Electropolymerization of Oligothienylferrocene Complexes: Spectroscopic and Electrochemical Characterization

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The new complexes 1,1′-bis(5-(2,2′-bithienyl))ferrocene (**2**) and 1,1′-bis(5-(2,2′:5′,2″-terthienyl))ferrocene (**3**) have been synthesized by coupling 1,1′-bis(2-thienyl)ferrocene (**1**) with 2-bromothiophene and 5-bromo-2,2′-bithiophene, respectively. The cyclic voltammograms of **1**−**3** contain a reversible $Fe^{II/III}$ wave with $E_{1/2}$ between 0.37 and 0.46 V vs SCE and irreversible thiophene-based oxidation waves at higher potentials. These compounds can be electrochemically oxidized to yield solutions of the monocations $\mathbf{1}^+$−$\mathbf{3}^+$. The visible−near-IR spectra of these monocations all contain low-energy bands due to an oligothienyl group to Fe^{III} charge-transfer transition. The absorption maxima and intensities of these bands correlate to the length of the conjugation in the oligothienyl group. Above the thiophene oxidation potential and by careful exclusion of water, **2** and **3** electropolymerize resulting in the deposition of electrochromic films on the electrode surface. The films are golden-red and stable when neutral and become black upon oxidation. The cyclic voltammetry of the film growth process and the formation of electroactive films indicate that the films are conductive. Spectroelectrochemical characterization of the films demonstrates that broad, low-energy absorptions appear upon oxidation of the ferrocenyl centers and that stronger and much broader bands appear upon full oxidation of the films.

Introduction

Conjugated polymers which contain transition metal centers in the polymer backbone are an interesting class of materials. The presence of the metal is expected to significantly impact upon the electronic conductivity and magnetic properties of such materials and may lead to their application in electroluminescent devices, sensors, and storage devices. Conjugated polymers which contain metals such as Pt,[1] Rh,[2] Au,[3] and Ru[4] in the backbone have been prepared; however, a great deal of the work in this field has focused on the incorporation of ferrocenyl groups into polymers.[5] Ferrocene is an ideal candidate for such studies due to its ease of substitution with a range of functional groups and its stability in both Fe^{II} and Fe^{III} oxidation states.

Polymers containing directly linked ferrocene centers have been prepared,[6] as well as those containing hydrocarbon,[7] alkene,[8] aromatic,[9] ER_2 (E = Si, Ge, and Sn), P, and S bridges.[5,10] The electronic behavior of these materials has been investigated using cyclic voltammetry and conductivity measurements. Cyclic voltammetry reveals the extent and nature of the interaction between ferrocene centers, and bulk conductivity measurements may be used to ascertain the charge delocalization in doped polymers. Many studies on linked ferrocene dimers and oligomers have also been reported and have been recently reviewed.[11]

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(1) (a) Takahashi, S.; Kariya, M.; Yatake, T.; Sonogashira, K.; Hagihara, N. *Macromolecules* **1978**, *11*, 1063−1066. (b) Lewis, J.; Khan, M. S.; Kakkar, A. K.; Johnson, B. F. G.; Marder, T. B.; Fyfe, H. B.; Wittmann, F.; Friend, R. H.; Dray, A. E. *J. Organomet. Chem.* **1992**, *425*, 165−176. (c) Chawdhury, N.; Köhler, A.; Friend, R. H.; Younus, M.; Long, N. J.; Raithby, P. R.; Lewis, J. *Macromolecules* **1998**, *31*, 722−727.

(2) Fyfe, H. B.; Miekuz, M.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1991**, 188−190.

(3) Irwin, M. J.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 3541−3547.

(4) (a) Davies, S. J.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Organomet. Chem.* **1991**, *414*, C51−C53. (b) Faulkner, C. W.; Ingham, S. L.; Khan, M. S.; Lewis, J.; Long, N. J.; Raithby, P. R. *J. Organomet. Chem.* **1994**, *482*, 139−145.

(5) Manners, I. *Adv. Organomet. Chem.* **1995**, *37*, 131−168.

(6) (a) Cowan, D. O.; Park, J.; Pittman, C. U.; Sasaki, Y.; Mukherjee, T. K.; Diamond, N. A. *J. Am. Chem. Soc.* **1972**, *94*, 5110−5112. (b) Yamamoto, T.; Sanechika, K.; Yamamoto, A.; Katada, M.; Motoyama, I.; Sano, H. *Inorg. Chim. Acta* **1983**, *73*, 75−82.

(7) (a) Neuse, E. W.; Trifan, D. S. *J. Am. Chem. Soc.* **1963**, *85*, 1952−1958. (b) Nelson, J. M.; Rengel, H.; Manners, I. *J. Am. Chem. Soc.* **1993**, *115*, 7035−7036. (c) Nelson, J. M.; Nguyen, P.; Petersen, R.; Rengel, H.; Macdonald, P. M.; Lough, A. J.; Manners, I.; Raju, N. P.; Greedan, J. E.; Barlow, S.; O'Hare, D. *Chem. Eur. J.* **1997**, *3*, 573−584.

(8) (a) Bayer, R.; Pöhlmann, T.; Nuyken, O. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 359−364. (b) Buretea, M. A.; Tilley, T. D. *Organometallics* **1997**, *16*, 1507−1510.

(9) (a) Morikita, T.; Maruyama, T.; Yamamoto, T.; Kubota, K.; Katada, M. *Inorg. Chim. Acta* **1998**, *269*, 310−312. (b) Funaki, H.; Aramaki, K.; Nishihara, H. *Synth. Met.* **1995**, *74*, 59−64. (c) Arnold, R.; Matchett, S. A.; Rosenblum, M. *Organometallics* **1988**, *7*, 2261−2266. (d) Yamamoto, T.; Morikita, T.; Maruyama, T.; Kubota, K.; Katada, M. *Macromolecules* **1997**, *30*, 5390−5396. (e) Knapp, R.; Velten, U.; Rehahn, M. *Polymer* **1998**, *39*, 5827−5838. (f) Nugent, H. M.; Rosenblum, M.; Klemarczyk, P. *J. Am. Chem. Soc.* **1993**, *115*, 3848−3849.

(10) (a) Tanaka, M.; Hayashi, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 334−336. (b) Foucher, D. A.; Honeyman, C. H.; Nelson, J. M.; Tang, B. Z.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1702−1711.

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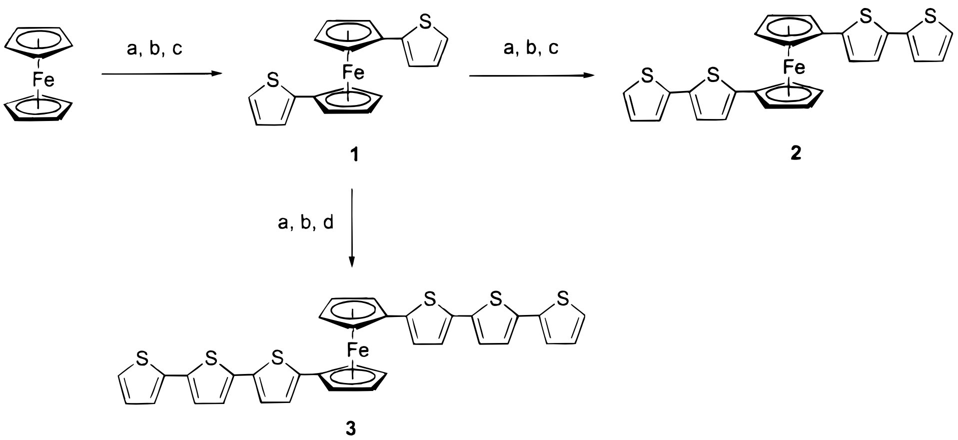
Scheme 1[a]



[a] Reagents: (a) BuLi, TMEDA, THF/hexanes; (b) $ZnCl_2$, THF; (c) 2-bromothiophene, $Pd(PPh_3)_4$, THF; (d) 5-bromo-2,2′-bithiophene, $Pd(PPh_3)_4$, THF.

Table 1. UV−Visible−Near-IR and Cyclic Voltammetry Data

complex	UV−vis−near-IR λ (nm) (ϵ ($M^{-1}cm^{-1}$))[a]	$E_{1/2}$ (1)[b] vs SCE	$E_{p,a}$ (2)[b] vs SCE
1	460 (830), 306 (17 000)	0.46	-
2	466 (2 800, sh), 344 (35 000)	0.45	1.33
3	384 (55 000)	0.37	0.93
2,2′-bithiophene[c]	302 (12 470)	-	1.31
2,2′:5′,2″-terthiophene[c]	355 (25 050)	-	1.05
$\mathbf{1}^+$	275 (18 000), 365 (9 000), 480 (3 800), 815 (900, sh), 945 (1 200)		
$\mathbf{2}^+$	345 (21 000), 450 (9 600), 560 (3 700, sh), 1 175 (2 300)		
$\mathbf{3}^+$	385 (51 000), 505 (13 000, sh), 585 (7 800, sh), 1 305 (3 500)		

[a] CH_2Cl_2, 20 °C. [b] Conditions: Pt working electrode; 20 °C; CH_2Cl_2; scan rate = 50 mV/s (except for **3**: 70 °C; $ClCH_2CH_2Cl$). [c] UV−vis: ref 26; cyclic voltammetry (ref 27).

Electronic conductivity in ferrocene-containing polymers can arise either by delocalization of charge along the backbone, analogous to the behavior of organic conducting polymers such as polythiophene, or by charge hopping between localized redox centers within the polymer. Manners and co-workers have concluded that for the poly(ferrocenylsilanes) investigated by their group, conductivity is a result of intersite redox hopping.[5]

Hybrid polymers containing both ferrocenyl and oligothienyl groups in the backbone are of interest because they allow the investigation of an intermediate regime in which both redox hopping and charge delocalization are possible. Several groups have investigated the electrochemical behavior and conductivity of polythiophene derivatives containing pendant ferrocene groups,[12] and the magnetic properties of a hybrid polymer, poly(1,1′-ferrocenylene-3′-hexyl-2′,5−5′,2″-terthienyl-2,2″-ylene) have been examined.[13] The conductivity of this latter polymer, when doped with tetracyanoethylene (TCNE) is 10^{-8} S cm^{-1}; however, this is apparently inconsistent with a four-point probe conductivity measurement on a closely related material, poly(ferrocenyl terthienylene), which when doped with $FeCl_3$ gave a value of 10^{-3} S cm^{-1}.[14]

We reasoned that longer oligothiophene bridges may enhance delocalization of charge in these materials, and postulated that this can be accomplished by constructing monomers containing two or three linked thienyl groups. Coupling of these monomers would then yield materials containing bridges between adjacent ferrocenyl centers of four or six thiophene units. We report herein the preparation and electropolymerization of 1,1′-bis(5-(2,2′-bithienyl))ferrocene (**2**) and 1,1′-bis(5-(2,2′:5′,2″-terthienyl))ferrocene (**3**) and the spectroscopic and electrochemical characterization of these compounds and the electropolymerized films.

Results and Discussion

Syntheses. Complexes **2** and **3** were synthesized by the coupling of **1** with 2-bromothiophene and 5-bromo-2,2′-bithiophene, respectively (Scheme 1). Complex **1** has been previously synthesized,[14,15] while **2** and **3** are new compounds. Compound **2** was obtained as an orange solid which is soluble in CH_2Cl_2 and was purified by chromatography on silica gel. The solubility of **3** at room temperature in most organic solvents is poor; however, its solubility increases at slightly elevated temperatures so characterization and electrochemistry could be conducted. Compounds **2** and **3** were characterized by ^1H NMR spectroscopy and elemental analysis. The UV−vis absorption and cyclic voltammetry data for **1**−**3** are collected in Table 1.

Electrochemistry. Compounds **1**−**3** are all expected to show electroactivity both due to the $Fe^{II/III}$ couple and oxidation of the thiophene groups. Oxidized thiophene

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(11) Barlow, S.; O'Hare, D. *Chem. Rev.* **1997**, *97*, 637−669.

(12) (a) Zotti, G.; Schiavon, G.; Zecchin, S.; Berlin, A.; Pagani, G.; Canavesi, A. *Synth. Met.* **1996**, *76*, 255−258. (b) Zotti, G.; Schiavon, G.; Zecchin, S.; Berlin, A.; Pagani, G.; Canavesi, A. *Langmuir* **1997**, *13*, 2694−2698. (c) Back, R.; Lennox, R. B. *Langmuir* **1992**, *8*, 959−64.

(13) Hmyene, M.; Yassar, A.; Escorne, M.; Percheron-Guegan, A.; Garnier, F. *Adv. Mater.* **1994**, *6*, 564−568.

(14) Garnier, F.; Yassar, A. U.S. Patent 5 272 238, 1993.

(15) Wolfgang, H.; Andrejewski, D. German Patent DE3703771, 1988.

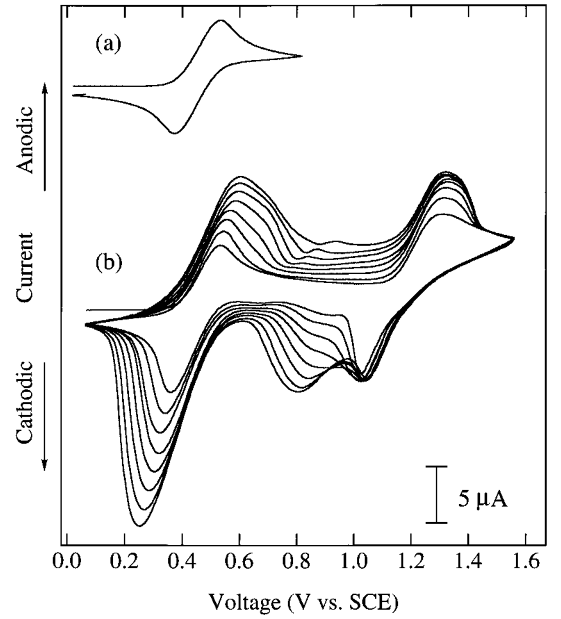

Figure 1. Cyclic voltammogram of **2** at 20 °C in CH_2Cl_2 containing 0.6 M [n-Bu_4N]PF_6 at a Pt working electrode (a) between 0 and 0.8 V and (b) multiple scans between 0 and 1.6 V. Scan rate = 50 mV/s.

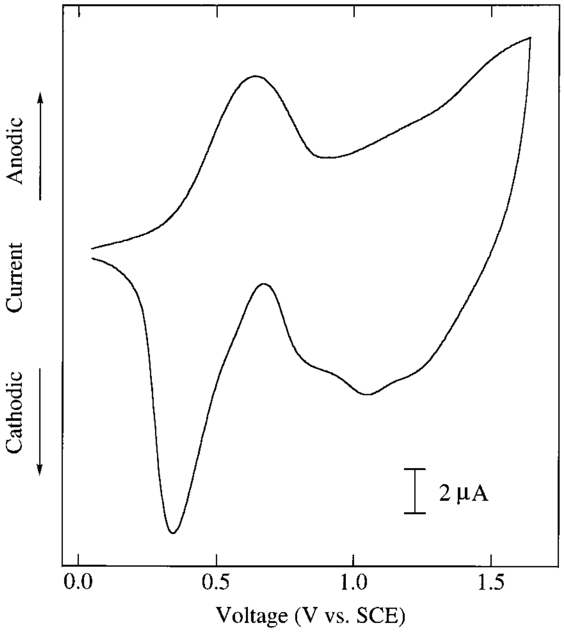

Figure 2. Cyclic voltammogram of poly-**2** at a Pt working electrode at 20 °C in CH_2Cl_2 containing 0.6 M [n-Bu_4N]PF_6. Scan rate = 50 mV/s.

groups typically couple to yield oligomers or polymers, and the solubility of the resulting materials is often poor unless solubilizing side-chains are present in the monomers. A cyclic voltammogram of **1** at 20 °C in CH_2Cl_2 containing 0.1 M [n-Bu_4N]PF_6 shows only one reversible oxidation wave with $E_{1/2}$ = 0.46 V vs SCE, due to the $Fe^{II/III}$ redox couple. Previous attempts by others to electropolymerize this monomer were also unsuccessful.[15] Cyclic voltammetry of a solution of **2** at 20 °C in CH_2Cl_2 containing 0.6 M [n-Bu_4N]PF_6 reveals two oxidation waves in the range 0−1.5 V vs SCE. The lower potential wave with $E_{1/2}$ = 0.45 V vs SCE is reversible and assigned to the $Fe^{II/III}$ redox couple (Figure 1a).

The higher potential wave at 1.33 V vs SCE is electrochemically irreversible and coupled to a reduction feature at 1.05 V (Figure 1b); this wave is assigned to a thiophene-based oxidation. Similar electrochemical behavior was observed in a series of [CpRu(η^5-oligothiophene)]PF_6 complexes.[16] In the absence of water, scanning several times over the potential range 0−1.5 V results in the appearance of an electrochromic film on the electrode surface. The film is golden-red and stable when neutral, but becomes black when oxidized. Scanning from 0 to 0.7 V, where only the ferrocenyl groups are oxidized, does not result in any deposition.

The cyclic voltammogram of the electropolymerization process (Figure 1b) is consistent with the growth of a conducting film on the electrode since the currents of both the ferrocenyl oxidation wave and a new reduction wave at 0.8 V increase with scan number. This new wave is assigned to the reduction of coupled monomers, expected to occur at a lower potential than reduction of the monomer alone due to more extended conjugation. Upon removal of the neutral film from solution and washing it thoroughly to remove any residual **2**, the cyclic voltammogram of the film in monomer-free solution shows a broad oxidation wave at 0.6 V which we attribute to the $Fe^{II/III}$ oxidation (Figure 2). The associated reduction at 0.35 V is sharper but is approximately equal in area to the oxidation wave. The voltammogram also contains a broad feature at higher potential which is assigned to oxidation of coupled oligothiophene moieties in the film. The films are stable to repeated cycling over the potential range 0−0.8 V, with only slight changes in the voltammogram during this process.

Due to the poor solubility of **3** in CH_2Cl_2 at room temperature the cyclic voltammogram of this compound was obtained in $ClCH_2CH_2Cl$ containing 0.6 M [n-Bu_4N]PF_6 at 70 °C. The voltammogram contains multiple waves in the range 0−1.2 V vs SCE, including a reversible $Fe^{II/III}$ wave with $E_{1/2}$ = 0.37 V (Figure 3a) and two irreversible waves at 0.93 and 1.03 V due to thiophene-based oxidations. The $Fe^{II/III}$ waves of **1**−**3** all appear at very similar potentials, indicating that this redox couple is not substantially affected by the length of the oligothiophene group. We observed a similar effect in a series of ruthenium bisacetylide complexes containing oligothienyl ligands.[17] Increasing the length of the oligothienyl group from **2** to **3** results in a decrease in the potential of the second oxidation wave by 0.40 V.

In the absence of water, scanning over the potential range 0 to 1.2 V results in the growth of a golden-red film on the electrode surface (Figure 3b). The cyclic voltammogram of the film in monomer-free solution, after removing it from the polymerization solution in the neutral form and washing with solvent, shows similar features to those observed for **2** (Figure 4). This cyclic voltammogram was obtained after scanning the film 10 times over the complete potential range. During these scans the intensity of the voltammogram increased until it stabilized as shown in Figure 4. After this treatment, the film is stable to repeated cycling over the potential range 0−1.5 V. The reasons for this

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(16) Graf, D. D.; Mann, K. R. *Inorg. Chem.* **1997**, *36*, 150−157.

(17) Zhu, Y.; Millet, D. B.; Wolf, M. O.; Rettig, S. J. *Organometallics* **1999**, *18*, 1930−1938.

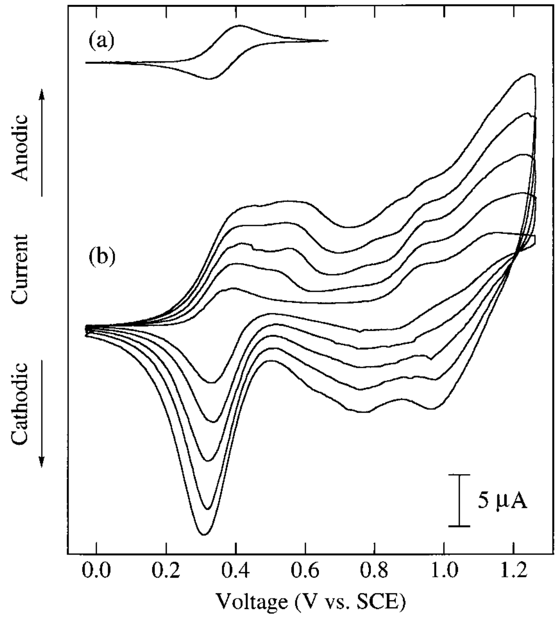

Figure 3. Cyclic voltammogram of **3** at 70 °C in $ClCH_2CH_2Cl$ containing 0.6 M [n-Bu_4N]PF_6 at a Pt working electrode (a) between 0 and 0.7 V and (b) multiple scans between 0 and 1.3 V. Scan rate = 50 mV/s.

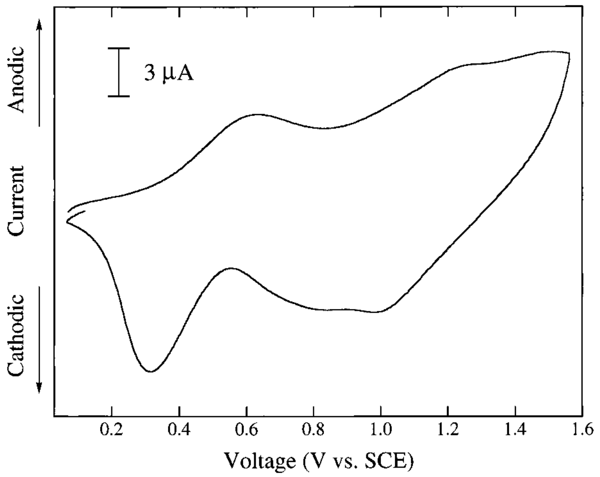

Figure 4. Cyclic voltammogram of poly-**3** at a Pt working electrode at 20 °C in CH_2Cl_2 containing 0.6 M [n-Bu_4N]PF_6. Scan rate = 50 mV/s.

unusual increase in intensity are not known at this time.

The thicknesses of the electropolymerized **2** (poly-**2**) and **3** (poly-**3**) films were estimated from the cyclic voltammetry. The number of monomer units in the films was determined from the area under the ferrocenyl redox waves. Assuming a density of 1.1 g cm^{-3}, the same as that of electropolymerized polythiophene,[18] we obtain a thickness of 0.4 μm for both the poly-**2** film in Figure 2 and the poly-**3** film in Figure 4.

It is very important that the electropolymerizations of **2** and **3** are carried out under rigorous exclusion of water. The presence of even small amounts of water results in the formation of brittle black deposits which stop growing after 2−3 scans. The $Fe^{II/III}$ wave disappears after the first scan, which suggests that water reacts to give an insulating film which prevents the $Fe^{II/III}$ redox couple in dissolved monomer from being observed.

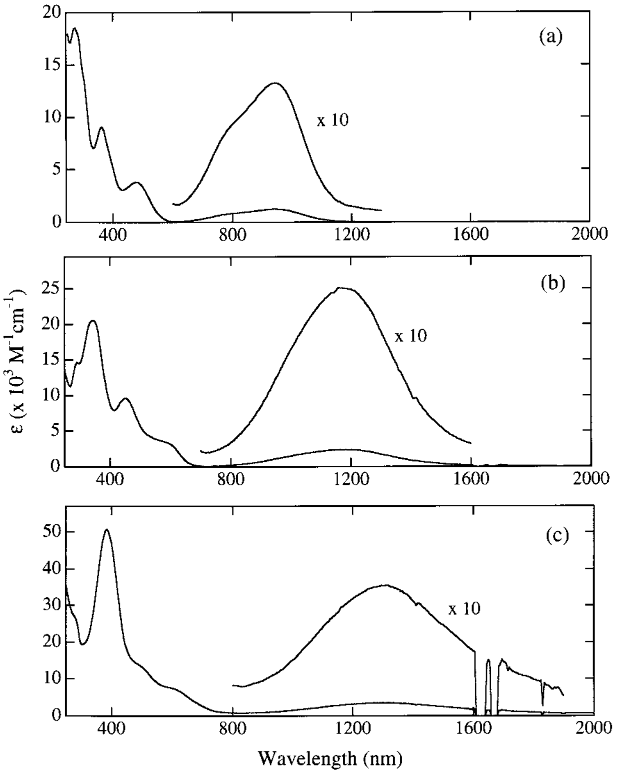

Figure 5. Visible−near-IR spectra of (a) **1**$^+$, (b) **2**$^+$, and (c) **3**$^+$ in CH_2Cl_2 containing 0.13 M [n-Bu_4N]PF_6.

Visible−Near-IR Spectroscopy of 1$^+$−3$^+$. The mechanism of charge transport in poly-**2** and poly-**3** will depend on the level of oxidation of the polymer. When only the ferrocenyl groups are oxidized, it is possible that transport would involve transfer of charge from the oligothienyl groups to the Fe^{III} centers in the polymer. Oxidation of the Fe^{II} in the monomers **1**−**3** allows us to model this process, since in this state ligand-to-metal charge transfer (LMCT) from the oligothienyl group to the Fe^{III} is possible. We have previously observed a low-energy LMCT from a terthienyl ligand to a Ru^{III} center in a ruthenium bis(terthienylacetylide) complex;[17] however, the instability of the less conjugated analogues prevented us from studying the dependence of this transition on the length of the oligothienyl ligand.

The UV−visible spectra of the neutral complexes **1**−**3** contain a strong absorption band assigned to the π−π* transition in the oligothienyl group. This band shifts to lower energy and becomes more intense as the length of the conjugation is increased. The weaker bands at 460 nm in the spectrum of **1** and the shoulder at 466 nm for **2** are assigned as Fe^{II} d−d transitions and appear very close to the ligand-field transition for ferrocene at 441 nm.[19] Solutions of the monocations **1**$^+$−**3**$^+$ were prepared by electrochemical oxidation in CH_2Cl_2 containing 0.13 M [n-Bu_4N]PF_6, and the visible−near-IR spectra were obtained (Figure 5). The spectra all contain several intense transitions between 300 and 800 nm, the strongest of which is assigned to the π−π*

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(18) *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; p 303.

(19) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979.

transitions in the oligothiophene ligand. These transitions appear at similar energy and have similar intensity to those for the corresponding neutral complexes **1**−**3**. The other bands between 300 and 800 nm are likely Cp → Fe^{III} LMCT transitions and are of similar intensity and energy as those in ferrocenium.[20]

The spectra of **1**$^+$−**3**$^+$ contain a broad low-energy band with λ_{max} between 945 and 1305 nm. The absorption maximum and intensity of this band are dependent on the length of the conjugation in the ligand. The band appears at highest energy (945 nm) and is least intense ($\epsilon = 1200$ M^{-1}cm^{-1}) for **1**$^+$ and is lowest in energy (1345 nm) and is most intense ($\epsilon = 3500$ M^{-1}cm^{-1}) for **3**$^+$. On the basis of this behavior, we assign this low-energy band to an oligothiophene → Fe^{III} LMCT transition. The difference in oxidation potential between the oligothienyl group and the metal center correlates to the energy of this LMCT transition; increased conjugation means the oligothienyl group can give up an electron more easily (lower oxidation potential) and the charge transfer to the oxidized metal center is more facile. In mixed-valent bimetallic complexes, the energy and intensity of the intervalence charge transfer (IVCT) transition are related to the delocalization of charge in the complex.[21] Analogously, the energy and intensity of the LMCT transition in **1**$^+$−**3**$^+$ are consistent with significant delocalization of charge in these complexes, and this delocalization is greatest for the complex with the most conjugated oligothienyl group (**3**$^+$).

Spectroelectrochemistry of Electropolymerized Films. To examine the effect of oxidation on the spectral characteristics of the electropolymerized films, we carried out in situ spectroelectrochemistry on poly-**2** and poly-**3** films on transparent indium tin oxide (ITO) electrodes. The cyclic voltammograms of these films were similar to those obtained on Pt electrodes, although the positions of all the peaks were slightly shifted due to the resistance of the ITO layer. To minimize IR drop in the solution due to the relatively large separations between the electrodes in the spectroelectrochemical cell, high electrolyte concentrations were used (1.3 M).

We collected optical spectra of the films at three potentials: reduced (~ −0.1 to 0 V), with the ferrocene oxidized (~ 0.7 to 0.8 V), and fully oxidized (~ 1.5 to 1.7 V). These spectra over the range 300−1600 nm are shown for poly-**2** and poly-**3**, respectively, in Figures 6 and 7. The spectra all show sharp absorptions at >1100 nm due to vibrational overtones from the electrolyte and solvent. The reduced films (~−0.1 to 0 V vs SCE) show a single broad band at 445 nm (poly-**2**) and 420 (poly-**3**) assigned to a π-π* transition of the oligothienyl group in the backbone. The absorption maxima for both films are close to those observed for polythiophene (between 418 and 480 nm, depending on the method of preparation).[22] The absorption maximum for poly-**3** is expected at lower energy than for poly-**2** due to the relative conjugation lengths in the two materials; however, the opposite is observed. This may be due to differences in the conditions (temperature and solvent) under which the two films are prepared. The conductivity of electropolymerized polythiophene films has been shown to be dependent on the conditions under which the films are prepared;[23] similar effects may influence the absorption maxima for the neutral poly-**2** and poly-**3** films.

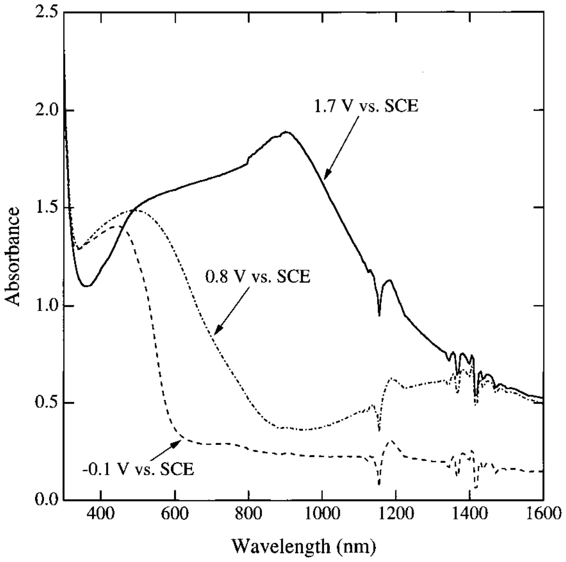

Figure 6. Spectroelectrochemistry of poly-**2** on an ITO electrode in CH_2Cl_2 containing 1.3 M [n-Bu_4N]PF_6.

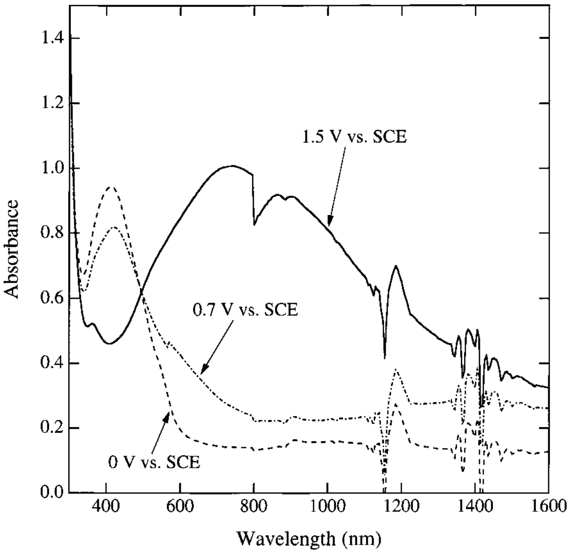

Figure 7. Spectroelectrochemistry of poly-**3** on an ITO electrode in CH_2Cl_2 containing 1.3 M [n-Bu_4N]PF_6.

Upon oxidation of the films to a potential at which the ferrocenyl groups are oxidized, several changes are observed in the spectra. In the case of poly-**2**, two bands are observed, at 495 and 1395 nm. The broad, higher energy band is predominantly due to the π−π* transition with contributions from Cp → Fe^{III} LMCT also possible; and the band with λ_{max} at 1395 nm is assigned as a charge-transfer band from the oligothiophene group to the Fe^{III}. It is interesting to compare this spectrum to that of **2**$^+$ in solution (Figure 4b). The lowest energy band shifts from 1175 nm in **2**$^+$ to 1395 nm in poly-**2** oxidized at 0.8 V, consistent with the charge-transfer originating from a more conjugated moiety in the

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(20) Sohn, Y. S.; Hendrickson, D. N.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 3603−3612.

(21) (a) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: New York, 1984. (b) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391−444.

(22) Ref 18, p 316.

(23) Hotta, S.; Hosaka, T.; Shimotsuma, W. *Synth. Met.* **1983**, *6*, 69−71.

polymer. Coupling of **2** should result in a tetrathienyl bridge between ferrocenyl groups, which is expected to result in a charge transfer band slightly lower in energy than that observed for $\mathbf{3}^+$ which contains a terthienyl group.

In the spectrum of poly-**3** oxidized at 0.7 V, the $\pi-\pi^*$ transition does not shift substantially from neutral poly-**3**, although a broad low-energy shoulder does appear, and a very weak, broad band in the near-IR is present. On the basis of the spectra of $\mathbf{2}^+$ and $\mathbf{3}^+$, as well as the spectrum of poly-**2** at 0.8 V, the absorption of poly-**3** at 0.7 V is expected to be more intense than observed. It is possible that the ferrocenyl centers are not completely oxidized at 0.7 V, resulting in a weaker absorption. Cycling the films twice between 0 and 0.7−0.8 V demonstrates that the spectral changes are completely reversible, consistent with the stability of the films over this potential range as shown in the cyclic voltammetry of the films on Pt electrodes.

Oxidation of both poly-**2** and poly-**3** films to 1.5−1.7 V vs SCE results in dramatic changes in the spectra. For both poly-**2** and poly-**3** a very broad absorption between 400 and 1600 nm appears. In contrast to the reversibility of the spectral changes upon oxidation to 0.7−0.8 V, these broad absorptions do not completely disappear when the oxidized film is reduced back to −0.1 to 0 V, indicating oxidation to 1.5−1.7 V results in some irreversible changes to the polymers. The appearance and positions of these broad bands suggest that they arise due to transitions to intergap states in the oxidized polymers. Oxidation or doping of polythiophene causes the interband absorption at 480 nm to decrease with the concomitant appearance of lower energy bands due to transitions between the valence band and localized levels in the band gap.[24]

Conclusions

The stability of ferrocene in both $\mathrm{Fe}^{\mathrm{II}}$ and $\mathrm{Fe}^{\mathrm{III}}$ oxidation states allows the electropolymerization of oligothienylferrocene complexes without decomposition. The growth of electroactive films on the electrode surface is consistent with the formation of a conductive material during the electropolymerization process. The reversible electrochromic behavior of these films is similar to that observed for other conducting polymers such as polythiophene.

Oxidation of the ferrocene group to ferrocenium in both the monomers and in the electropolymerized films results in the appearance of a low-energy charge-transfer transition. This band is due to a LMCT transition from the oligothienyl group to the $\mathrm{Fe}^{\mathrm{III}}$ center and is indicative of significant charge delocalization, which is enhanced with increasing conjugation in the oligothienyl group. It is possible that limited conductivity could arise from oxidation of only the ferrocenyl groups in the polymers, and such measurements are currently underway.

Experimental Section

General. All reactions were carried out under nitrogen using Schlenk techniques, unless noted otherwise. Tetrahydrofuran was dried by refluxing over sodium/benzophenone. *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) was purified by distillation from KOH and was stored over molecular sieves (4 Å). All other compounds were used as received. 5-Bromo-2,2′-bithiophene[25] and 1,1′-bis(2-thienyl)ferrocene[14] were prepared using literature procedures. ^{1}H NMR spectra were obtained on a Bruker WH-400 spectrometer and the spectra referenced to residual solvent.

1,1′-Bis(5-(2,2′-bithienyl))ferrocene (2). *n*-BuLi (3.5 mL, 1.6 M in hexanes, 5.6 mmol) was added via syringe at 0 °C to a solution of **1** (0.78 g, 2.3 mmol) and TMEDA (1.2 mL, 8.0 mmol) in a mixture of dry THF (20 mL) and hexanes (10 mL). The solution was heated at reflux for 2 h and then cooled to room temperature. A solution of anhydrous $\mathrm{ZnCl_2}$ (0.76 g, 0.56 mmol) in dry THF (20 mL) was then added via cannula, and the mixture was stirred for another 2 h. The mixture was added to a solution of 2-bromothiophene (0.86 g, 5.3 mmol) and $\mathrm{Pd(PPh_3)_4}$ (60 mg, 0.052 mmol) in dry THF (20 mL) via cannula, and the mixture was heated at 50 °C for 2 days with stirring. After the reaction mixture was cooled to room temperature, a solution of 1 M HCl (30 mL) was added to quench the reaction. The organic layer was collected, and the aqueous layer was extracted using methylene chloride (2 × 20 mL). The organic portions were combined and washed with distilled water (2 × 30 mL). The organic solution was dried over anhydrous $\mathrm{MgSO_4}$ and collected by filtration. Removal of the solvent gave a brownish red solid, which was purified by flash chromatography on silica gel using hexanes/methylene chloride (3:2 v/v) as eluant. Pure **2** was also obtained by crystallization from the methylene chloride solution by adding hexanes and cooling to −4 °C overnight. Yield: 0.39 g (34%). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 7.15 (dd, $J = 5.0$, 1.0 Hz, 2H), 7.05 (dd, $J = 3.5$, 1.0 Hz, 2H), 6.96 (dd, $J = 5.0$, 3.5 Hz, 2H), 6.87 (d, $J = 3.7$ Hz, 2H), 6.73 (d, $J = 3.7$ Hz, 2H), 4.47 (t, $J = 1.8$ Hz, 4H), 4.24 (t, $J = 1.8$ Hz, 4H). Anal. Calcd $\mathrm{C_{26}H_{18}S_4Fe}$: C 60.69, H 3.53. Found: C 60.74, H 3.42.

1,1′-Bis(5-(2,2′:5′,2″-terthienyl))ferrocene (3) was prepared as described for **2**, using 5-bromo-2,2′-bithiophene, instead of 2-bromothiophene. The product was obtained in >95% purity by crystallization either from hot toluene or chlorobenzene solution. Yield: 53%. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 6.98 (s, broad, 2H), 6.95 (dd, $J = 3.6$, 1.1 Hz, 2H), 6.80−6.83(m, 2H), 6.78 (d, $J = 3.7$, 2H), 6.71 (dd, $J = 5.1$, 1.1 Hz, 2H), 6.63 (dd, $J = 5.1$, 3.6 Hz, 2H), 6.53 (d, $J = 3.7$ Hz, 2H), 4.37 (t, $J = 1.8$ Hz, 4H), 4.01 (t, $J = 1.8$ Hz, 4H). Anal. Calcd $\mathrm{C_{34}H_{22}S_6Fe}$: C 60.16, H 3.27. Found: C 60.20, H 3.15.

Electrochemistry. Electrochemical measurements were conducted on a Pine AFCBP1 bipotentiostat using a Pt coil wire counter electrode and an Ag wire reference electrode. The working electrode was a Pt disk electrode with a diameter of 1.0 mm. The supporting electrolyte, $[(n\text{-Bu})_4]\mathrm{NPF_6}$, was purified by recrystallization three times from hot ethanol and dried in vacuo at 100 °C for one week. Methylene chloride and dichloroethane were dried by heating at reflux over calcium hydride, followed by distillation. Decamethylferrocene (−0.12 V vs SCE) was used as an internal standard for the electrochemical experiments. All electrochemical polymerizations were carried out under nitrogen, and the cells containing the electrodes and $[(n\text{-Bu})_4]\mathrm{NPF_6}$ were dried in vacuo at 90 °C overnight before addition of dry solvent. The polymer film was grown on the electrode by scanning over a suitable potential range (0−1.5 V vs SCE for **2**, and 0−1.2 V vs SCE for **3**). The electrochemical polymerization of **2** was carried out at 20 °C in a methylene chloride solution with an electrolyte concentration of 0.6 M, and the complex concentration was in a range of 5×10^{-3} to 1×10^{-2} M. The same experiments for **3** were carried out in a saturated solution of **3** in 1,2-dichloroethane with 0.6 M electrolyte at 70 °C.

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(24) Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem. Rev.* **1988**, *88*, 183−200.

(25) Bäuerle, P.; Würthner, F.; Götz, G.; Effenberger, F. *Synthesis* **1993**, 1099−1103.

(26) Van Pham, C.; Burkhardt, A.; Shabana, R.; Cunningham, D. D.; Mark, H. B.; Zimmer, H. *Phosphorus, Sulfur Silicon Relat. Elem.* **1989**, *46*, 153−168.

(27) Diaz, A. F.; Crowley, J.; Bargon, J.; Gardini, G. P.; Torrance, J. B. *J. Electroanal. Chem.* **1981**, *121*, 355−361.

Spectroelectrochemistry. A homemade spectroelectrochemical cell using a Pyrex cuvette into which an indium tin oxide (ITO) on glass working electrode could be inserted under inert atmosphere was used. Measurements were carried out on a Varian Cary 5 spectrometer. The polymer films were deposited on ITO electrodes from the same deposition solutions as used with the Pt electrodes, by scanning at 25 mV/s over a similar potential range (0−1.7 V vs SCE for **2**, and −0.2 to 1.3 V vs SCE for **3**). After the potential was reduced to 0 V, the films were removed from solution, rinsed with methylene chloride, and dried in vacuo for 1 h. The poly-**2** film was prepared at 20 °C, and the poly-**3** film at 55 °C. The film-coated electrodes were loaded into the previously dried cell containing $[(n\text{-Bu})_4]NPF_6$, along with a Pt counter electrode and an Ag wire reference electrode. The cell was dried in vacuo overnight at room temperature and dry methylene chloride was added until the electrolyte concentration was 1.3 M. The visible−near-IR spectrum was obtained at 20 °C after the film was held at a specific potential until no further change in current was observed (∼1 min), to allow the entire film to reach the potential.

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