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Copper-Mediated Polycondensations of Substituted Diiodoferrocenes and Bis(stannyl)ferrocenes: Synthesis and Properties of Soluble Polyferrocenylenes Containing Trimethylsilyl or Methyl Groups

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ABSTRACT: Low to moderate molecular weight substituted polyferrocenylenes $[(\eta^5\text{-}C_5H_3X)Fe(\eta^5\text{-}C_5H_3X)]_n$ (where **3a**−**3c**, X = H, $SiMe_3$, Me) were prepared from the Ullmann coupling reaction of the diiodoferrocenes, $(\eta^5\text{-}C_5H_3XI)_2Fe$ (**2a**−**2c**), with an excess of copper metal or alternatively CuCl-facilitated coupling of the bis(stannyl)ferrocene, $(\eta^5\text{-}C_5H_3SiMe_3SnBu_3)_2Fe$ (**1b**). The new monomers were characterized by ^1H and ^{13}C NMR spectroscopy, elemental analysis and mass spectrometry. A single-crystal X-ray diffraction study $(\eta^5\text{-}C_5H_3SiMe_3I)_2Fe$ (**2b**) shows the disubstituted cyclopentadienyl rings are eclipsed with the substituents staggered by 20°. The molecular weights (M_w) for the soluble homopolymers **3b** and **3c** were estimated by gel permeation chromatography in THF vs polystyrene standards and were found in the range from 2.0×10^3 to 1×10^4 with generally broad polydispersities (PDI > 2). Polymers **3b** and **3c** were characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis. The polymer thermal transition behavior and morphology of **3a**−**3c** were examined by differential scanning calorimetry (DSC) and by powder X-ray diffraction (PXRD). The amorphous nature of the disubstituted polymers **3b** and **3c** was evident by the presence of weak glass transitions and the absence of any melt transitions. In contrast, the semicrystalline nature of the largely insoluble polyferrocenylene **3a** led to the presence of a strong melt transition by DSC in addition to three sharp peaks in its the PXRD spectrum. The polymers **3b** and **3c** as well as their I_2 and TCNE oxidized products (**4b**, **4c** and **5b**, **5c**) were characterized by UV/vis/NIR spectroscopy. The neutral polymers **3b** and **3c** showed only weak d−d visible transition centered near $\lambda = 480$ nm, while the partially oxidized derivatives showed strong charge-transfer peaks in the visible $\lambda = 630-700$ nm) and broad intervalence charge-transfer transitions between $\lambda = 850$ and 1900 nm. Cyclic voltammetry of the neutral polymers **3b** and **3c** showed two well-separated oxidation waves with $\Delta E_{1/2}$ values of 485 and 460 mV s^{-1} respectively and were consistent with substantial interaction between neighboring metal centers. Mössbauer data of the partial oxidized dimethylferrocene polymer **5c** with TCNE at room temperature indicates that electron transfer is valence trapped with distinct Fe^{2+} and Fe^{3+} sites.

Introduction

Metallocenes are attracting growing attention as components of solid-state oligomeric and high polymeric materials with unusual electronic and physical properties.[1] In recent years, this has led to the substantial development of metallocene polymer chemistry where several examples of readily synthesized, processable organometallic polymers have been identified. In particular, alternating high molecular weight polymers containing a metallocene unit and a heteroatom of Si,[2,3,4,5] Ge,[6,7] Sn,[8] P,[9] S,[10] Se,[11] or B[12] prepared by thermal, anionic, or transition-metal-catalyzed polymerization of strained [1]metallocenophanes have been reported. While details of the electrochemistry and electronic properties of polyferrocenylsilanes and related polymers confirm substantial degrees of delocalization along their backbones,[13] a similar understanding for soluble polyferrocenylenes has not been reported.

Oligomers and short-chain linear polymers where the main chain consists only of ferrocene units have been known for nearly 40 years. In these materials, adjacent ferrocenes are directly connected through cyclopentadienyl (Cp) ring carbons with their iron centers located in close proximity. The interest in preparing processable polymeric materials of this type stems from the observation of a number of unusual electronic properties attributable to the extensive one-dimensional delocalization of iron centers along the main chain when partially or fully doped, including high conductivities (10^{-2} S cm^{-1}),[14] strong intervalence charge-transfer bands,[15] and an extensive degree of metal−metal interaction by cyclic voltammetry.[16] The promise, then, is that films of partially oxidized polyferrocenylenes containing both ferrocene and ferrocenium type units could function as polymeric conductors,[17] optoelectronic materials,[18] and, when fully oxidized, polymeric ferromagnetic coatings[19] suitable for read/write applications.

Polyferrocenylene is a particularly attractive synthetic target in that the potentially useful and unusual properties observed with other ferrocene-containing polymer systems suggest that these properties should be optimal in these species. In most ferrocene-containing polymers, the ferrocene unit is incorporated in the main chain and is separated by one or more bridging atoms. As a result, there is a reduced degree of electronic interaction between adjacent ferrocenes. For instance, in model biferrocenes and polyferrocenylenes the iron centers between ferrocene units are approximately 3.5−5.0 Å apart,[20] while on average the Fe−Fe distance for polyferrocenylsilanes lies between 5.5 and 6.5 Å.[21] The nature of these interactions is also different where electron transport or delocalization in polyferroce-

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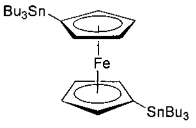
nylenes essentially occurs through Cp based pπ orbitals and metal-based dπ orbitals while polyferrocenylsilanes are linked through pπ−dπ−σ orbitals with addition of the bridging silicon group.

Until recently, convenient, reproducible routes to soluble polyferrocenylenes have not been available. Preparation of polyferrocenylene was first described by Korshak and Nesmeyanov in 1961.[22,23] Samples of polyferrocenylene were isolated in low yield from the reaction of molten ferrocene in the presence of *tert*-butylperoxide, where polyrecombination of ferrocene radicals is believed to occur. Number-average molecular weights, M_n, were reported to vary between 2500 and 7000; however, the exact structure of this polymer was not determined and likely contains multilinked ferrocenes and methylene and oxygen bridges as well as mixed oxidation state species. The polycondensation synthesis of low molecular weight linear polyferrocenylene was also described by Rosenberg and co-workers, where the transition-metal-catalyzed coupling of dilithioferrocene−tmeda ($Fe(\eta^5\text{-}C_5H_4Li)_2\cdot$tmeda) in the presence of either $CoCl_2$ or $CuCl_2$ was carried out.[24] Investigations into the use of ferrocenyl cuprates[25,26] and related species as monomers for polycondensation has been extensively explored but has not resulted in any substantial increase in the degree of polymerization or yield of polyferrocenylene. Organocopper chemistry was employed by Neuse and co-workers in 1979 to afford low molecular weight polyferrocenylene from the catalytic oxidative coupling of equimolar amounts of $Fe(\eta^5\text{-}C_5H_4\text{-}Li)_2\cdot$tmeda and $Fe(\eta^5\text{-}C_5H_4I)_2$ with CuI.[27] Rausch had also reported earlier the successful solid-state synthesis of oligomeric ferrocenes from the Ullmann coupling reaction of $Fe(\eta^5\text{-}C_5H_4I)_2$ with excess copper metal.[28] The preparation of moderate molecular weight ($M_n = 4600$), semicrystalline samples of polyferrocenylene by Yamamoto et al. in 1980 was carried out using the dehalogenation polymerization of either $Fe(\eta^5\text{-}C_5H_4I)_2$ or $Fe(\eta^5\text{-}C_5H_4Br)_2$ with activated magnesium metal.[29] All of the above preparative routes to polyferrocenylenes result in either very low molecular weight or intractable materials that are at best only partial characterized and are difficult to prepare and reproduce. More recently, reasonably well characterized oligomeric and polymeric ferrocenylenes were prepared by Nishihara et al. from the reaction of dihexylfulvalene dianion with $[FeCl_2\cdot 2THF]$.[16] A polymer of $M_w > 4000$ was separated by recycling HPLC, along with a substantial yield of oligomeric material. Successful preparation of insoluble ferrocene containing polymers from the Pd-catalyzed coupling of diiodoferrocene with alkynyltrimethylstannanes was recently reported by Dixneuf and co-workers.[30]

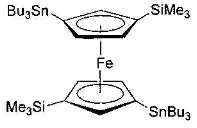
In this report, we have reinvestigated a number of the previously explored routes to the preparation of polyferrocenylenes and report on those findings. We also detail the preparation of the first examples of moderate molecular weight, soluble polyferrocenylenes by organocopper-based chemistry involving Ullmann condensation and Ullmann coupling polymerizations.

Results and Discussion

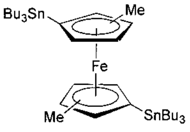
Synthesis of Bis(stannyl)ferrocenes $Fe(\eta^5\text{-}C_5H_4SnBu_3)_2$ (1a), $Fe(\eta^5\text{-}C_5H_3SiMe_3SnBu_3)_2$ (1b), $Fe(\eta^5\text{-}C_5H_3MeSnBu_3)_2$ (1c) and Diiodoferrocenes $Fe(\eta^5\text{-}C_5H_4I)_2$ (2a), $Fe(\eta^5\text{-}C_5H_3SiMe_3I)_2$ (2b), $Fe(\eta^5\text{-}C_5H_3MeI)_2$ (2c) Monomers. The synthesis of the bis(tri-*n*-butylstannyl)ferrocenes **1a**−**c** was carried out using the similar synthetic methodology outlined by Wright[31] for compound **1a**. Reaction of the dilithiated ferrocene, bis(trimethysilyl)ferrocene, and dimethylferrocene precursors in hexane at −78 °C with tri-*n*-butylchlorostannane afforded the crude products **1a**−**1c** in good yield. While **1a** was readily vacuum distilled, attempts to distill the bulkier stannylferrocenes **1b** and **1c** resulted in degradation of the crude samples. Purification of the stannylferrocenes **1b** and **1c** by column chromatography also proved to be somewhat cumbersome, as previously noted by Butler in his work with related tin-containing ferrocenes.[32] In this case, while the separation of mono- and disubstituted products was straightforward, traces of tetrabutyltin and other tin salts were detected in the disubstituted products even after repeated column purification. Attempts to purify **1c** were also hindered by the lack of regioselectivity in the lithiation of dimethylferrocene. Compounds **1b** and **1c** were therefore used in the iodination or Ullmann coupling reactions without further extensive purification.



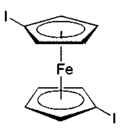
1a



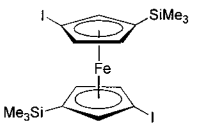
1b



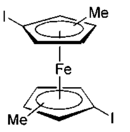
1c



2a



2b



2c

The new diiodoferrocenes **2b** and **2c** were prepared using a variation of the halogen/organotin exchange reaction reported by Butler for **2a**.[32] Using the bis(tri-*n*-butylstannyl)ferrocenes **1a**−**1c** as starting materials, direct iodination to the crude products **2a**−**2c** is afforded by reaction with 2 molar equiv of iodine at 0 °C in dichloromethane. The organic phases containing the crude products are then reduced with aqueous sodium thiosulfate and filtered through neutral alumina. After removal of the solvent, dark amber oils were recovered. Further purification to remove residual tin salts was afforded by redissolving the crude product in methanol and adding potassium fluoride. The bright yellow slurries were filtered through neutral alumina. After further washing and an additional chromatographic step, the pure diiodoferrocenes **2a** and **2c** were obtained as dark amber oils, while **2b** was isolated as amber crystals. Overall reaction yields starting from the base ferrocenes ranged from 30% for **2b** to 70% for **2c**.

Characterization of Bis(stannyl)ferrocenes 1a−1c and the Diiodoferrocenes 2a−2c. The identities of the difunctional monomers **1a**, **1b**, and **1c** were confirmed by ^1H and ^{13}C NMR analysis. Characterization of all the unique peaks in **1a** and **1b** was straightforward, and in the case of **1b**, the analysis showed chemical shifts very similar to those reported for other tetrasubstituted ferrocenes with bis(trimethylsilyl) functionality attached to the cyclopentadienyl ring.[33] As previously reported by ourselves[34] and others,[35] the lithiation of the cyclopentadienyl rings of 1,1′-dimethylferrocene is not regioselective, yielding in 1,2- and 1,3-substituted species for each of the cyclopentadienyl

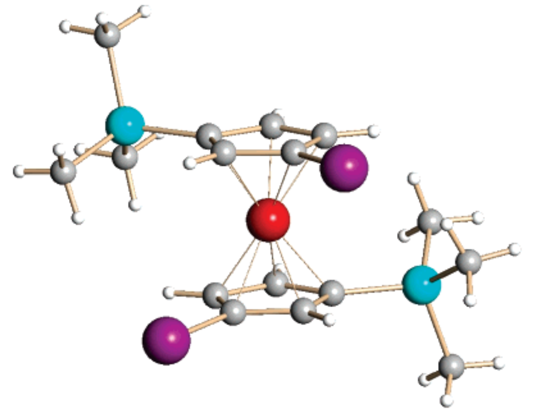
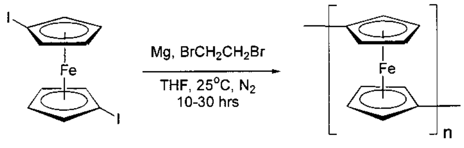


Figure 1. View of the diiodo monomer, **2b**.

Scheme 1



2a **3a**

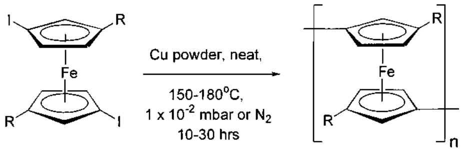
rings, resulting in several possible new ferrocenyl isomers of **1c** containing both methyl and tri-*n*-butylstannyl groups. The diiodoferrocenes **2a** and **2c** were recovered as air-stable amber oils while **2b** formed dark amber crystals (see Figure 1). The monomers were characterized by ^1H and ^{13}C NMR and the elemental analysis was determined for the new products **2b** and **2c**. As reported earlier,[36] a single-crystal X-ray diffraction of **2b** reveals eclipsed Cp rings with the two groups occupying the 1,3 positions, respectively. The trimethylsilyl and diiodo groups are staggered by 141.0(4) and 69.6(3)°, respectively. The structure of compound **2b** details a staggered conformation to accommodate the presence of both the bulky trimethylsilyl and iodo groups on each cyclopentadienyl ring. The top and bottom Cp carbons are essentially eclipsed, with the trimethylsilyl and diiodo staggered by approximately 20° with respect to one another. All of the trimethylsilyl and iodo substituents lie in the planes of the cyclopentadienyl ring carbons.

Preparation of Polyferrocenylenes. Three general strategies where employed for preparation of polyferrocenylenes **3a**–**3c**. The first was to replicate the use of Mg-coupling polymerizations of dihaloferrocenes used successfully by Yamamoto[29] to prepare **3a**, the second was to reinvestigate the use of Cu-mediated couplings used by Rausch[28] in the preparation of oligoferrocenes, and the third was to explore the CuCl-mediated Ullmann reactions of bis(stannyl)ferrocenes, borrowing similar methodology from Piers[37] in his high yield preparation of carbon–carbon bonds in alkenyltrimethylstannane species.

Preparation of Polymers 3a–3c: Ullmann Coupling of Fe(η^5-C_5H_3XI)$_2$ Diiodoferrocenes To Yield the Polyferrocenylenes [Fe(η^5-C_5H_3X)$_2$]$_n$. The first efforts to prepare processable polyferrocenylenes utilized the Mg-type coupling reactions employed by Yamamoto.[29] In that work, high purity diiodoferrocene was reacted with activated Mg metal in the presence of dibromoethane to prepare largely insoluble, but highly crystalline polyferrocenylenes (Scheme 1).

Similar attempts with all three monomers **2a**–**2c** were undertaken; however, polymer was only detected in the case of **2a**. As in Yamamoto's work,[29] we were able to isolate the insoluble polymer **3a** in good yield and confirmed the crystalline nature of this product by PXRD. In the reactions of **2b** and **2c** under the same conditions, only starting materials were recovered. The lack of reactivity is somewhat surprising given the expected difference between the more electron-rich **2c** monomer and the comparatively electron-poor **2b**. The failure to polymerize may, however, be related to difficulty in accessing the iodine in the presence of the sterically hindering Me and $SiMe_3$ groups.

Scheme 2



Where R = SiMe$_3$ or Me
2b, 2c **3b, 3c**

In the 1970s, Rausch[28] had reported the Ullmann coupling reactions between mono- and diiodoferrocenes with an excess of activated Cu metal to give high yields of oligoferrocenes. The relative bulk and electronic nature of the groups attached to the cyclopentadienyl rings in **2b** and **2c**, would be expected to have a significant impact on the relative rate and degree of polymerization for these species. We employed Rausch's synthetic methodology for the polymerization of the highly purified monomers **2b** and **2c**. Reactions of neat **2b** and **2c** in the presence of Cu metal at elevated temperatures (>150 °C) yielded a mixture of oligomeric and polymeric materials after heating for several hours (Scheme 2). Unlike the highly crystalline **3a**, the new polymers **3b** and **3c** were readily solublized in THF and could be filtered to remove excess Cu metal and CuI salts.

After filtration, the polymers were recovered by precipitation into either methanol or hexanes. In the case of **3b**, the polymers were found to generally be of low molecular weight (M_w < 4000) with some degree of oligomeric materials detectable by GPC and mass spectrometry. No difference in the degree of polymerization was observed if recrystallized **2b** were used instead of the recovered monomer solids. The **3b** polymers were recovered as dark red powders, were found to be sparingly soluble in hexanes, methanol, or ether solvents and could be cast into brittle films from THF or toluene. The Ullmann coupling of **2c** under identical polymerization conditions to **2b** yielded comparatively high molecular weight polymers **3c**. These materials were readily isolated from any unreacted starting materials and recovered as golden powders. The ^1H NMR of **3c** polymer (see Figure 2) shows the presence of a single broad peak (3.5–4.5 ppm) corresponding to the cyclopentadienyl ring protons, as well as a distinguishable peak for the Me groups attached to the ring at higher field (1.2–2.5 ppm). A typical GPC trace of the new polyferrocenylenes is shown in Figure 3, indicating broad polydispersities typical of condensation polymerization. Molecular weight data for the polymers **3b** and **3c** is shown in Table 1. In most cases, the recovered materials displayed characteristics of high polymers (i.e., film forming) and the degree of polymerization was between 5 and 35 ferrocene repeat units.

In an attempt to explore possible new routes to polyferrocenylenes, the CuCl-assisted coupling of bis-

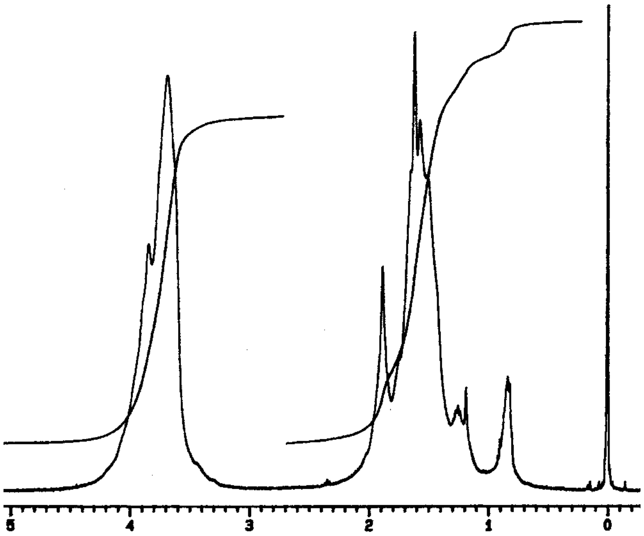


Figure 2. ^{1}H NMR (400 MHz, $CDCl_3$) of a moderate molecular weight polymer, **3c**.

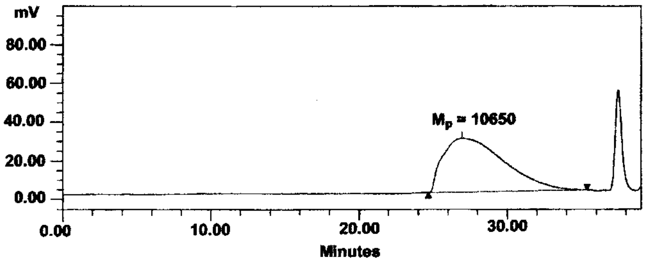


Figure 3. GPC trace of moderate molecular weight polymer **3c** prepared from the Ullmann condensation reaction of **2c**.

Table 1. GPC Data for Polyferrocenylenes 3b and 3c

monom used	polym formed	reacn temp, °C (time, h); coupling method	M_w	M_n	M_p	PDI	yld, %
2c	**3c**	160 (22); Cu	5230	1740	8770	3.01	48
2c	**3c**	175 (vac, 22); Cu	5040	2730	10 010	1.84	45
2c	**3c**	150 (17); Cu	3660	1620	3710	2.25	57
2c	**3c**	150 (17); Cu	5160	2320	3870	2.23	51
2c	**3c**	150 (vac, 17); Cu	8600	3590	10 650	2.40	55
2c	**3c**	160 (vac, 17); Cu	4340	2600	5530	1.61	44
2b	**3b**	150 (17); Cu	2560	1890	1900	1.35	71
2b	**3b**	150 (17); Cu/CuCl	2010	1530	1840	1.31	54
2b	**3b**	150 (17); Cu	2150	1660	1850	1.30	34
2b	**3b**	150 (20); CuCl	3430	1860	1560	1.84	39
1b	**3b**	80 (17); CuCl	2410	1650	2100	1.45	27
1b	**3b**	80 (17); CuCl/phen	2270	1870	2220	1.21	44
1b	**3b**	60 (17); CuCl	2740	1870	1790	1.46	37

(stannyl)ferrocene **1b** was investigated (Scheme 3). Piers et al. recently reported[37] on the CuCl intramolecular coupling of bis(alkenyl)stannanes. While the mechanistic details for this reaction are still largely unknown, it is believed to proceed via Cu insertion into carbon−tin bond of one the trimethylstannyl groups, proceeded by the elimination of $ClSnMe_3$. This alkenyl cuprate species can then undergo additional reaction with CuCl to provide carbon−carbon bond formation. In our case, monomer **1b** was reacted along with an excess of CuCl in DMF at 70 °C. Low molecular weight polymer **3b** was recovered in all cases and the molecular weight data for these reactions provided in Table 1. As with Piers's observation,[37] this reaction probably proceeds with the elimination of the trialkyltin chloride, $ClSnBu_3$, and the in situ generation of a mixed ferrocenyltin cuprate. In the presence of additional CuCl, this species can undergo further condensation to form intermolecular Cp−Cp bonds resulting in polymeric material. To our knowledge, this is the first example of Cu-promoted coupling of bis(stannyl)ferrocenes to yield polymer.

Scheme 3

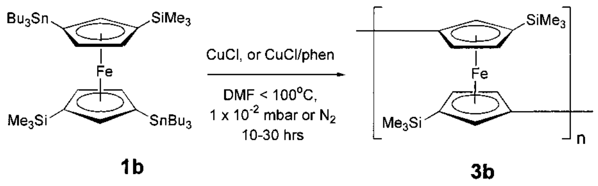


Table 2. Thermal Transition Data for Polyferrocenylenes 3a−3c

polymer	T_g, °C	T_m, °C
3a	75	112
3b	45	
3c	59	

Electron Impact Mass Spectroscopic Investigation of Polymers 3b and 3c. Because of the inherent difficulty in carrying out end group determination by NMR for the multiisomer polymer **3c**, the possible fragmentation pathways of polyferrocenylenes containing trimethylsilyl (**3b**) and methyl (**3c**) functionality were investigated by electron impact (EI) and fast atom bombardment (FAB) mass spectrometry. Analysis of **3b** by EI mass spectrometry revealed fragments as high as m/z = 2225 amu, corresponding to the linear heptamer with one missing trimethylsilyl substituent. Hydrogen-terminated oligomers from the biferrocene to the hexamer were also observed in the FAB mass spectra. In the case of polymer prepared from CuCl-mediated coupling of bis(stannyl)ferrocene **1b**, a complementary set of linear trimethylsilyl oligomers containing tri-*n*-butylstannyl end groups was identified. The detected oligo/polymer species also showed losses of $Si(CH_3)_3$ (m/z = 73 amu) and $Sn(C_4H_9)_3$ (m/z = 290 amu) fragments. This would suggest that, for coupling reactions with the less pure bis(stannyl)ferrocene **1b**, two different end-terminated polymers exist throughout the condensation polymerization. Additionally, the tri-*n*-butylstannyl group survives the coupling reactions, indicating a lower reactivity in comparison to the diiodo species.

Analysis of the mass spectra produced by the ionization of **3c** did not reveal any iodoferrocenyl species or fragments. This would suggest that all of the iodine groups from the monomer was effectively consumed during reaction or subsequent polymer workup. The highest m/z peak observed at 1697 amu is assigned to the octamer with a hydrogen-terminated end group. Fragmentation of the polymer then proceeds either through the loss of the iron containing fragment, $FeC_5H_3CH_3$ (m/z = 134 amu), followed by the subsequent cleavage of a $C_5H_3CH_3$ fragment (m/z = 78 amu), or by the loss of methylated Cp ring itself. This fragmentation pattern is observed for the methylated oligoferrocenes, n = 2−6. The strong intensity peak at m/z = 424 amu corresponds to the doubly bridged tetramethylbiferrocene.

Thermal Transition Behavior and Morphology. The thermal transition behavior of polymers **3a**−**c** was studied by DSC. The glass transitions for the polyferrocenylenes **3a**−**c** are reported in Table 2. For these polymers, the T_g is observed to decrease with increasing bulkiness of the substituents on the cyclopentadienyl

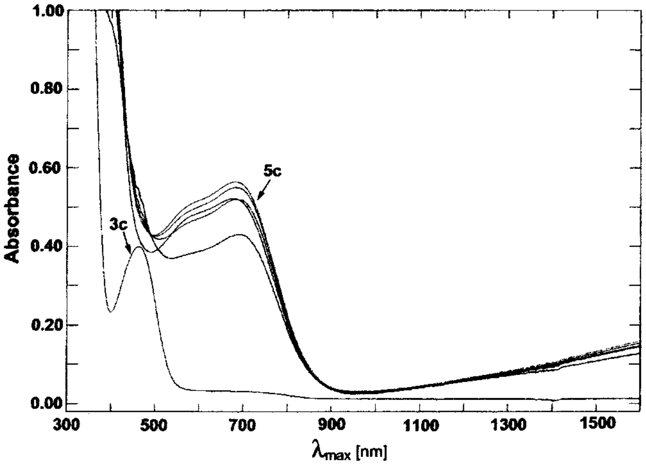


Figure 4. Spectrophotometric titration of polymer **3c** in CH_2Cl_2 with TCNE.

rings. The lower T_g for **3b** is unexpected, as intuitively the decreasing conformational flexibility of trimethylsilyl groups in **3b** compared to the methyl groups in **3c** would be expected to increase chain rigidity. Polymer **3a** was the only polymer to show a strong melt transition. Further investigation of polymer morphology of **3a** was obtained by powder X-ray diffraction (PXRD) which confirmed the crystalline nature of this polymer.[29] Three diffraction peaks with similar intensities and d spacings (5.38, 4.43, and 4.14 Å) are in excellent agreement with those previously identified by Yamamoto.[14] The d spacing of 5.38 Å was assigned to the relative Fe−Fe distance in the polymer. This is considerably smaller than that reported for polyferrocenylsilanes where the Fe−Fe distance of ≈6.0 Å was determined in crystal structures of oligomers and by PXRD.[21] Two broad peaks were found in the PXRD of **3b**, with 2θ values of ca. 16 and ca. 8°. The amorphous nature of **3c** was confirmed with a single broad amorphous halo at $2\theta \approx 13°$.

Electronic properties of Polyferrocenylenes 3b and 3c. The electronic properties of polymers **3b** and **3c** were examined by cyclic voltammetry, UV/vis/NIR, and Mössbauer spectroscopy.

(i) UV/Vis/NIR Spectroscopy. The solution UV/vis/NIR spectroscopy of the unoxidized polymers **3b** and **3c** is typical of most ferrocene and polyferrocene containing materials with λ_{max} of 470 nm (ϵ = 100 M^{-1} cm^{-1}) for **3c** and a slightly red-shifted λ_{max} for **3b** at 480 nm (ϵ = 280 M^{-1} cm^{-1}).[38] When titrated with oxidants I_2 or TCNE, the polymers showed the dramatic red shifting to 650−700 nm in the visible spectrum typical of oxidized ferrocenium species, along with broad, but weak, intervalence charge-transfer bands between 850 and 1900 nm (see Figure 4). The appearance of these broad IT bands is typical of ferrocene polymers with extensive delocalization of charge along the backbone.[38,39] The partially oxidized polymers remained soluble in polar solvents, such as dichloromethane or acetonitrile. Attempts to achieve fully chemically oxidized polymers was unsuccessful, even in the presence of a large excess of oxidizing agent. Spectrophotometric titrations of **3b** and **3c** with TCNE or I_2 (Scheme 4) to the partially oxidized polymers were carried out, however, in all cases the absence of IT bands corresponding to a fully chemically oxidized polymer was never achieved.

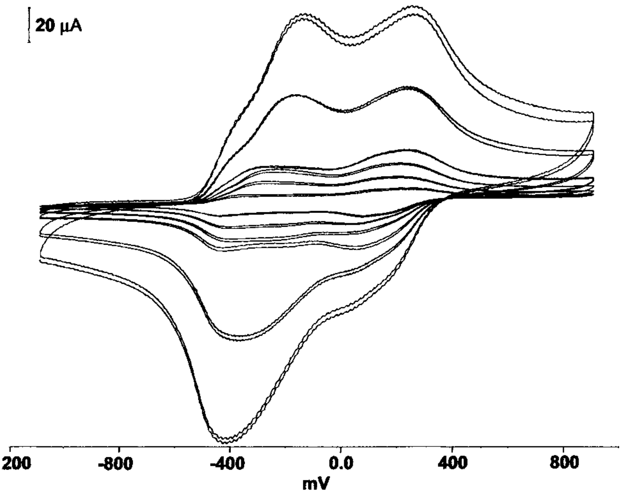
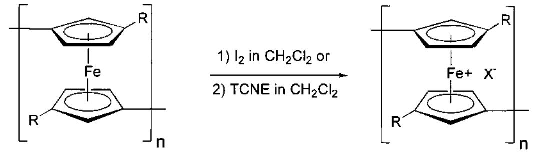


Figure 5. Cyclic voltammogram for the polymer **3c** in dichloromethane at scan rates from 50 to 1000 mV/s.

Scheme 4



3b, 3c

4b = R = $SiMe_3$, X = I_3^-
4c = R = Me, X = I_3^-
5b = R = $SiMe_3$, X = $TCNE^-$
5c = R = Me, X = $TCNE^-$

(ii) Cyclic Voltammetric Analysis of Polymers 3b and 3c. Electrochemical studies of dimers, oligomers or polymers of ferrocene units separated by a single spacer element of SiR_2, GeR_2, SnR_2, or PR (where R = alkyl, aryl or halo group) display two reversible redox waves in their cyclic voltammograms.[13] The extent of this separation has been shown to be a function of the heteroelement, the substituents attached to the heteroelement and the nature and number of substituent groups on the cyclopentadienyl rings of ferrocene itself.[13] The two wave phenomena have been attributed to the oxidation of alternating iron centers at the lower applied potential ($^1E_{1/2}$) followed by an oxidation of the remaining iron centers at a higher potential ($^2E_{1/2}$). The separation between the two waves, $\Delta E_{1/2}$, has been used as a gauge of the electronic interaction between neighboring iron centers. A representative cyclic voltammogram for polymers **3c** is shown in Figure 5, and data are given in Table 3. Clearly visibly in both voltammograms is the appearance of two distinguishable redox peaks. This suggests strongly, that unlike the electrochemistry reported for polyferrocenylene[40,41] **3a** and 1,1′-dihexyl-polyferrocenylene,[16] **6**, the extent of polymerization in polymers **3a** and **3b** is sufficient to reveal polymeric rather than oligomeric behavior. The peak to peak separation ($\Delta E_{1/2}$) of **3b** and **3c** was found to be 485 and 465 mV, respectively. In contrast to the

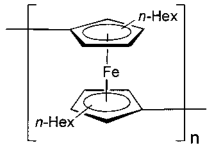


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Table 3. Cyclic Voltammetry Data for Polyferrocenylenes 3b and 3c

polymer	scan rate, mV s^{-1}	$^1E_{1/2}$ ^{b}	$^2E_{1/2}$ ^{b}	ΔE^c
3b	25	−392	158	551
3b	50	−338	122	460
3b	100	−326	131	456
3b	250	−356	146	502
3b	500	−285	174	459
3b	1000	−282	198	480
3c	50	−266	168	433
3c	100	−272	181	453
3c	250	−284	161	483
3c	500	−279	152	462
3c	1000	−300	158	493

[a] Data obtained by analysis at 22 °C of CH_2Cl_2 solutions which were $\approx 5 \times 10^{-3}$ *M* in polymer and 0.1 *M* in $[NBu_4][PF_6]$. $^1E_{1/2}$ and $^2E_{1/2}$ are the half-wave oxidation potentials for the first and second oxidation waves in the polymer CV's, respectively, and are given in volts vs the ferrocene/ferrocenium ion couple at $E = 0.00$ V by definition. $\Delta E = {}^1E_{1/2} - {}^2E_{1/2}$.

Table 4. Mössbauer Data for Polyferrocenylenes

compound; equiv of TCNE	T (K)	oxidation state of Fe	ΔE_q (mm s^{-1})	δ (mm s^{-1})	ref
3a	301	(Fe^{2+})	2.22	0.46	14
3b	301	(Fe^{2+})	2.25	0.47	*a*
3c	301	(Fe^{2+})	2.34	0.45	*a*
5a; 0.81	78	(Fe^{2+})	2.17	0.45	14
		(Fe^{3+})	0.72	0.57	
5a; 0.81	301	$(Fe^{2.5+})$	≈1.5	≈0.61	14
5c; 0.52	301	(Fe^{2+})	2.17	0.449	*a*
		(Fe^{3+})	0.664	0.442	
5c; 0.94	301	(Fe^{2+})	2.17	0.464	*a*
		(Fe^{3+})	0.533	0.395	
6	78	(Fe^{2+})	2.25	0.51	43
		(Fe^{3+})	*b*	0.42	
$[Fe(\eta\text{-}C_5H_4)_2SiMe_2]_n$	77	(Fe^{2+})	2.35	0.41(1)	46

[a] This work. [b] Not reported.

electrochemical behavior reported for **3a** by Sanechika et al.[41] where at least three or more peaks were observed in the cyclic voltammogram, the voltammograms of **3b** and **3c** display electrochemical behavior similar to that reported for polyferrocenylsilanes.[3] This may suggest that that the multipeak behavior of **3a** observed by Sanechikia et al.[41] is probably due to either a high ratio of lower oligomeric materials present in solution or that deposition on to the gold electrode is occurring as a result of the poor solubility of **3a**.

Mössbauer Spectra of Polyferrocenylenes 3b, 3c, and 5c. Studies of model mixed valence biferrocenes by Dong et al.[42] has shown the intricate dependency of rates of electron-transfer delocalization to the degree of ring-tilt in these structures, the nature of the counterion, and the type of substitution at the cyclopentadienyl ring. In this work, we have found that the quadrapolar splitting, ΔE_q, and the isomer shifts, δ, of the new polymers **3b** and **3c** (listed in Table 4) and their oxidized counterparts are typical of other neutral or oxidized ferrocenes, oligoferrocenes,[43] and the polyferrocenylene **3a**.[14] As shown from the representative Mössbauer spectra in Figure 6, when the polymer **3c** is partially oxidized with either approximately half or 1 equiv of TCNE respectively, the oxidized polymer **5c** was found to not delocalize on the Mössbauer time scale (10^{-7} s^{-1}). This might suggest that greater delocalization may be achieved with a different counterion or that the overall amorphous nature of **3a** and **3b** slows electron transfer sufficiently to have distinct Fe^{2+} and Fe^{3+} environments.

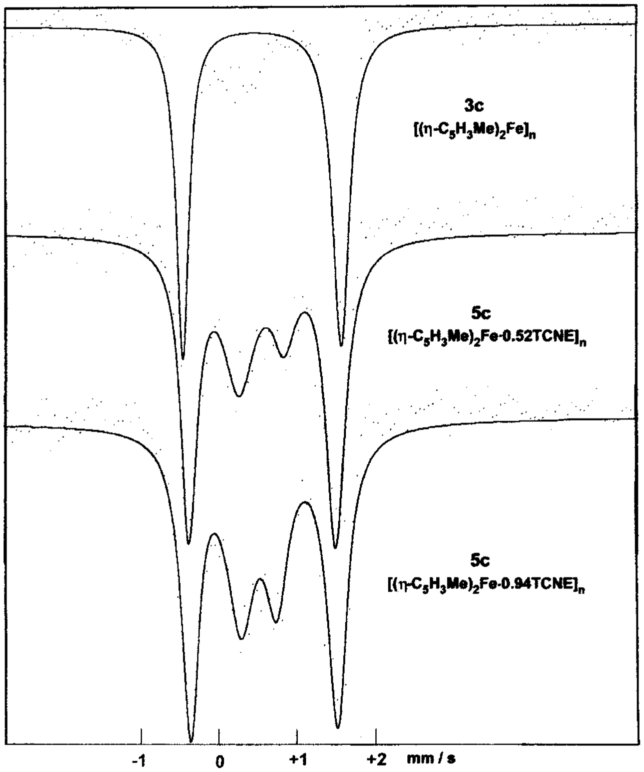

Figure 6. Mössbauer spectra of **3c** (top), partially oxidized **5c** with 0.52 equiv of TCNE (middle), and **5c** oxidized with 0.94 equiv of TCNE (bottom).

Conclusion

We have detailed the preparation and characterization of soluble, low to moderate molecular weight, film-forming polyferrocenylenes. Copper-mediated polymerizations of methylated and trimethylsilylated diiodoferrocenes and bis(stannyl)ferrocenes yielded new polyferrocenylenes after prolonged reaction periods. Polymers with methyl substituents attached to the cyclopentadienyl rings were found to yield higher molecular weights on average compared to those with trimethylsilyl groups. These polyferrocenylenes show distinct, reversible, two-wave separations of ca. 0.5 V that is suggestive of enhanced metal to metal communication in the polymer backbone. However, TCNE adducts were found to be valence trapped on the Mössbauer time scale at room temperature.

Experimental Section

All air- or moisture-sensitive operations were performed under inert atmosphere (Argon) using Schlenk line techniques or an Innovative Technologies glovebox. Ferrocene, tetramethylethylendiamine, trimethylsilyl chloride (98%), tri-*n*-butyltin chloride (98%), iodine (98%), copper powder (98%), cuprous chloride (99.995%) and 1,1′-dimethylferrocene (85%) were purchased from Aldrich. Potassium fluoride was purchased from Lancaster. All compounds were used as received except for the ferrocene which was further purified by Soxhlett extraction with hexanes. Hexanes were distilled from a sodium dispersion. Dilithioferrocene[44] and 1,1′-bis(trimethylsilyl)ferrocene[33] starting materials were prepared by standard preparative methods.

Equipment. Nuclear magnetic resonance spectroscopy was performed on a Bruker AMX-400 or 300 MHz for ^1H and 100 MHz ^{13}C NMR. UV/vis/NIR spectra were obtained from a Cary 5 UV−vis−NIR spectrophotometer. DSC analyses were performed at a heating rate of 10 °C/min under prepurified N_2 using a DuPont Instruments DSC10 differential scanning calorimeter. Mass Spectra were obtained with the use of a VG 70−250S mass spectrometer operating in an electron impact (El) mode. Elemental analyses were performed by Canadian Microanalytical Service, Delta, B.C., Canada. Wide-angle X-ray scattering data were obtained at 25 °C using Siemens D5000 diffractometer employing Ni-filtered Cu Kα ($\lambda = 1.54178$ Å) radiation. Samples were scanned at step widths of 0.02° with 1.0 s per step in the Bragg angle range 3−35°. Samples were prepared by spreading finely ground polymer on grooved glass slides. Cyclic voltammograms were recorded with a PAR model 273 potentiostat. A platinum-working electrode was used in conjunction with a tungsten auxiliary electrode and a silver wire reference electrode in a Luggin capillary. All potentials are relative to the ferrocene/ferrocenium ion couple at 0.00 V, which was used as an internal reference. Methylene chloride distilled from P_2O_5, $[Bu_4N][ClO_4]$ electrolyte was used, and the analyses were carried out under argon after rigorous deoxygenation of the analyte solutions. Molecular weight estimates were made via gel permeation chromatography using a Waters Associates liquid chromatograph equipped with a 510 HPLC pump, an automatic sampling injector and tray, and four in-series Ultrastyragel columns with pore sizes between 102 and 106 Å and a Waters 410 differential refractometer. A flow rate of 1.0 mL/min was used, and samples were dissolved and filtered in THF prior to injection. Polystyrene standards were used for calibration purposes. Room-temperature ^{57}Fe Mössbauer spectra were obtained using a Ranger Scientific Vt-1200 instrument using an MS-1200 digital channel analyzer. The γ-source was a 6 mCi ^{57}Co sample supplied by Amersham. The data were collected in a -15.8 to $+ 15.8$ mm s^{-1} range and referenced to Fe foil.

Synthesis of 1,1′-Bis(tri-*n*-butylstannyl)ferrocene (1a). **1a** was prepared by the method reported by Wright.[31]

Synthesis of 1,1′-Bis(tri-*n*-butylstannyl)-3,3′-bis(trimethylsilyl)ferrocene (1b). To 1,1′-bis(trimethylsilyl)ferrocene (54. 6 g, 0.165 mol) was added 1.6 M ^{n}BuLi in hexanes (320 mL, 0.512 mol). To the resulting solution was added TMEDA (32.2 mL, 0.496 mol) dropwise over a period of 20 min. The dark red solution was allowed to stir for 72 h.[45] The resulting suspension was cooled to −78 °C, and $ClSn(n\text{-}Bu)_3$ (166.73 g, 0.512 mol) was added dropwise over a period of 30 min. After the addition was completed, the mixture was allowed to warm up to ambient temperature and mixed for a further 15 h. The resulting suspension was filtered and the solid washed with hexanes (200 mL). The solvent was removed under reduced pressure yielding a dark red oil. Further purification was accomplished by distillation of the lower boiling compounds under reduced pressure to a temperature not exceeding 180 °C. The remaining residue was then passed through a neutral alumina column with hexanes as eluent. After removal of solvent, the dark-red liquid was washed twice with methanol (200 mL). Drying of the dark red liquid yielded **1b** (105.92 g, 70.7%). ^{1}H NMR (400 MHz, $CDCl_3$/TMS) chemical shifts in ppm: 4.14 (m, 2H, Cp), 4.09 (m, 2H, Cp), 3.92 (m, 2H, Cp), 1.53 (m, 6 H, $Sn{-}CH_2C\mathit{H}_2CH_2CH_3$), 1.33 (m, 6 H, $Sn{-}CH_2CH_2C\mathit{H}_2CH_3$), 1.03 (m, 6 H, $Sn{-}C\mathit{H}_2CH_2CH_2CH_3$), 0.92 (m, 9 H, $Sn{-}CH_2CH_2CH_2C\mathit{H}_3$), 0.23 (s, 9 H, $SiC\mathit{H}_3$). ^{13}C NMR (100 MHz, $CDCl_3$/TMS) chemical shift values in ppm: 79.4 (s, Cp), 77.1 (s, Cp), 74.5 (s, Cp), 73.8 (s, Cp-$SnBu_3$), 72.3 (s, Cp-$SiMe_3$), 29.2 (m, $Sn{-}CH_2CH_2\mathit{C}H_2CH_3$), 27.5 (t, $Sn{-}CH_2\mathit{C}H_2CH_2CH_3$), 13.7 (s, $Sn{-}CH_2CH_2CH_2\mathit{C}H_3$), 10.3 (t, $Sn{-}\mathit{C}H_2CH_2CH_2CH_3$), 0.37 (s, $Si\mathit{C}H_3$). Mass spectroscopy (El, 70 eV), *m/z* (%): 908 (100, M^+), 291 (18.7, Bu_3Sn^+).

Note: Further purification of this monomer to remove residual tin salts was unsuccessful, and the compound was used as is for conversion to the diiodo species and to polymer.

Synthesis of Dimethylbis(tri-*n*-butylstannyl)ferrocene (1c). To 1,1′-(dimethyl)ferrocene (9.0 g, 0.042 mol) was added 1.6 M ^{n}BuLi in hexanes (52.5 mL, 0.084 mol). To the resulting solution was added TMEDA (5.45 mL, 0.084 mol) dropwise over a period of 20 min. The dark red solution was allowed to stir for 72 h. The resulting suspension was cooled to −78 °C, and $ClSn(n\text{-}Bu)_3$ (28.64 g, 0.088 mol) was added dropwise over a period of 30 min. After the addition was completed, the mixture was allowed to warm up to ambient temperature and mixed for a further 15 h. The resulting suspension was filtered and the solid washed with hexanes (100 mL). The solvent was removed under reduced pressure, yielding a dark red oil. Further purification was accomplished by distillation of the lower boiling compounds under reduced pressure to a temperature not exceeding 180 °C. The remaining residue was then passed through a neutral alumina column with hexanes as eluent. After removal of solvent, the dark-red liquid was washed twice with methanol (100 mL). Drying of the dark red liquid yielded **1c** (23.6 g, 70.8%). ^{1}H NMR chemical shifts, ppm: major clustering of peaks at 4.24−3.53, 2.12−1.87, 1.72−0.84. ^{13}C chemical shifts, ppm: major clustering of peaks at 89−85, 79−71, 30−27, 16−13, 10.4−10.1.

Note: Further purification of this monomer to remove residual tin salts was unsuccessful, and the compound was used as is for conversion to the diiodo species and to polymer.

Synthesis of Diiodoferrocenes 2a−c. Diiodoferrocenes **2a**−**c** were prepared by the halogen/organotin exchange reaction established by Butler[32] for **2a** with further purification being required for compounds **2b** and **2c**.

Synthesis of 1,1′-Diiodoferrocene (2a). Compound **2a** was synthesized and purified according to the known literature.[32]

Synthesis of 1,1′-Diiodo-3,3′-bis(trimethylsilyl)ferrocene 2b. To a stirred solution of **1b** (80.9 g, 0.089 mol) in CH_2Cl_2 (450 mL) cooled to 0 °C was added iodine (49.9 g, 0.196 mol). The dark green-brown solution was allowed to warm up to ambient temperature and allowed to stir for 18 h. The dark red-brown solution was washed with l M sodium thiosulfate solution (2 × 200 mL aliquots). The organic phase was then filtered through neutral alumina and the solvent removed to yield a dark amber oil. The oil was redissolved in methanol (300 mL) to which was added potassium fluoride (20 g, 0.344 mol). After the mixture was stirred for 10 min a thick, bright yellow slurry formed. The slurry was filtered through neutral alumina and the solvent removed to leave an orange residue. The residue was extracted with diethyl ether (300 mL). The etheric solution was washed three times with water (200 mL). The organic phase was dried and purified by column chromatography using hexanes as eluent. After removing the solvent dark amber crystals of **2b** (15.4 g, 29.7%) formed from the resulting oil. ^{1}H NMR (400 MHz, $CDCl_3$/TMS) chemical shift values in ppm: 4.53 (m, 2 H, Cp), 3.93 (m, 4 H, Cp), 3.89 (m, 4 H, Cp), 0.27 (s, 18 H, $Si{-}C\mathit{H}_3$). ^{13}C NMR (100 MHz, $CDCl_3$/TMS) chemical shift values in ppm: 87.9 (s, Cp), 78.2 (s, Cp), 76.0 (s, Cp-Si), 74.4 (s, Cp), 42.6 (s, Cp-I), 0.19 (s, $Si\mathit{C}H_3$). Mass spectroscopy (El, 70 eV), *m/z* (%): 582 (100, M^+), 440 (26, M-CH_3, I). High-resolution MS for $C_{16}H_{24}FeSi_2I_2$: calculated, 581.8856; measured, 581.8837. Anal. Calcd: C, 33.01, H, 4.16. Found: C, 33.23; H, 4.03. Melting point: 69.2 °C.

Synthesis of 1,1′-Diiodobis(methyl)ferrocene (2c). To a stirred solution of **1c** (23.6 g, 0.030 mol) in CH_2CI_2 (125 mL) cooled to −78 °C was added iodine (15.5 g, 0.061 mol). The dark green solution was allowed to warm up to ambient temperature and allowed to stir for 18 h. The dark green organic phase was washed with l M sodium thiosulfate solution (2 × 75 mL aliquots). The organic phase was then filtered through neutral alumina and the solvent removed to yield a dark amber oil. The oil was redissolved in methanol (100 mL) to which was added potassium fluoride (4 g, 0.069 mol). After stirring for 10 min a thick, bright yellow slurry formed. The slurry was filtered through neutral alumina and the solvent removed to leave an orange residue. The residue was extracted with diethyl ether (100 mL). The etheric solution was washed three times with water (75 mL). The organic phase was dried and purified by column chromatography using hexanes as eluent. After removing the solvent an amber oil of **2c** (12.3 g, 86.7%). ^{1}H NMR (400 MHz, $CDCl_3$/TMS) chemical shift values in ppm: 4.28−3.86 (m, 6 H for all isomers, Cp), 2.00−1.90 (m, 6 H for all isomers Me). ^{13}C NMR (100 MHz, $CDCl_3$/TMS) chemical shift values in ppm: 87−71 (s, for all isomers, Cp), 41.8−41.3 (s, for all isomers Cp-I), 14.6−12.9 (s, for all isomers, Me). Mass spectroscopy (El, 70 eV), *m/z* (%): 466 (100, M^+), 339 (13.6, M^+- I). High-resolution MS $C_{12}H_{12}FeI_2$: calculated, 465.8378; measured, 465.8389. Anal. Calcd: C, 30.94; H, 2.60. Found: C, 30.09; H, 2.49.

Synthesis of Polyferrocenylene 3a by Mg Coupling of 2a. This reaction was similar to that used by Yamamoto. Earlier attempts to prepare **3a** in higher dilution failed.

To 0.2 g of finely divided Mg powder in 50 mL round-bottom flask under N_2 was added 2.0 g (0.045 mol) of **2a**, and 12 mL of dried THF containing 0.35 mL (8.5×10^{-4} mol) of 1,2′-dibromoethane. The reaction was stirred for 3 h and became noticeably viscous. An additional 10 mL of THF was added and the reaction stirred overnight. The sample was filtered to remove excess Mg metal and salts and was then precipitated into an excess of methanol (200 mL). The resulting yellow powder could not be redissolved in THF or in other polar solvents. The yield of the THF insoluble fraction was 0.77 g (91%). No GPC of this material was obtained. The product was characterized by PXRD, which showed crystalline peaks at positions similar to those reported by Yamamoto.

Note: Attempts to polymerize the monomers **3b** and **3c** under the same conditions as **3a** were unsuccessful resulting in most cases in the recovery of unreacted monomer.

Synthesis of 1,1′-Polydimethylferrocenylene (3c) via Copper-Mediated Reductive Coupling. An isomeric mixture of neat diiodo monomer **2c** (23.3 g, 0.05 mol) and copper powder (31.8 g, 0.5 mol) was heated to 165 °C under a static vacuum (1.3×10^{-2} mbar) for 25 h. The crude ferrocene polymer **3c** was extracted from the solid mixture with THF using a Soxhlett extractor. The polymeric solution was concentrated (ca. 20 mL) and precipitated into methanol (900 mL). The pale yellow polymer was reprecipitated into methanol two more times. In the final precipitation the THF solution of **3c** was filtered through a 0.2 μm filter prior to addition to methanol. The polymer was isolated as a yellow-orange powder (5.04 g, 47.5%). ^{1}H NMR (400 MHz, $CDCl_3$/TMS) chemical shift values in ppm: 3.75 (br s, 6 H for all isomers, Cp), 1.60 (m, 6 H, for all isomers, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$/TMS) chemical shift values in ppm: 83.8−80.9 (for all ipso isomers, Cp-CH_3), 72.3−66.1 (for all isomers, Cp), 14.6−13.6 (m, for all isomers, CH_3). Anal. Calcd: C, 67.96; H, 5.70. Found: C, 66.78; H, 5.88. GPC estimated $M_w = 5233$, $M_n = 1736$, PDI = 3.0l. $T_g = 52.2$ °C. End group and oligomer detection: Polymeric samples were evaluated by electron impact and fast atom bombardment to determine the species present in the polymeric residue.

Tetramethylbiferrocene, $[Fe(\eta^5\text{-}C_5H_3CH_3)_2]_2$: $m/z = M^+$, 424 amu. Linear hydrogen-terminated methylated ferrocenes, $\{(\eta^5\text{-}C_5H_4CH_3)Fe(\eta^5\text{-}C_5H_4CH_3)\}_2[Fe(\eta^5\text{-}C_5H_4CH_3)_2]_n$: M^+, 638 amu, where $n = 1$, linear trimer; M^+, 849 amu, where $n = 2$, linear tetramer; M^+, 1059 amu, where $n = 3$, linear pentamer; M^+, 1271 amu, where $n = 4$, linear hexamer; M^+, 1485 amu, where $n = 5$, linear heptamer; M^+, 1696 amu, where $n = 6$, linear octamer.

Note: All molecular ions for the linear oligoferrocenes were always accompanied by a second peak at a slightly lower m/z ratio corresponding to the loss of the methylated cyclopentadienyl ring at 78 amu below the molecular ion.

Synthesis of 1,1′-Polybis(trimethylsilyl)ferrocenylene (3b) via Copper-Mediated Reductive Coupling of Bis(trimethylsilyl)diiodoferrocene (2b). An isomeric mixture of neat diiodo monomer **2b** (0.70 g, 0.0012 mol) and copper powder (0.76 g, 0.012 mol) was heated to 150 °C under a static vacuum (1.5×10^{-2} mbar) for 17.5 h. The crude ferrocene polymer **3b** was extracted from the solid mixture with THF (25 mL) and precipitated into methanol (300 mL). An orange-tan polymer was reprecipitated into methanol two more times. In the final precipitation, the THF solution of **3b** was filtered through a 0.2 μm filter prior to addition to methanol. The polymer was isolated as an orange-tan powder (0.190 g, 54.3%). ^{1}H NMR and ^{13}C NMR chemical shifts are similar to those reported by other polymerization methods. Anal. Calcd: C, 58.53; H, 7.36. Found: C, 56.30; H, 7.36. GPC: estimated $M_w = 2460$, $M_n = 1856$, PDI = 1.3. $T_g = 52.2$ °C.

Synthesis of 1,1′-Poly-3,3′-bis(trimethylsilyl)ferrocene (3b) via CuCl-Mediated Coupling of the Bis(stannyl)-ferrocene 1b. A stirred mixture of the bis(stannyl)ferrocene **1b**, (20.8 g, 0.0229 mol) and CuCl (11 g, 0.111 mol) in DMF (75 mL) was heated to 70 °C for 25 h. The solution was concentrated (ca. 15 mL) and precipitated into methanol (900 mL). The polymer was isolated and redissolved in THF (50 mL). The polymer solution was then filtered, concentrated (20 mL) and precipitated into methanol. The polymer was redissolved in THF (15 mL), filtered through a 0.2 um filter and reprecipitated once again into methanol (500 mL). **3b** was isolated as an orange-brown powder (2.74 g, 36.3%). ^{1}H NMR (400 MHz, $CDCl_3$/TMS) chemical shift values in ppm: 4.7−3.00 (br m, 6 H, Cp), +0.5 to −0.2 (br s, 18 H SiCH_3). ^{13}C NMR (100 MHz, $J = 145$ Hz $CDCl_3$/TMS) chemical shift values in ppm: 72−68 (br unresolved peak, Cp), 0.04 (br s, SiCH_3). Anal. Not determined due to the presence of mixed polymer species. GPC: estimated $M_w = 2410$, $M_n = 1400$, PDI = 1.72. $T_g = 36.7$ °C. End group and oligomer detection: Polymeric samples were evaluated by electron impact and fast atom bombardment to determine the species present in the polymeric residue. Tetra(trimethylsilyl)biferrocene, $[Fe(\eta^5\text{-}C_5H_3SiMe_3)_2]_2$: m/z M^+, 656 amu. Linear hydrogen-terminated trimethylsilylated ferrocenes, $\{(\eta^5\text{-}C_5H_4SiMe_3)Fe(\eta^5\text{-}C_5H_4SiMe_3)\}_2[Fe(\eta^5\text{-}C_5H_4SiMe_3)_2]_n$: M^+, 986 amu, where $n = 1$, linear trimer; M^+, 1314 amu, where $n = 2$, linear tetramer; M^+, 1642 amu, where $n = 3$, linear pentamer; M^+ 1970 amu, where $n = 4$, linear hexamer; $M^+ - SiMe_3$, 2225 amu, where $n = 5$. Linear tributylstannyl terminated trimethylsilylated ferrocenes, $\{(\eta^5\text{-}C_5H_3SiMe_3\text{-}SnBu_3)Fe(\eta^5\text{-}C_5H_4SiMe_3)\}_2[Fe(\eta^5\text{-}C_5H_4SiMe_3)_2]_n$: M^+, 947 amu, where $n = 0$, linear dimer; M^+, 1275 amu, where $n = 1$, linear trimer; M^+, 1603 amu, where $n = 2$, linear tetramer; M^+, 1932 amu, where $n = 3$, linear pentamer.

Note: All molecular ions for the linear oligo(bistrimethylsily)ferrocenes were accompanied by a second peak at a slightly lower m/z ratio corresponding to the loss of the trimethylsilyl group at −73 below the molecular ion.

Oxidation of Polymers 3b and 3c. Polymers **3b** and **3c** were oxidized with iodine and TCNE by the addition of the polymer solutions in CH_2Cl_2 into the corresponding solution of oxidant in CH_2CI_2. An excess of oxidant was used in each case and removed by sublimation. The oxidation of polymer **3c** with iodine as oxidant is provided as a general procedure. Mass balance estimates calculated from the elemental analysis were used to determine the compositions and degree of oxidation.

Preparation of $[Fe(\eta^5\text{-}C_5H_3CH_3)_2]_n[I_3]_x$ (4c). To a stirred solution of iodine (6 g, 0.047 mol) in CH_2Cl_2 (50 mL) was added dropwise a solution of **3c** (1.0 g, 0.0047 mol) in CH_2Cl_2 (10 mL) under aerobic conditions. The mixture was mixed for 18 h. The CH_2Cl_2 was removed under reduced pressures and unreacted I_2 removed by sublimation under reduced pressure with gentle heating (60 °C) over a period of 24 h leaving a black powder **4c** (1.94 g, 69.5%) and a composition with just over 80% of all the Fe^{2+} sites oxidized to Fe^{3+}. Anal. Calcd ($[Fe(\eta^5\text{-}C_5H_3CH_3)_2]_{1.0}[I_3]_{0.81}$): C, 29.88; H, 2.51. Found: C, 29.90; H, 2.53. Spectroscopic titration data: $\lambda_{max} = 700$ nm ($\epsilon = 100$ M^{-1} cm^{-1}), $\lambda_{max} \approx 1700$ nm ($\epsilon = 60$ M^{-1} cm^{-1}).

Preparation of $[Fe(\eta^5\text{-}C_5H_3CH_3)_2]_n[TCNE]_x$ (5c). For $[Fe(\eta^5\text{-}C_5H_3CH_3)_2]_n[TCNE]_x$ (**5c**), the same methodology was applied to the oxidation of **3c** with tetracyanoethylene (TCNE) with a few modifications. The polymer was oxidized under an inert atmosphere using 3 equiv of TCNE. After using a similar workup, a black powder was isolated (1.49 g, 93.1%), with a composition with nearly all of the Fe^{2+} sites oxidized to Fe^{3+}, $[Fe(\eta^5\text{-}C_5H_3CH_3)_2]_{1.0}[TCNE]_{0.94}$. Anal. Calcd: C, 60.14; H, 3.60; N, 15.58. Found: C, 62.25; H, 3.81; N, 15.38. Spectroscopic titration data: $\lambda_{max} = 690$ nm ($\epsilon = 380$ M^{-1} cm^{-1}), $\lambda_{max} \approx 1700$ nm ($\epsilon = 69$ M^{-1} cm^{-1}).

Preparation of $[Fe(\eta^5\text{-}C_5H_3SiMe_3)_2]_n[I_3]_x$ (4b). For **4b** the same methodology as used above was applied to the oxidation of **3b** with iodine with a few modifications. The polymer was oxidized under an inert atmosphere using 5 equiv of I_2. A similar workup afforded a black powder (0.54 g, 75%) and a composition with 84% of all the Fe^{2+} sites oxidized to Fe^{3+}. Anal. Calcd ($[Fe(\eta^5\text{-}C_5H_3SiMe_3)_2]_{1.0}[I_3]_{0.84}$): C, 32.20; H, 4.05. Found: C, 32.19; H, 3.82. Spectroscopic titration data (note:

all transitions were very weak): $\lambda_{max} = 690$ nm ($\epsilon = 50$ M^{-1} cm^{-1}), $\lambda_{max} \approx 1700$ nm ($\epsilon = 5$ M^{-1} cm^{-1}).

Preparation of [Fe(η^5-$C_5H_3SiMe_3$)$_2$]$_n$[TCNE]$_x$ (5b). For [Fe(η^5-$C_5H_3SiMe_3$)$_2$]$_n$[TCNE]$_x$ (**5b**), the same methodology was applied to the oxidation of **3b** with tetracyanoethylene (TCNE) with a few modifications. The polymer was oxidized under an inert atmosphere using 3 equiv of TCNE. After using a workup similar to that for **3c**, a black powder was isolated (0.61 g, 88%), with a composition having 97% of all the Fe^{2+} sites oxidized to Fe^{3+}. Anal. Calcd ([Fe(η^5-$C_5H_3SiMe_3$)$_2$]$_{1.0}$[TCNE]$_{0.97}$): C, 56.04; H, 5.11; N, 11.86. Found: C, 56.68; H, 5.25; N, 11.85. Spectroscopic titration data: $\lambda_{max} = 690$ nm ($\epsilon = 200$ M^{-1} cm^{-1}), $\lambda_{max} \approx 1700$ nm ($\epsilon = 50$ M^{-1} cm^{-1}).

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Supporting Information Available: Text giving additional characterization data for the known ferrocene monomers **1a** and **2a** is provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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