4-methylcyclopentadienyl)-arenes have been prepared from the sequential lithiation of dibromoarenes followed by reaction with 3-hexyl-4-methylcyclopenta-2-ene-1-one. The dicarbinol is then dehydrated with p-toluenesulfonic acid to give the bis(3-hexyl-4-methylcyclopentadienyl)arene. Poly-(3,3′-dihexyl-4,4′-dimethyl-1,1′-ferrocenylenearylene)s were prepared via the reaction of dilithio bis(3-hexyl-4-methylcycylopentadienide)arylenes and iron(II) iodide in THF. The organic bridging ligands and polymers were characterized by DSC, GPC, NMR, CV, UV−vis, and TGA.

Conjugated polymers have received much attention for their electroactive and magnetic properties for use in applications, e.g., NLO,[1] light-emitting diodes (LEDs),[2] electrochromic thin films,[3] and thin-film transistors (TFTs).[4] The combination of the electroactivity of ferrocene with the electronic properties of conjugated polymers is an attractive strategy for enhancing the physical and electronic properties of the resultant hybrid polymers.[5] Electronic delocalization along the polymeric chain may also enhance the communication between metal centers, thus allowing the magnetic and spectroscopic properties to be fine tuned for specific applications. The nature of the bridging ligands influences the degree of delocalization.

One of the most challenging aspects of designing soluble, conjugated metallocene polymers has been the synthesis of suitable bis(cyclopentadienyl)arenes that can be made conveniently from relatively inexpensive precursors and that are versatile synthons for a variety of metallocene polymers. In this communication, we report the synthesis of new bridging ligands, 1,4-bis(3-hexyl-4-methylcylopentadienyl)benzene and 2,5-bis(3-hexyl-4-methylcylopentadienyl)thiophene, that are designed to impart solubility and processability to conjugated poly(metallocenes).

Scheme 1



(i) 1.0 eq. BuLi, then **1**. (ii) $LiN(SiMe_3)_2$. (iii)FeI_2.

2-Nonenoic acid was converted to isopropyl-2-nonenoate via the condensation of the acid and 2-propanol with a catalytic amount of sulfuric acid in 95% yield.[6] The ester was then converted to 3-hexyl-4-methylcyclopent-2-en-1-one, **1**, by reacting the ester with polyphosphoric acid (PPA) at 100 °C for 12 h.[7] Compounds **2** and **3** were realized by the reaction of 1,4-dibromobenzene or 2,5-dibromothiophene with 1 equiv of n-butyllithium in diethyl ether to afford the monolithiated monobromoarene, which was then allowed to react with 3-hexyl-4-methylcyclopent-2-en-1-one. Addition of a second equivalent of n-butyllithium and a second equivalent of 3-hexyl-4-methylcyclopent-2-en-1-one resulted in the dicarbinol arene, which gave **2** or **3** (Scheme 1) upon subsequent dehydration with *p*-toluenesulfonic acid in 21−52% yield.[5c,d] Compound **2** is a light yellow solid,

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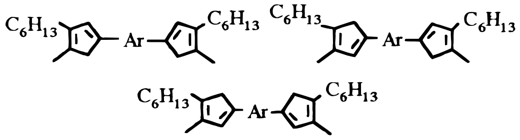
Scheme 2



which may be recrystallized from hexanes. As determined by ^{1}H NMR, compound **2** crystallizes as three isomers that are tentatively assigned to those shown in Scheme 2. Compound **3** is a liquid down to −40 °C but may be purified by flash chromatography over silica gel with hexanes as the eluent. ^{1}H NMR assignments of compound **3** are complicated by the presence of many of the 25 possible isomers corresponding to the various positions of the double bonds in the Cp rings.

Compounds **2** and **3** were then converted to their respective dilithio salts with 2 equiv of lithium bis(trimethylsilyl)amide in THF. These were allowed to react with an equimolar amount of ferrous iodide, and the reaction mixture was heated to reflux for at least 4 days before being poured into methanol to precipitate the polymers, **4** and **5** (Scheme 1). The dilithium salt of **2** precipitates from THF solution, resulting in a stoichiometric imbalance if an equimolar amount of FeI_2 is added all at once. The nonstoichiometry results in the formation of a large amount of cyclic dimers, trimers, and other higher oligomers in addition to polymer **4**. However, if the FeI_2 is added in small increments over the interval of several days, then the cyclization problem is lessened.

Polymers **4** and **5** were collected in 70% and 50% yields, respectively. Polymer **4** is an orange-red solid that forms brittle films. GPC analysis (polystyrene standards) of **4** indicates $M_n = 4{,}000$, $M_w = 42{,}000$, and PDI = 10.5. Polymer **5** is a deep red, tacky solid. Similar GPC analysis of **5** gives $M_n = 3{,}600$, $M_w = 52{,}600$, and PDI = 14.6. Thermogravimetric analysis (TGA heating rate = 40 °C/min) reveals the very high thermal stability of these materials: only 5% weight losses were observed at 406 and 440 °C for **4** and **5**, respectively. The char yields of **4** and **5** were 28% and 25% at 900 °C, respectively. These values are close to those that would be obtained if the char consisted of FeC. UV−vis spectra of **4** and **5** exhibit strong "band II" absorptions at 460 ($\epsilon = 2000$ M^{-1}/cm) and 468 nm ($\epsilon = 2800$ M^{-1}/cm), respectively.[8] Cyclic voltammetry of the polymers in methylene chloride with 0.1 M Bu_4NPF_6 supporting electrolyte reveal moderate electronic communication between metal ferrocene moieties. Both polymers exhibit two reversible waves of equal intensity (Figure 1). These waves have been attributed to the oxidation of alternate iron centers along the polymer backbone at the first wave, $^1E_{1/2} = -0.24$ (**4**) and −0.20 V (**5**), followed by oxidation of the remaining iron centers at higher potential, $^2E_{1/2} = -0.07$ V (**4**) and −0.01 V (**5**). Polymer **4** exhibits $\Delta E = (^2E_{1/2} - {}^1E_{1/2}) = 170$ mV, while **5** has $\Delta E = 190$ mV. The quantity, ΔE, is a measure of the degree of interaction between the iron centers. In **4** and **5**, ΔE is large, especially in view of the large Fe−Fe distances involved, and the relatively large interactions may be attributed to the effects of the conjugated, aromatic system that links the ferrocene units in the polymers. The iron−iron distances, calculated for the most stable, *trans*-conformation of rings, and the corresponding ΔE's for some ferrocene dimers and polymers are **4** 8.96 Å, $[C_2H_2(C_{10}H_9Fe)]_n$ ($\Delta E = 250$ mV) 7.03 Å,[9] $[(C_4H_4(C_{10}H_9Fe)_2]$ ($\Delta E = 129$ mV) 9.21 Å,[10] $[S_2(C_4H_9C_5H_4)(C_5H_4)Fe]_n$ ($\Delta E = 290$ mV) 8.62 Å,[11] $[C_2H_4(C_{10}H_8Fe)]_n$ ($\Delta E = 90$ mV) 7.70 Å,[12] $[SiMe_2(C_{10}H_8Fe)]_n$ ($\Delta E = 250$ mV) 6.30 Å,[13] and $C_6H_4[(C_2C_5H_4)(C_5H_5)Fe]_n$ ($\Delta E \approx 0$ mV) 13.7 Å.[14] ΔE is also related to the comproportionation constant (K_c) according to eq 1, where ΔE is in mV and $T = 298$ K.[15] The K_c's for **4** and **5** are 750

$$K_c = \exp(F\Delta E/RT) = \exp(\Delta E/25.69) \qquad (1)$$

and 1630, respectively, and are comparable to that of diferrocenyl acetylene, $K_c = 160$, whose one-electron-oxidized species is classified as a class II mixed-valence complex.[16] For **4**, plots of current vs square root of scan rate were linear over the range of scan rates employed, indicative of diffusion-controlled electron transfer. Thick films of the polymers were formed on the electrode by dipping the electrode in a polymer solution, removing the excess solution by shaking, and allowing the solvent to evaporate. Cyclic voltammetry of the thick films immersed in acetonitrile containing 0.1 M Bu_4NPF_6 supporting electrolyte do not show the sharp symmetrical reduction−oxidation peaks expected for an electrode-localized electroactive film. Instead, there is one unsymmetrical oxidation peak at 0.22 V for **4** and at 0.16 V for **5**. The films must be poorly solvated and highly resistive and are not oxidized until the break-in potential (E_{bp}) is reached and the electrolyte penetrates the film. The oxidized films were soluble in acetonitrile and quickly dissolved from the electrode, precluding studies of the cycling behavior.

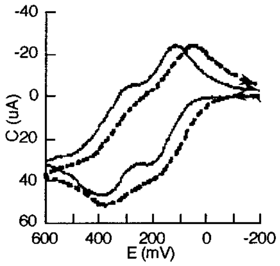


Figure 1. Cyclic voltammograms of **4** (—) and **5** (- - -). Data obtained at 23 °C in CH_2Cl_2 solutions of 0.1 M NBu_4PF_6 supporting electrolyte at a scan rate of 100 mV/s.

Polymers **4** and **5** may be oxidized chemically with 1.5 equiv of elemental iodine to give the polyferrocenium triiodides, **6** and **7**.[5e,17] The magnetic behavior of the

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iodine-oxidized oligomers has been investigated. Amorphous powders of **6** and **7** were first cooled in a zero field, and the magnetic susceptibilty was measured in a field of 0.1 T from 5 to 300 K in a SQUID. For the oxidized thienylene polymer, **7**, the susceptibility data are well-represented by Curie−Weiss behavior, $\chi = C/(T - \theta)$ where $C = N\mu_{\mathrm{eff}}^2/3k \approx \mu_{\mathrm{eff}}^2/8$. The value of μ_{eff} at 300 K is 2.23, and $\theta = -2.6$ K. For the polymer, **6**, a plot of χ^{-1} vs T shows a negative curvature over the entire temperature range. This type of behavior, as well as other anomalies which have been observed previously for ferrocene polymers and oligomers,[12,17] has been ascribed to the effects of large temperature-independent paramagnetism, to very large antiferromagnetic coupling, or even to ferromagnetic interactions. We believe these explanations are erroneous, and the correct interpretation arises as follows.

Hendrickson et al. showed some years ago that low symmetry distortions that lift the degeneracy of the $^2E_{2g}$ ground state of Fc^+ give rise to a temperature-dependent magnetic moment.[18] The theoretical expression for χ is complex, but the *functional* form for the magnetic moment is quite simple: $\mu_{\mathrm{eff}} = bT + C$ (see Figure 1 in ref 18). Substitution of this functional form for μ_{eff} in the Curie−Weiss equation gives a good fit to the data with the values $\chi = (0.00341T + 2.36)^2/8(T + 3.2)$, as shown in Figure 2. Thus, at 300 K, $\mu_{\mathrm{eff}} = 3.38\ \mu_{\mathrm{B}}$ and $\theta = -3.2$ K. Although the derived value for μ_{eff} is slightly larger than those usually observed for ferricinium compounds (2.3−2.6 μ_{B}), we believe this explanation of the observed magnetic behavior is most consistent with the known aspects of ferricinium-ion magnetism and gives physically reasonable values for the antiferromagnetic coupling.

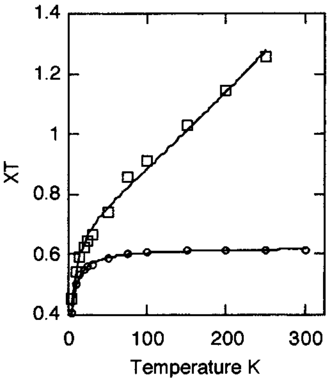

Figure 2. Plot of χT vs T for **6** (□) and **7** (○).

A new general route to a variety of processable, conjugated poly(metallocene)s has been developed. Polymers based on the 3,3′-dihexyl-4,4′-dimethyl-1,1′-ferrocenylarylene repeat unit have been synthesized in good yield. These polymers exhibit a surprisingly large electronic communication between the metal centers, high solubility, and good film-forming properties. A physically reasonable model for the magnetic bahavior of the oxidized poly(aryleneferrocenylene)s was developed.

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Supporting Information Available: Text giving the typical experimental procedures, a table of half-wave potentials, and graphs of UV−vis spectra and CV curves (4 pages). Ordering information is given on any current masthead page.

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