Synthesis of Oligoferrocenylenearylenes and the X-Ray Structure of 1,4-Bis(tricarbonylmethyltungstentetramethylcyclopentadienyl)benzene

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Abstract: Soluble oligo-(1,1′-ferrocenylene-2,5-dihexylphenylene) and oligo-(1,1′-ferrocenylene-2,5-didodecyloxylphenylene) were prepared by the Suzuki coupling of the ferrocene diboronic acid and the 1,4-phenylene diiodide. Direct reaction of lithium 1,4-bis(tetramethylcyclopentadienide)benzene or lithium 2,5-bis(tetramethylcyclopentadienide)thiophene with Fe(II) halides afforded insoluble ferrocenylenearylene oligomers, and with $W(CO)_6$ followed by MeI gave a model dimer whose crystal structure was determined. The magnetic properties of the ferrocene oligomers exhibit anomalous behavior that is explained in terms of the properties of the individual ferrocene groups, rather than to cooperative behavior.

Key words: organometallic polymers, ferrocene, magnetism, structure, charge transfer

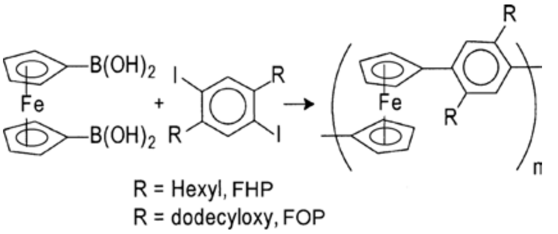
Introduction

Conjugated organometallic polymers (COP) have received much attention for their electroactive and magnetic properties for use in applications, e.g., NLO,[1] electrochromic thin films,[2] macrocyclic precursors,[3] molecular magnets,[4–6] electrochemical sensors,[7] and photoconductors.[8] The combination of the electroactivity of transition metals with the electronic properties of conjugated polymers is an attractive strategy for enhancing the physical and electronic properties of the resultant hybrid polymers.[9] Electronic delocalization along the polymeric chain may be influenced by the nature of the bridging ligands and may be used to enhance the communication between metal centers, thus allowing the magnetic and spectroscopic properties to be fine tuned for specific applications.

Polyferrocenes have been synthesized via a number of routes, including: ring opening polymerization,[10,11] atom abstraction polymerization,[12] Heck coupling,[13] polycondensation of bis(fulvalene) dianions with ferrous halide,[14] transition-metal catalyzed coupling of dihaloarenes and diethynylferrocenes,[15] acyclic diene metathesis,[11] and Knoevenagel condensation.[16] Here, we report two routes: Suzuki coupling of ferrocene diboronic acid and diiodoarenes, and direct condensation of arylenebis(cyclopentadienide)s and Fe(II) halides.

Suzuki Coupling Route to Oligo(ferrocenylene-arylene)s

Oligo[1,1′-ferrocenylene-1,4-(2,5-dihexylphenylene)] (FHP) and oligo(1,1′-ferrocenylene-1,4-(2,5-didodecyloxyphenylene) (FOP) were prepared by the palladium-catalyzed coupling of 1,1′-ferrocene diboronic acid and 1,4-dialkyl(oxy)-2,5-diiodobenzene in DME/3 M NaOH(aq) solvent system (Scheme 1). The palladium catalyst was 1,1′-bis(diphenylphosphino)ferrocenedichloropalladium(II) dichloromethane adduct (dppf).[17] FHP and FOP were isolated in 70% and 89% yields, respectively. The physical appearance of the oligomers is striking as FHP is dark, while FOP is yellow.



Scheme 1

End group analysis, with the assumption of only Cp end groups, of FHP's terminal Cp resonances vs. internal Cp resonances by ^{1}H NMR was carried out for the material isolated by the precipitation procedure described in the experimental section. The ratio of the integrated areas gave a number average degree of polymerization (DP) of 12 repeat units. However, gel permeation chromatography (GPC) of FHP and FOP indicated a DP of only 5 repeat units as determined from M_n. Microanalysis of the oligomers eliminated the discrepancy between ^{1}H NMR and GPC data. The analyses of FHP and FOP were consistent with one iodophenyl end group per chain. Hence, ^{1}H NMR end group analysis assuming only Cp end groups would estimate a DP twice as large as actually present.

The low molecular weights of the oligomers are attributed to the decomposition of ferrocene diboronic to ferrocene boronic acid under basic conditions. The rate of base induced cleavage of B–C bond is slow, but the rate of palladium-catalyzed carbon–carbon bond formation is only slightly greater under polymerization conditions. Although we have not actually tried, the degree of polymer-

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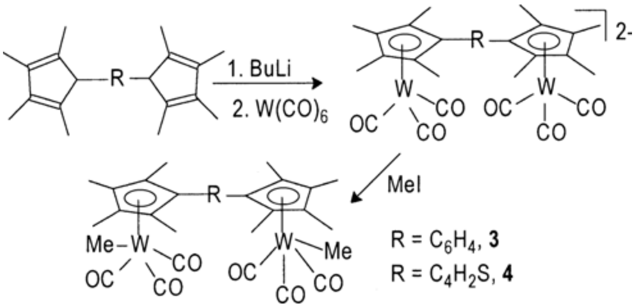
ization might be improved if the functional groups of 1,1′-ferrocene diboronic acid and diiodobenzenes were exchanged and the diboronic acid converted to its ethylene or propylene ester. Placement of the borate ester on the arene would impart solubility in organic solvents and preclude the need for aqueous base, thus decreasing or eliminating the borate ester decomposition.

Condensation of Bis(cyclopentadienide)s Anions with Fe(II) Halides

The second approach to the synthesis of conjugated ferrocenylenearylenes involved the reactions of bis(cyclopentadienide)arene anions with metal(II) halides. In order to develop the method and establish some structural parameters of the materials, two model tungsten tricarbonyl compounds were synthesized according to Scheme 2. 1,4-Bis(tetramethylcyclopentadienyl)benzene (**1**) and 2,5-bis(tetramethylcyclopentadienyl)thiophene (**2**) were dilithiated with two equivalents of butyl lithium in DMF. To these respective solutions, tungsten hexacarbonyl was added, and the mixture was heated to reflux for two hours to afford the ditungsten dianion. The DMF was then removed and THF was added as well as a tenfold excess of methyl iodide. Subsequent workup afforded $\{[Me_4CpW(CO)_3Me]_2C_6H_4\}$ (**3**) and $\{[Me_4CpW(CO)_3Me]_2C_4H_2S\}$ (**4**) in 60 and 30% yields respectively. Both **3** and **4** are yellow, air stable compounds.



Scheme 2

Crystals of **3** suitable for X-ray diffractometry were grown by allowing a concentrated solution of hexane to stand at room temperature for several days. The observed space group was P-1(#2) with Z = 2 (two independent molecules per unit cell, each of which lies on an inversion center). The metrical details of both molecules are nearly identical, and the bond lengths and angles associated with the $CpW(CO)_3Me$ group are not remarkable: bond lengths, W–Me = 2.31 Å, W–CO = 1.99 Å, nearly linear W–C–O (171–177 deg.). As shown in Figures 1 and 2, the Cp rings are essentially coplanar, the W-groups are *anti* to each other, and the central phenylene group is twisted by 36° (molecule 1) and 39° (molecule 2).

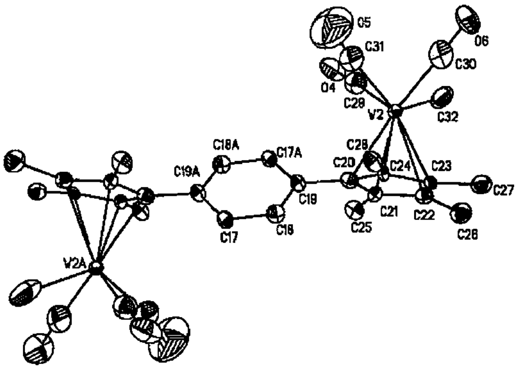


Figure 1 ORTEP drawing of **3** (molecule no. 2)

Although compounds **3** and **4** were prepared as model compounds, these compounds could also serve as synthons for organometallic polymers based on the $W(CO)_3$ group. For example, the methyl groups could be eliminated to form polymers with direct W–W bonds,[18] or the methyl groups could be replaced by bridges between the tungsten atoms, e.g., ethynylene, 1,4-diethynylphenylene, etc.[19,20] A small-scale ^1H NMR photolysis experiment was performed on compound **3** in deuterated benzene with the aim of demonstating homolytic cleavage of the methyl–tungsten bond to yield ethane and tungsten–tungsten bonded polymer. The NMR tube containing **3** and deuterated benzene was subjected to UV light for two hours. NMR spectra were taken ca. every thirty minutes.

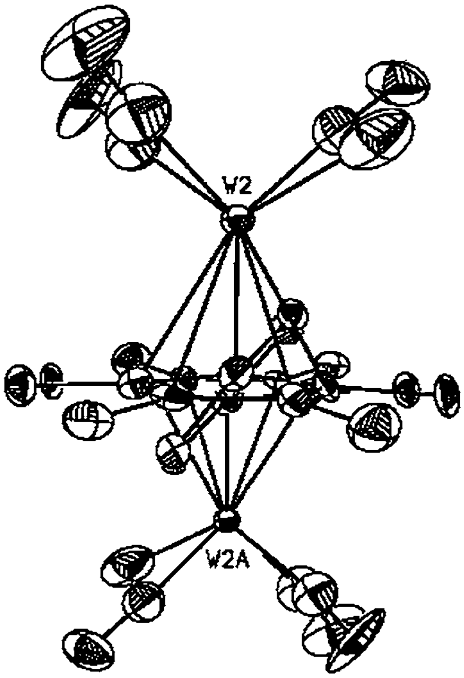


Figure 2 ORTEP drawing of **3** with the view down the long axis of the molecule showing tilt of the phenylene ring

The proton signals of **3** steadily decreased in intensity in relation to that of silicone grease (internal standard), a new signal attributed to ethane formed from the coup-

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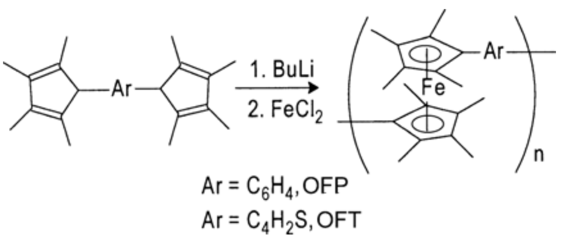
ling of methyl radicals generated by homolysis of the W–Me bond appeared at 0.8 ppm, and a small amount of brown precipitate formed at the bottom of the NMR tube. The brown precipitate may be polymeric [–$W(CO)_3Cp^*C_4H_2Cp^*(CO)_3W$–] with tungsten–tungsten single bonds along the backbone, but due to its insolubility and the small amount the precipitate was not characterized.

The dilithiated bis(tetramethylcyclopentendienyl)arene monomers, **1** and **2**, were allowed to react with an equimolar amount of anhydrous $FeCl_2$ or anhydrous FeI_2 and refluxed for 12 to 24 hours (Scheme 3). A red precipitate was observed to form in the reaction mixture. At the end of the reaction time, the mixture was poured into methanol to complete the precipitation of the product. Oligo(octamethyl-1,1′-ferrocenylene-1,4-phenylene) (OFP) and oligo(octamethyl-1,1′-ferrocenylene-2,5-thienylene) (OFT) were collected in 90 and 80% yields, respectively. The oligo(octamethylferrocenylenearylene)s are brick red powders that are insoluble in all organic solvents, as is a related polymer, poly(octamethyl-1,1′-ferrocenylenedimethylsilylene).[5]



Scheme 3

Thermogravimetric analysis (TGA, heating rate of 40 °C/min, N_2 atmosphere) showed that all of the Fc-containing oligomers are thermally stable to over 400 °C. The onset of decomposition was determined from the temperature at which a 5% weight loss was observed.

UV/Vis spectra of FHP and FOP (Figure 3) exhibited strong Band II (d-d) absorptions at 437 nm ($\varepsilon = 2010\ M^{-1}cm^{-1}$) and 458 nm ($\varepsilon = 2410\ M^{-1}cm^{-1}$), respectively.[21] We assign the peak at 346 nm (FOP) to an MLCT band rather than to a ligand-based $\pi\rightarrow\pi^*$ transition because of its low sensitivity to the nature of the attached arene.[22] FHP does not show a strong absorption at 330 nm, but a shoulder is seen near 300 nm on the side of the intense $\pi\rightarrow\pi^*$ peak at 230 nm. Satisfactory UV-vis spectra of OFP and OFT were not obtained due the insoluble nature of the oligomers. Spangler has studied the electronic spectrum of a series of diferrocenylpolyenes of the general formula F_c–$(CH{=}CH)_n$–F_c, where F_c = ferrocenyl group and n = 1–6.[23] He found that the molar extinction coefficients of the π-π^* absorption of the vinylene bridge increases with greater n, as does molar extinction coeffecients of the ferrocene d-d band, showing that the ferrocene moiety is not an independent chromophore, and that there is significant ligand π^* character in the 'd-d' transition.

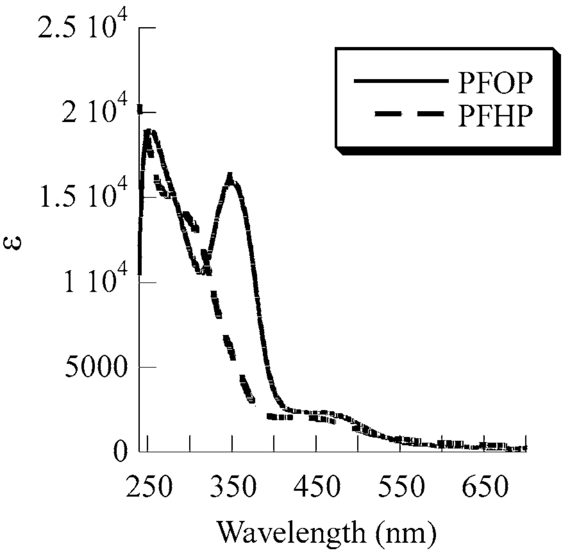
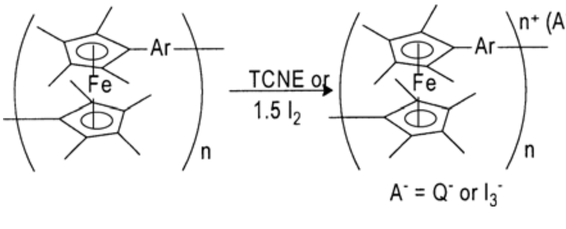


Figure 3 UV/Vis absorption spectra of (a) HFP and (b) FOP

The ferrocene-based oligomers may be oxidized to ferrocenium oligomers by a number of oxidizing agents, e.g. trifluoroacetic acid, nitric acid, tetracyanoethylene (TCNE), or iodine (Scheme 4).[9,18] OFP and OFT may be oxidized with TCNE to produce OFP-Q-100 and OFT-Q-100, or with 1.5 moles of iodine per mole of iron to give OFT-I3-100 and OFP-I3-100 (the appended letter designates the anion, and the number designates that all the Fc centers were oxidized to Fc^+). In the oxidation procedure, the neutral oligomer was slurried with dichloromethane and an oxidant/dichloromethane solution was added. The mixture immediately turned dark brown or black and was allowed to stir at room temperature for one day, during which time the oxidized oligomer dissolved. The solution was filtered, and the solvent removed. The residue was washed with ether and dissolved again in dichloromethane. Finally, the oxidized oligomer was precipitated from solution by addition of hexanes.



Scheme 4

The conversion of OFT to OFT-Q-100 or OFT-I3-100 is nearly quantitative, as was OFP to OFP-I3-100, but TCNE oxidation of OFP gave OFP-Q-100 in only 30% yield. The poor yield may be due to the insolubility of higher molecular weight oligomer despite oxidation. FT-IR spectroscopy showed that the $[TCNE]^-$ radical anion in the oxidized material had reacted with the atmosphere to give the ions shown in Scheme 5. The $[TCNE]^-$ radical anion is characterized by absorptions at 2144 cm^{-1} and 2183 cm^{-1}. How-

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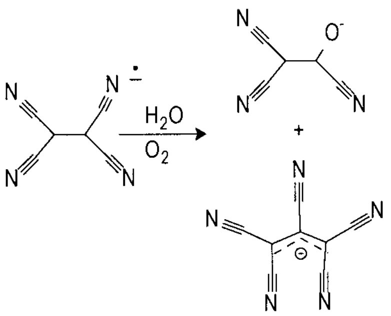
ever, these absorptions are absent in both OFP-Q-100 and OFT-Q-100, but absorptions at 2198, 1598, and 1504 cm^{-1}, indicative of the presence of tricyanoethenolate and pentacyanopropenide ions, known decomposition products of $[TCNE]^-$, were observed. The absorption at 2198 cm^{-1} may be attributed to coincidental absorbances of tricyanoethenolate and pentacyanopropenide ions, while absorptions at 1598 cm^{-1} and 1504 cm^{-1} are assigned to tricyanoethenolate and pentacyanopropenide ions, respectively.[24,25]



Scheme 5

The UV/Vis spectra of OFP-Q-100 and OFT-Q-100 also are consistent with the presence of the $[TCNE]^-$ radical anion decomposition products. Absorptions at 397 nm and 417 nm are indicative of the presence of pentacyanopropenide ion, and a third transition at 297 nm is assigned to the tricyanoethenolate ion. No absorptions consistent with the presence of $[TCNE]^-$ were found.[26,27] Fits of carbon and nitrogen microanalyses for OFP-Q-100 and OFT-Q-100 indicate values for Q that are consistent with a 4:1 ratio of tricyanoethanolate and pentacyanopropenide anions. The spectra of OFP-I3-100 and OFT-I3-100 each exhibited band II absorptions at 542 nm and an MLCT band near 360 nm (Table 1).

Table 1 UV/Vis Data for Neutral and Oxidized Metallocene Materials[a]

Compound[a]	Band II	MLCT
FHP	437 (2010)	300 (sh, 14,000)
FOP	458 (2410)	346 (8000)
OFP-I3-100	542 (2900)	361 (15,600)
OFT-I3-100	542 (1700)	363 (17,800)

[a] The solvent was CH_2Cl_2 for all materials. s = shoulder. All values are reported as λ_{max} in nm and ε in M^{-1} cm^{-1}.

Cyclic voltammetry of the oligomers with 0.1 M Bu_4NPF_6 electrolyte in methylene chloride indicated the presence of moderate electronic communication between ferrocene moieties by exhibiting two reversible waves of equal intensity. These waves have been attributed to the oxidation of alternate metal centers along the oligomer backbone at the first wave ($E = {}^1E_{1/2}$) followed by oxidation of the remaining metal centers at the higher potential ($E = {}^2E_{1/2}$).[28] A more sophisticated approach attributes the presence of two peaks to the 'density of redox states' as a function of potential.[29,30] The latter approach is much more useful in explaining the comproportionation-disproportionation behavior of partially oxidized polymer chains.[30] The separation of the two waves, ΔE, provides a measure of the electronic interaction between the iron centers in the oligomer backbone, and may be expressed as a comproportionation constant (K_c) according to the Equation, where ΔE is in mV and T = 298 K.[31]

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

Equation

Table 2 collects the observed oxidation potentials, ΔE, and the calculated values of Kc. FHP has a ΔE = 160 mV and for FOP the value is 210 mV. The Kc's calculated for FHP and FOP are 500 and 3550, respectively. The corresponding values of Kc for OFP and OFT were obtained from solutions of the soluble, oxidized materials, OFP-Q-100 and OFT-Q-100 and are 160 and 5400. When the metal–metal distances (ca. 9 Å in *trans* configuration, or 8.3 Å in twisted *cis* configuration) are taken into account, these comproportionation constants are rather large, especially when compared to compounds, e.g., diferrocenyl acetylene, $K_c = 160$, whose one-electron oxidized species is classified as a class II type of mixed valence complex (class II materials have values, $0 < Kc < 10^5$; class III have $Kc > 10^5$ and exhibit complete electron delocalization between metal centers).[32]

Table 2 Cyclic Voltammetry Data for Metallocene Compounds[a]

Oligomer	${}^1E_{1/2}$[b]	${}^2E_{1/2}$[b]	ΔE (V)[c]	Kc[d]
FOP	–0.17	0.04	0.21	3550
FHP	–0.01	0.15	0.16	500
OFP-Q-100	–0.37	–0.24	0.13	160
OFT-Q-100	–0.43	–0.15	0.28	5400

[a] Electrolyte: 0.1 M in $Bu_4N^+PF_6^-$, scan rate, 200 mV/s, T = 23 °C.
[b] ${}^1E_{1/2}$, ${}^2E_{1/2}$ = potentials for 1st and 2nd CV waves, volts vs. the Fc/Fc^+ couple set at E = 0.00 V. To convert to NHE, add 0.40 V.[33]
[c] $\Delta E = {}^2E_{1/2} - {}^1E_{1/2}$.
[d] $K_c = \exp(F\Delta E/RT) = \exp(\Delta E/25.69)$.

Magnetic Behavior

The magnetic susceptibility of the TCNE and iodine oxidized oligomers has been investigated. The powdered samples were first cooled in a zero field, and the magnetic susceptibility measured in a field of 0.1 T from 5K to 300 K in a SQUID magnetometer. The susceptibility data obtained for OFT-Q-100 are well represented by Curie–Weiss behavior, $\chi = C/(T-\Theta)$ where $C = N\mu_{eff}^2/3k \approx \mu_{eff}^2/8$. The fully oxidized phenylene oligomers, OFP-Q-100 and OFP-I3-100, as well as OFT-I3-100 exhibited plots of

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χ^{-1} vs. T that showed a negative curvature over the entire temperature range, as shown in Figure 4 (and implicitly shown in Figure 5). This type of behavior, as well as other anomalies that have been observed previously for ferrocene polymers and oligomers, has been ascribed to the effects of a large antiferromagnetic coupling,[34] or even to ferromagnetic interactions.[35] Southard and Curtis argued that this odd magnetic behavior is most likely associated with the complex magnetic behavior of the $^2E_{2g}$ ground state of the Fc^+ ion itself.[30] Hendrickson et al. showed earlier that low symmetry distortions that lift the degeneracy of the $^2E_{2g}$ ground state of ferrocenium cation give rise to a temperature dependent magnetic moment: $\mu = bT+\zeta$, as shown at the high temperature limit in Figure 5.[36] Substitution of this expression for μ_{eff} into the Curie–Weiss equation and subsequent least-squares fitting to the data gives the solid lines shown in Figures 4. The best-fit parameters, b, ζ, and Θ are collected in Table 3.

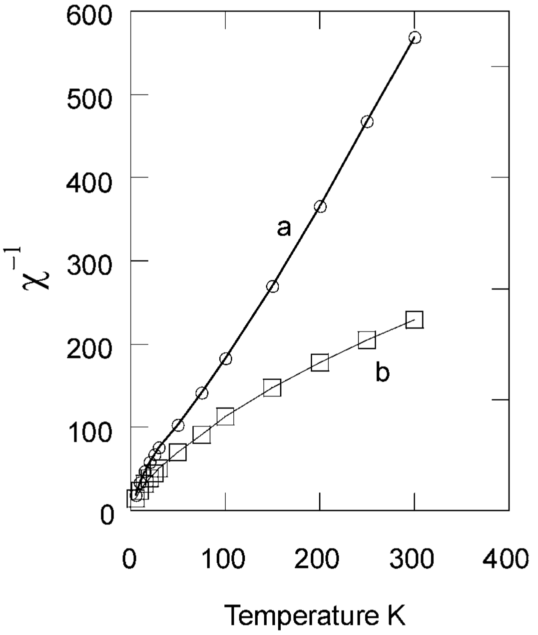

Figure 4 χ^{-1} vs. T (K) for (a) **OFT-Q** and (b) **OFT-I**

Thus, the effective magnetic moment, μ_{eff}, of the ferrocenium ion with a distorted $^2E_{2g}$ state split by a distortion, δ, would be expected to be temperature dependent. However, μ_{eff} of many ferrocenium salts is temperature independent. The lack of temperature dependence of μ_{eff} has been attributed to one of two possible effects by Hendrickson et al.: 1) thermal population of a low-lying electronic state, such as the $^2A_{1g}$ state, corresponding to the d^5 configuration, $a_{1g1}e_{2g2}$, or 2) a temperature dependent, low symmetry distortion.[36] Either effect may lead to cancellation of the μ_{eff} temperature dependence. The χT vs. T curves of all fully oxidized phenylene oligomers and OFT-I3-100 were found to be temperature dependent, hence either the thermal population of the $^2A_{1g}$ was negligible or the low symmetry distortions are constant over the entire temperature range studied.

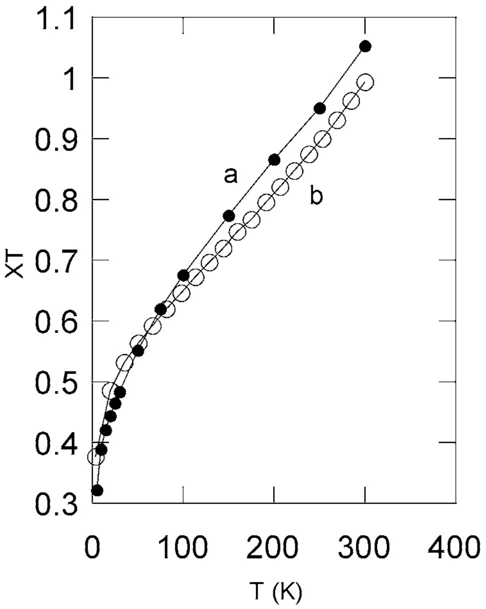

Figure 5 χT vs T for (a) **OFP-I** and (b) **OFP-Q**

Table 3 Magnetic Properties of Oxidized Fc-Ologomers

Compound	μ_{eff}[a]	Θ (K)	10^3b[b]	ζ[b]
OFP-Q-100	3.05	–2.0	2.11	2.42
OFP-I3-100	2.97	–2.1	2.79	2.13
OFT-Q-100	2.29	–14.5	-	-
OFT-I3-100	3.32	–8.8	2.89	2.45

[a] Diamagnetic corrections used: OFP-Q-100 -280×10^{-6} emu/mol; OFP-I3-100 -378 10^{-6}; OFT-Q-100 -363 10^{-6} emu/mol; OFP-I3-100 -357×10^{-6} emu/mol.

[b] $\mu = bT + \zeta$.

Conclusions

The reaction of arene bis(cyclopentadienide) anions with metal salts has been shown to be an effective route to conjugated polymeric and oligomeric metallocenes. Less symmetric substitution patterns and/or longer alkyl side-chain substituents lead to more soluble materials that can be more readily characterized and fabricated into useful shapes, e.g., thin films.[30]

Drying of solvents, descriptions of general experimental techniques, and intrumentation has been described previously.[30] The reagents, 1,4-bis(tetramethylcyclopentadienyl)benzene,[9b] 2,3,4,5-tetramethylcyclopent-2-enone[37] and ferrocene diboronic acid[38] were prepared by published procedures. All other reagents were purchased from Aldrich Chemical Company, Lancaster, Janssen, or Strem Chemical, Inc. Elemental analyses were done by the Microanalysis Laboratory, Department of Chemistry, The University of Michigan, or Galbraith Laboratories, Knoxville, TN.

FHP

Ferrocene diboronic acid (1.00 g, 3.65 mmol), 2,5-dihexyl-1,4-diiodobenzene (1.82 g, 3.65 mmol) and [1,1′-bis(diphenylphosphi-

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no)ferrocnene]palladium(II) chloride·dichloromethane adduct (0.200 g, 0.26 mmol) were placed in a flask containing DME (30 mL) and 3 M aq NaOH (6 mL) under N_2. The mixture was refluxed for 5 d. The resulting solution was precipitated into MeOH, filtered, dissolved in a minimum amount of CH_2Cl_2, and chromatagraphed through silica gel with hexane as eluent with increasing proportions of CH_2Cl_2 followed by Et_2O. Two bands were collected from the CH_2Cl_2 and Et_2O washes respectively. Removal of solvent from the CH_2Cl_2 fraction gave a dark oil (800 mg, 50%).

^{1}H NMR (300 MHz, 25 °C, C_6D_6): δ = 7.83 (br s, 2 H), 4.56 (br m, 4 H), 4.27 (br m, 4 H), 4.10 (s, 1 H), 2.88 (br t, 4 H), 1.67 (br m, 4 H), 1.28 (br s, 12 H), 0.88 (br t, 6 H).

Anal. Calcd for $[C_{28}H_{36}Fe]_n$: C, 78.48; H, 8.47; Fe, 13.03. Found: C, 75.34; H, 8.09; Fe, 12.77.

Solvent removal from the Et_2O fraction gave a black solid (300 mg, 20%).

Thermogravimetric analysis: 5% weight loss at 411 °C; 29% char yield at 900 °C.

Gel Permeation Chromatography (THF, polystyrene standard, 1 mL/min, UV detection): M_n = 2700; M_w = 5600; PDI = 2.1; DP = 13.

UV/Vis ($CHCl_3$): λ_{max} (ε) = 282 (14,130), 430 nm (2,000).

^{1}H NMR (300 MHz, 25 °C, C_6D_6): δ = 7.83 (br s, 2 H), 4.56 (br m, 4 H), 4.27 (br m, 4 H), 4.10 (s, 1 H), 2.88 (br t, 4 H), 1.67 (br m, 4 H), 1.28 (br s, 12 H), 0.88 (br t, 6 H).

Anal. Calcd for $[C_{28}H_{36}Fe]_n$: C, 78.48; H, 8.47; Fe 13.03. Found: C, 73.96; H, 7.92; Fe, 11.28.

1,4-Didodecyloxy-2,5-diiodobenzene

Silver trifluoroacetate (2.7 g, 12.2 mmol), I_2 (3.1 g, 12.2 mmol), and 1,4-didodecyloxybenzene (2.5 g, 6.05 mmol) were placed in a flask containing CH_2Cl_2 (100 mL). The mixture was allowed to stir for 1 h, during which time large amounts of AgI precipitated. The AgI was removed by filtration, and the organic layer was washed with 10% aq $NaHSO_3$ (2 × 100 mL) and dried ($MgSO_4$). Filtration, solvent removal, and crystallization from EtOH (2 × 100 mL) gave 2.8 g (70%) of irregular pink crystals.

^{1}H NMR (300 MHz, 25 °C, C_6D_6): δ = 7.08 (s, 2 H), 3.33 (t, 4 H), 1.55 (q, 4 H), 1.32 (br m, 36 H), 0.92 (t, 6 H).

Anal. Calcd for $C_{30}H_{52}I_2O_2$: C, 51.58; H, 7.50. Found: C, 52.01 ; H, 7.67.

FOP

Ferrocene diboronic acid (1.00 g, 3.65 mmol), 1,4-didodecyloxy-2,5-diiodobenzene (2.55 g, 3.65 mmol), and [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) dichloromethane adduct (0.20 g, 0.26 mmol) were placed into a flask containing DME (30 mL) and 3 M aq NaOH (6 mL) under N_2. The mixture was refluxed for 7 d. The black mixture was twice precipitated into MeOH giving 2.04 g (90% yield) of yellow solid.

Thermogravimetric Analysis: 5% weight loss 428 °C; 26.7% char yield at 900 °C.

Gel Permeation Chromatography (THF, polystyrene standard, 1 mL/min, UV): M_n = 3270; M_w = 5340; PDI = 1.6; DP = 8.5.

FT-IR (KBr): 3044 (CH aromatic stretch), 2922, 2853 (CH alkyl stretch), 1455 (C=C aromatic stretch), 1213 (CH alkyl bend), 820 cm^{-1} (CH Cp bend).

UV/Vis ($CHCl_3$): λ_{max} (ε): = 251 (9,530), 346 (8,040), 459 nm (1,190).

^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): δ = 6.82 (br, 2 H), 4.77–4.68 (br m, 4 H), 4.26–4.13 (br m, 4 H), 3.81 (br m, 4 H), 1.82 (br m, 4 H), 1.29 (br s, 36 H), 0.89 (br s, 6 H).

Anal. Calcd for $[C_{40}H_{60}FeO_2]_n$: C, 76.40; H, 9.62; Fe, 8.88. Found: C, 74.90; H 9.51; Fe 8.40.

$[C_5Me_4WMe(CO)_3]_2C_6H_4$ (3)

1,4-Bis(tetramethylcyclopentadienyl)benzene (200 mg, 0.63 mmol) was placed in an 100 mL Schlenk flask. DMF (20 mL) was transferred via cannula and 2.5 M BuLi (0.53 mL) was added dropwise. The orange solution was stirred for 1 h before tungsten carbonyl (475 mg, 1.35 mmol) was added. The mixture was refluxed for 2 h. The DMF was removed, THF (20 mL) was added via cannula, and MeI (940 mg, 7.00 mmol) was added dropwise. The black solution was refluxed for 1 h. The solution was cooled, the THF removed, and the residue washed with MeOH (50 mL) and hexanes (50 mL) The tungsten dimer was collected by filtration to give a light yellow solid (330 mg, 60%).

FT-IR (KBr): 2002 (C=O stretch), 1898 cm^{-1} (C=O stretch).

^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): δ = 7.24 (s, 4 H, C_6H_4), 2.04 (s, 12 H, CH_3), 2.01 (s, 12 H, CH_3), 0.26 (s, 6 H, WCH_3).

^{13}C NMR (75 MHz, 25 °C, C_6D_6): δ = 219.52, 132.62, 131.77, 110.01, 103.99, 11.14, 10.09, –22.60.

MS: *m/z*: Found 882. Calcd for $C_{32}H_{34}O_6W_2$: 882.

Anal. Calcd for $C_{32}H_{34}O_6W_2$: C, 43.55; H, 3.88. Found: C, 43.18; H, 4.04.

$[C_5Me_4WMe(CO)_3]_2C_4H_2S$ (4)

Prepared as above from 2,5-bis(tetramethylcyclopentadienyl)thiophene (100 mg, 0.31 mmol) and 2.5 M BuLi (0.25 mL) to give a light yellow solid (100 mg, 32%).

FT-IR (KBr): 2003 (C=O stretch), 1903 (C=O stretch), 1893 cm^{-1} (C=O stretch).

^{1}H NMR (300 MHz, 25 °C, C_6D_6): δ = 6.76 (s, 2 H, C_4H_2S), 1.79 (s, 12 H, CH_3), 1.46 (s, 12 H, CH_3), 0.46 (s, 6 H, WCH_3).

^{13}C NMR (75 MHz, 25 °C, C_6D_6): δ = 218.99, 137.00, 130.19, 105.04, 104.04, 11.18, 10.15, –22.62.

MS: *m/z* = Found: 888. Calcd for $C_{30}H_{32}O_6W_2S$: 888.

Anal. Calcd for $C_{30}H_{32}O_6W_2S$: C, 40.56; H, 3.63. Found: C, 41.17; H, 3.83.

Crystallography for $[C_5Me_4WMe(CO)_3]_2C_6H_{4\,(3)}$

Crystals suitable for diffractometry were grown by allowing a concentrated solution in hexanes to stand at r.t. for several days. Crystallographic data: Triclinic, P-1(#2), Z = 4, Unit cell dimensions, a = 9.8710(10) Å, b = 11.266(2) Å, c = 13.627(2) Å, α = 92.770(10)º, β = 94.370(10º, γ = 90.120(10º, Volume, 1509.2(4) Å^{3,} Density (calcd.) 1.942 g/cm^3 Reflections collected, 7115, Independent reflections, 5909 [R_{int} = 0.1101], Refinement method, Full-matrix least-squares on F^2, Goodness-of-fit on F^2 0.979, Final R indices [I>2σ(I)], R1 = 0.0697, wR2 = 0.1723. There are 2 independent molecules in the crystal lattice, each on inversion centers.

OFP

1,4-Bis(tetramethylcyclopentadienyl)benzene (500 mg, 1.57 mmol) was placed in a 100 mL Schlenk flask. THF (30 mL) was added via cannula and the solution was cooled to –78 °C before 2.5 M BuLi (1.29 mL) was added dropwise. The yellow solution was allowed to warm to r.t. and stirred for 1 h. $FeCl_2$ (200 mg, 1.57 mmol) was added, and the solution was refluxed for 3 h. A brick red precipitate formed. The mixture was cooled to r.t., poured into MeOH (250 mL), and the precipitate collected by filtration resulting in a brick red powder (540 mg, 90%). The material was very insoluble in all organic solvents. The oligomer was oxidized easily by many oxidizing agents; e.g. HNO_3, triflouroacetic acid, HCl, TCNE.

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Thermogravimetic analysis: 5% weight loss at 438C; 56.4% char yield at 900C.

FT-IR (KBr): 3044 (CH aromatic stretch), 2972, 2946, 2904, 2862 (CH alkyl stretch), 1524, 1448 (C=C aromatic stretch), 1376 cm^{-1} (CH alkyl bend).

Anal. Calcd for $C_{24}H_{28}Fe$: C, 77.42; H, 7.58: Fe 15.00. Found: C, 75.15; H, 7.52; Fe, 12.4 (15.00).

OFP-Q-100

OFP (100 mg, 0.268 mmol) was placed into a 100 mL Schlenk flask, and TCNE (38 mg, 0.291 mmol) dissolved in CH_2Cl_2 (10 mL) was added via cannula. The slurry immediately darkened to deep green, and the mixture was allowed to stir for 18 h. The CH_2Cl_2 was removed, and the residue was washed with Et_2O (2 × 50 mL). The residue was redissolved in CH_2Cl_2, the solution was filtered, and the product precipitated by addition of petroleum ether (bp 40–60 °C). Filtration resulted in 37 mg (30%) of dark green OFP-Q-100.

FT-IR (KBr): 2199 (CN stretch), 1599 (C=C stretch), 1505 cm^{-1} (C–C–C stretch).

UV/Vis ($CHCl_3$): λ_{max} (ε) = 261 (21,310), 298 (21,260), 326 (9,500), 397 (9,670), 417 (8,740), 463 nm (3,550).

Anal. Calcd for $[(C_{10}Me_8Fe)C_6H_4](C_5N_3O)_{0.83}(C_8N_5)_{0.17}$: C, 71.09; H, 5.66; N, 9.38. Found: C, 71.49; H, 5.71; N, 10.17.

OFP-I3-100

OFP (50 mg, 0.134 mmol) was placed into an 100 mL Schlenk flask and I_2 (61 mg, 0.201 mmol) dissolved in CH_2Cl_2 (10 mL), was added via cannula. The slurry immediately darkened to deep brown, and the mixture was allowed to stir for 18 h. Filtration resulted in 80 mg (80% yield) of dark brown OFP-I3-100.

FT-IR (KBr): 3044 (CH aromatic stretch), 2959, 2923, 2855 (CH alkyl stretch), 1471, 1456 (C=C aromatic stretch), 1376 cm^{-1} (CH alkyl bend).

UV/Vis ($CHCl_3$): λ_{max} (ε) = 234 (15,150), 293 (31,200), 361 (15,640), 542 nm (2,860).

Anal. Calcd for $[(C_{10}Me_8Fe)C_6H_4](I_3)$: C, 38.28; H, 3.75; I, 50.55. Found: C, 39.63; H, 3.83; I, 50.50.

2,5-$(C_5Me_4H)_2C_4H_2S$

2,5-Dibromothiophene (4.38 g, 18.1 mmol) was placed in a 250 mL Schlenk flask under N_2. Anhyd Et_2O (50 mL) was added via cannula, the solution was cooled to –78 °C, and 2.5 M BuLi in hexanes (8 mL) was added dropwise. After the solution was stirred for 20 min, a white precipitate formed. 2,3,4,5-Tetramethylcyclopent-2-enone (2.5 g, 18 mmol) was added dropwise, causing the precipitate to redissolve. The solution was heated to reflux for 1 h, and then cooled to –78 °C. More 2.5 M BuLi (8 mL) was added, causing a white precipitate to form slowly. The mixture was stirred for 1 h at r.t. Additional 2,3,4,5-tetramethylcyclopent-2-enone (5 g, 36 mmol) was added dropwise, causing the precipitate to dissolve. The solution was stirred for 1 h at r.t., then refluxed for 30 min. After cooling to r.t. and quenching with sat. aq NH_4Cl (2 × 100 mL), the aqueous phase was extracted with Et_2O (2 × 30 mL), and the combined Et_2O fractions were dried ($MgSO_4$). The solution was concentrated to about 30 mL, and *p*-toluenesulfonic acid monohydrate (700 mg) was added. After stirring for 10 min, a precipitate was observed. The stirring was continued for 2 h, after which time sufficient Et_2O was added to dissolve all of the precipitate. The Et_2O solution was washed with H_2O (3 × 100 mL) and dried ($MgSO_4$). The Et_2O was removed to give the yellow solid product which was recrystallized from EtOH (1.14 g, 20%).

^{1}H NMR (300 MHz, 25 °C, CD_2Cl_2): δ = 6.82 (s, 2 H, C_4H_2S), 3.07 (br m, 2 H, C_5Me_4H), 2.14 (s, 6 H, CH_3), 1.92 (s, 6 H, CH_3), 1.85 (s, 6 H, CH_3), 1.14 (d, 6 H, CH_3).

MS: *m/z*: Found: 324. Calcd for $(C_5Me_4H)_2C_4H_2S$: 324.

Anal. Calcd for $(C_5Me_4H)_2C_4H_2S$: C, 81.42; H, 8.70. Found: C, 81.29; H, 8.73.

OFT

2,5-Bis(tetramethylcyclopentadienyl)thiophene (500 mg, 1.54 mmol) was placed in an 100 mL Schlenk flask. THF (30 mL) was added via cannula and the solution was cooled to –78 °C before 2.5 M BuLi (1.25 mL, 3.1 mmol) was added dropwise. The yellow solution was allowed to warm to r.t. and stirred for 1 h. $FeCl_2$ (195 mg, 1.54 mmol) was added, and the solution was refluxed for 12 h. A brick red precipitate formed. The mixture was cooled to r.t., poured into MeOH (250 mL), and the product was collected by filtration resulting in 470 mg (82% yield) of brick red powder. The material was very insoluble in all organic solvents. The oligomer was oxidized easily by a variety of oxidizing agents; e.g. HNO_3, trifluoroacetic acid, HCl, TCNE, benzoquinone, etc.

Thermogravimetric Analysis: 5% weight loss at 457 °C; 41.6% char yield at 900 °C.

FT-IR (KBr): 3044 (CH aromatic stretch), 2970, 2946, 2905, 2867 (CH alkyl stretch), 1378 cm^{-1} (CH alkyl bend).

MS-FAB: *m/z* = Found: 702, 1080, 1458, 1838. Calcd for $[Fe(C_{10}Me_8C_4H_2S)(C_{10}Me_8H_2C_4H_2S)]$: 702; $[Fe_2(C_{10}Me_8C_4H_2S)_2(C_{10}Me_8H_2C_4H_2S)]$: 1080; $[Fe_3(C_{10}Me_8C_4H_2S)_3(C_{10}Me_8H_2C_4H_2S)]$: 1458; $[Fe_4(C_{10}Me_8C_4H_2S)_4(C_{10}Me_8H_2C_4H_2S)]$: 1838.

Anal. Calcd for $C_{22}H_{26}FeS$: C, 69.84; H, 6.93; Fe, 14.80. Found: C, 67.40; H, 6.92; Fe, 14.10.

OFT-Q-100

OFT (50 mg, 0.132 mmol) was placed into an 100 mL Schlenk flask and TCNE (19 mg, 0.146 mmol), dissolved CH_2Cl_2 (10 mL), was added via cannula. The slurry immediately darkened to deep green, and the mixture was allowed to stir for 18 h. The CH_2Cl_2 was removed, the residue was washed with Et_2O (2 × 50 mL) and redissolved in CH_2Cl_2. The solution was filtered, and the product was precipitated by addition of petroleum ether (bp 40–60 °C). Filtration resulted in 47 mg (80% yield) of dark brown OFT-Q-100 being collected.

FT-IR (KBr): 2198 (C≡N stretch), 1598 (C=O stretch), 1504 cm^{-1} (C–C–C stretch).

UV/Vis ($CHCl_3$): λ_{max} (ε) = 233 (7,950), 300 (14,900), 397 (7,300), 417 (6,480), 463 nm (2,780).

Anal. Calcd for $[(C_{10}Me_8Fe)C_4H_2S](C_5N_3O)_{0.81}(C_8N_5)_{0.19}$: C, 65.22; H, 5.24; N, 9.27. Found: C, 64.64; H, 5.24; N, 9.02.

OFT-I3-100

OFT (50 mg, 0.132 mmol) was placed into an 100 mL Schlenk flask, and I_2 (61 mg, 0.201 mmol), dissolved CH_2Cl_2 (10 mL), was added via cannula. The slurry immediately darkened to deep green, and the mixture was allowed to stir for 18 h. The CH_2Cl_2 was removed, the residue was washed with Et_2O (2 × 50 mL) and redissolved in CH_2Cl_2. The solution was filtered, and the product was precipitated by addition of petroleum ether (bp 40–60 °C). Filtration resulted in 105 mg (99% yield) of dark brown OFT-I3-100.

FT-IR (KBr): 3044 (CH aromatic stretch), 2924, 2854, (CH alkyl stretch), 1651, 1630 (C=C alkene, thiophene), 1468, 1447 (C=C aromatic stretch), 1378 cm^{-1} (CH alkyl bend).

UV/Vis ($CHCl_3$): λ_{max} (ε): 235 (26,570), 295 (29,850), 363 (17,770), 542 nm (1,670).

Anal. Calcd for $[(C_{10}Me_8Fe)(C_4H_2S](I_3)$: C, 34.81; H, 3.45. Found: C, 34.49; H, 3.35.

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