Oxidation of Ferrocenyl End-Substituted Oligothiophenes

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A ferrocenyl end-substituted terthiophenes derivative and a sexithiophene derivative were prepared as model compounds for a molecular wire. Electrochemical measurements and absorption spectroscopy were performed to elucidate the oxidation process and the oxidized states of those model compounds. The first oxidation of the model compounds took place in the ferrocene moieties (terminals). The resultant oxidized species in the ferrocene moieties seeped into the oligothiophene moieties (wires) and spread over two or three thiophene rings. Further oxidation of the ferrocenyl-terthiophene derivative did not occur, whereas that of the ferrocenyl-sexithiophene derivative produced an oxidized species, such as a cation radical in the sexithiophene moiety.

Molecular electronics has attracted a great deal of attention recently, since exhibiting potential applications for integrated molecular-sized circuits, which will downsize today's microcircuits and operate at far greater speeds.[1] In order to construct various molecular-electronic circuits, it will be necessary to divide the circuits into units. The most fundamental unit is a molecular wire accompanied by terminals. Ferrocene is a promising candidate for the terminals, owing to high stability in both the oxidized and neutral states and its charge-transport ability. One expects that the wire would be made of a π-conjugated material.[2] Several researchers have prepared diferrocenyl-polyenes,[3] a diferrocenyl-oligo(phenylenevinylene),[4] and diferrocenyl-arenes,[5] among others, which should be regarded as model compounds consisting of a wire (a π-conjugated system) and terminals (ferrocenyl groups). The charge transfer between the terminals decayed with increasing metal–metal distance and was scarcely detected for a distance of six conjugated double bonds.[3] However, there have been no reports regarding charge transfer from the ferrocene moieties to the π-conjugated systems, molecular wires. Recently, our and Wolf's groups have synthesized diferrocenyl-terthiophenes with alkyl or methoxy groups as model compounds for a molecular wire, and have discussed the charge transfers between the terminal and the wire,[6,7] or between both terminals,[8] in their reports. In this work, we prepared diferrocenyl-dihexyl-terthiophene (**F3F**) and diferrocenyl-tetrahexyl-sexithiophene (**F6F**) as model compounds for a molecular wire (Fig. 1). **F6F** includes a wire with a longer conjugation length than **F3F**. In addition, dihexyl-dimethyl-terthiophene (**M3M**), ferrocenyl-dihexyl-methyl-terthiophene (**F3M**), tetrahexyl-dimethyl-sexithiophene (**M6M**), and ferrocenyl-tetrahexyl-methyl-sexithiophene (**F6M**) were prepared as reference compounds (Fig. 1). The oxidation processes and the oxidized states of these compounds were investigated by cyclic voltammetry, coulometry, and electronic absorption spectroscopy. The results reveal the concrete feature of the oxidized species yielded in the ferrocene moieties (the terminals).

Oxidation Process

The oxidation processes of model compounds for a molecular wire were investigated by cyclic voltammetry and the controlled potential coulometry of ferrocene, the terthiophene derivatives, and the sexithiophene derivatives. Electrochemical measurements were carried out in dichloromethane solutions containing 2.0×10^{-3} M of each compound and 0.1 M of tetrabutylammonium perchlorate. In the cyclic voltammograms, the potential was swept at a rate of 100 mV/s.

The electrochemical data are summarized in Table 1. The cyclic voltammograms of ferrocene and the series of terthiophene derivatives show only one reversible redox wave. The redox potentials ($E^{1}{}_{1/2}$) of the terthiophene derivatives substituted with one ferrocene group and two ferrocene groups (**F3M** and **F3F**) are almost the same as that of ferrocene, and are apparently different from that of the methyl end-substituted terthiophene derivative (**M3M**). The controlled potential coulometry of the oxidation waves of the ferrocenyl-terthiophenes was conducted at 0.20 V vs ferrocene/ferricinium (Fc/Fc^{+}) and gave coulometric n-values (n_a): 1.1 Faraday per mole (about one-electron oxidation) for **F3M** and n_a: 2.1 Faraday per mole (about two-electron oxidation) for **F3F**. These results indicate that the redox waves of the ferrocenyl-terthiophenes correspond to the redox process of the ferrocene moieties in the molecules.

The cyclic voltammograms of the series of sexithiophene derivatives reveal two or three reversible redox waves. The first redox waves of the sexithiophene derivatives substituted with one ferrocene group and two ferrocene groups (**F6M** and **F6F**) were observed at almost the same potential as that at which the redox wave of ferrocene. In addition, controlled potential coulometry of the first oxidation waves of the ferrocenyl-sexithiophenes was conducted at 0.20 V vs Fc/Fc^{+}, and gave n_a: 1.1 Faraday per mole (about one-electron oxidation) for **F6M** and n_a: 2.0 Faraday per mole (about two-electron oxidation) for **F6F**. These results suggest that the first oxidation

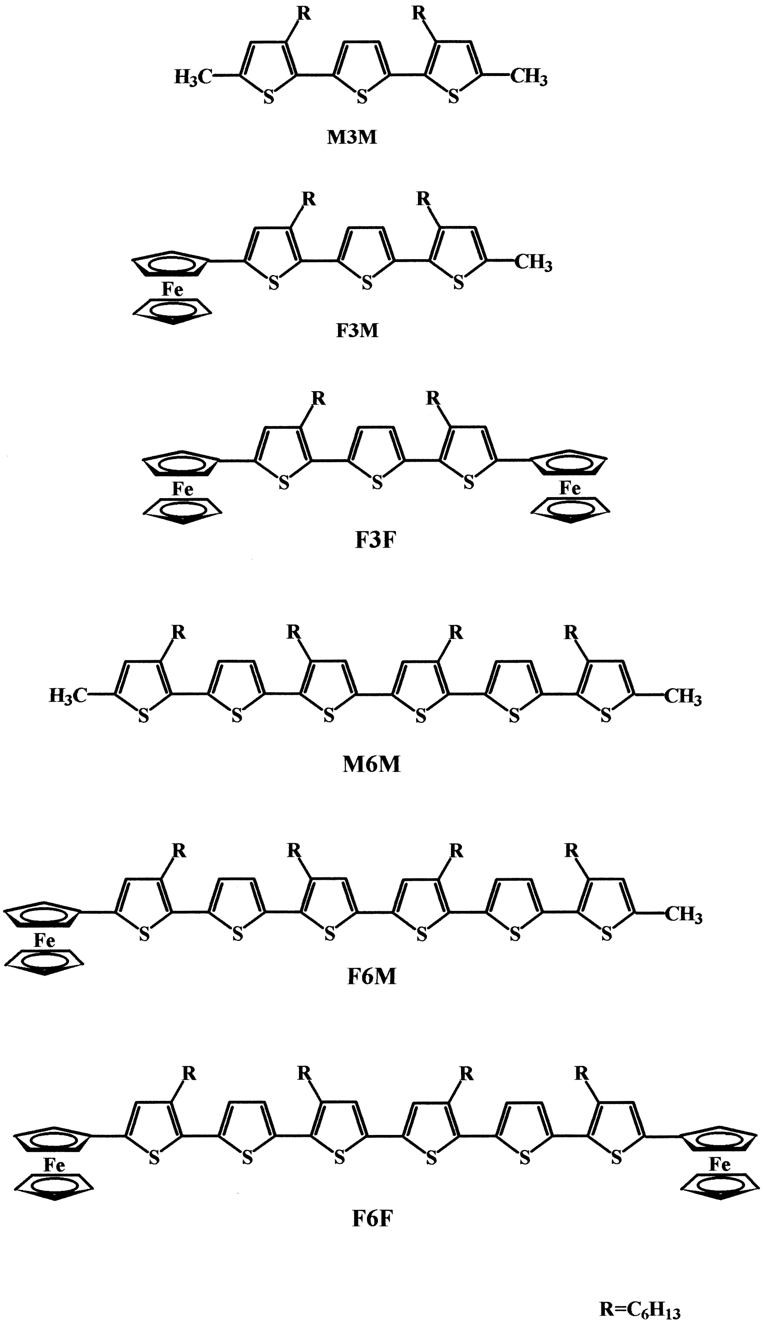

Fig. 1. Methyl-oligothiophene and ferrocenyl-oligothiophene derivatives.

takes place in the ferrocene moieties. On the other hand, the second redox potentials of the ferrocenyl-sexithiophenes are slightly higher than the first redox potential of the methyl end-substituted sexithiophene derivative (**M6M**), but closer to the first redox potential of **M6M** than that of ferrocene. These results allow us to speculate that the second oxidation of the ferrocenyl-sexithiophenes occurs in the sexithiophene moieties and that the ferricinium ion moieties produced by the first oxidation of the ferrocenyl-sexithiophenes interact with the sexithiophenes moieties linked to them.

Oxidized States

In order to clarify the interaction between the ferricinium ion and the oligothiophene moieties, the neutral and oxidized states of ferrocene, the terthiophenes derivatives, and the sexithiophene derivatives were investigated by electronic absorption spectroscopy. Dichloromethane solutions containing each compound (2.8×10^{-5} M for the terthiophene derivatives, 1.4×10^{-5} M for the sexithiophene derivatives) were oxidized with a stoichiometric amount of $FeCl_3$.[9]

The electronic absorption spectra of neutral and one-electron oxidized ferrocene showed no distinct band. The absorption bands attributable to ferrocene and ferricinium ion are undetectable in a dilute solution, such as in this case, because of their small optical densities, ferrocene: ε_{max} 87 (2.8 eV), ε_{max} 50 (3.8 eV); ferricinium ion: ε_{max} 400 (2.0 eV).

Table 1. Data from Cyclic Voltammetory and Controlled Potential Coulometrey

Compound	$E^1_{1/2}$ a)	$E^1_{p,a}-E^1_{p,c}$ b)	n^1_a c)	$E^2_{1/2}$ a)	$E^2_{p,a}-E^2_{p,c}$ b)	$E^3_{1/2}$ a)	$E^3_{p,a}-E^3_{p,c}$ b)
	V vs Fc/Fc$^+$	mV	Faradays/mol	V vs Fc/Fc$^+$	mV	V vs Fc/Fc$^+$	mV
Ferrocene	0.00	170	1.1	—	—	—	—
M3M	0.43	120	—	—	—	—	—
F3M	−0.01	160	1.1	—	—	—	—
F3F	0.01	180	2.1	—	—	—	—
M6M	0.25	160	—	0.42	140	—	—
F6M	0.01	130	1.1	0.30	— d)	0.44	— d)
F6F	0.03	160	2.0	0.35	190	—	—

a) $E^n_{1/2}$ are the *n* th redox potentials.

b) $E^n_{p,a}$ and $E^n_{p,c}$ are the *n* th anodic and the *n* th cathodic peak potentials, respectively.

c) n_a are coulometric *n*-values for the first oxidation.

d) The value is uncertain on account of overlapping waves.

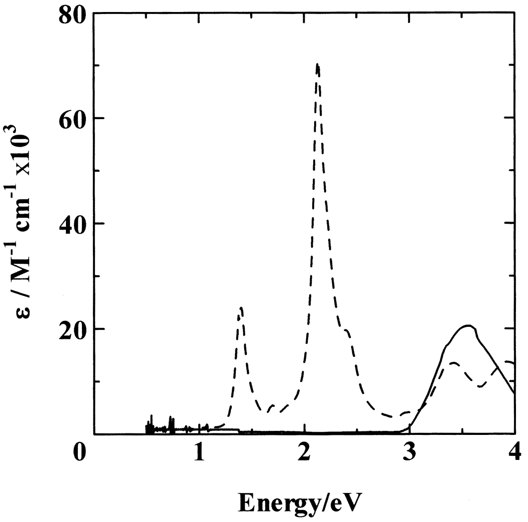

Fig. 2. Electronic absorption spectra neutral and oxidized **M3M**; neutral one (solid line), one-electron oxidized one (dashed line).

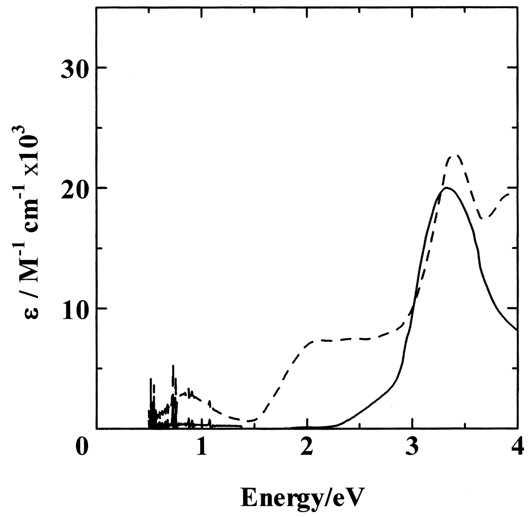

Fig. 3. Electronic absorption spectra neutral and oxidized **F3M**; neutral one (solid line), one-electron oxidized one (dashed line).

Oxidized States of Terthiophenes Derivatives. Figure 2 shows the electronic absorption spectra of neutral and one-electron oxidized **M3M**. The spectrum of neutral **M3M** has a π–π^* transition band at about 3.6 eV. The one-electron oxidation of **M3M** results in the appearance of two strong bands at 1.4 and 2.2 eV with a shoulder or a tailing on the high-energy side. This spectral change during one-electron oxidation closely resembles that of previously reported di(trimethylsilyl)terthiophene, and should be interpreted in terms of the production of a cation radical (polaron) in the terthiophene moiety.[10]

The spectra of the neutral and oxidized ferrocenyl-terthiophenes are shown in Fig. 3 (for **F3M**) and Fig. 4 (for **F3F**). The π–π^* transition bands were observed at 3.3 eV (for **F3M**) and 3.1 eV (for **F3F**). When **F3M** and **F3F** are one-electron oxidized in solution, two broad bands below 3 eV (0.8 and 2.2 eV) and two strong bands above 3 eV (3.4 and 4.0 eV) appear. The bands above 3 eV would be mainly attributable to ferric chloride and related substances, such as iron(II) chloride. The bands below 3 eV that are attributable to the oxidized ferrocenyl-terthiophenes show considerable optical densities (ε_{max} 3000 at 0.8 eV, ε_{max} 7300 at 2.2 eV) for **F3M** and (ε_{max} 3300 at 0.8 eV, ε_{max} 9500 at 2.2 eV) for **F3F**. The densities are remarkably higher than that of the absorption band for isolated ferricinium ion. It can be presumed from the results mentioned in "*Oxidation process*" that the one-electron oxidations of **F3M** and **F3F** occur in the ferrocene moieties. These results imply that the oxidized states are not localized in the ferricinium ion moiety. In addition, the spectral feature is quite different from that of one-electron oxidized **M3M**, indicating that the oxidized species produced in the ferrocene moiety does not completely transfer to the oligothiophene moiety to yield a cation radical (polaron). Moreover, the intervalence band, the ferrocene–ferrocene interaction band, has been observed as a broad single band in the near-IR region (0.7–0.8 eV) for diferrocenyl-polyene.[3] The two bands below 3 eV were not only observed in one-electron oxidized **F3F** (diferrocenyl-terthiophene), but also in one-electron oxidized **F3M** (monoferrocenyl-terthiophene). Therefore, the two bands would be not an intervalence band. It seems reasonable to conclude that the two intense absorption bands are primarily attributable to seeping of the oxidized species from the ferrocene moiety into the

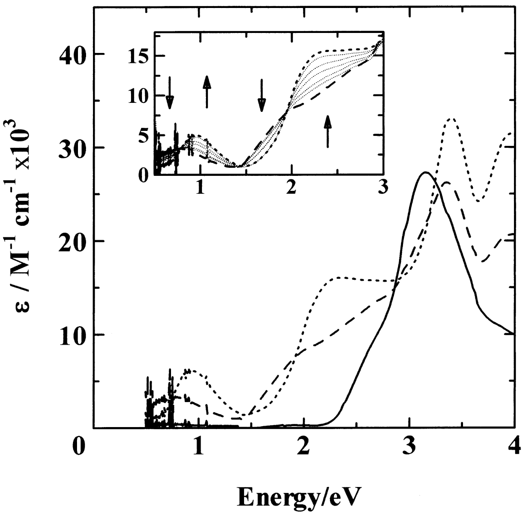

Fig. 4. Electronic absorption spectra neutral and oxidized **F3F**; neutral one (solid line), one-electron oxidized one (dashed line), two-electron oxidized one (dotted line). The inset is the spectral change of **F3F** during one-electron to two-electron oxidation.

neighboring terthiophene moiety.[11]

With a further addition of ferric chloride to the oxidized **F3F**, corresponding to the two-electron oxidation, two new broad bands grew at 1.0 and 2.3 eV. Isosbestic points in the spectral change were observed at 0.8, 1.4, 2.0, 3.0 eV during further oxidation (inset of Fig. 4). Two-electron oxidation would take place in the other ferrocene moiety of **F3F** according to the discussion in "*Oxidation process*". The isosbestic behavior shows that the oxidized species produced in both ferrocene moieties interact with each other, and are not isolated. This interaction allow us to presume that the oxidized species spreads over more than, or equal to, two thiophene rings of the terthiophene moiety from the ferricinium ion moiety.

Oxidized States of Sexithiophenes Derivatives. Figure 5 shows the electronic absorption spectra of neutral and oxidized **M6M** in dichloromethane. The spectrum of neutral **M6M** exhibits a π–π* transition band at 3.0 eV. With the one-electron oxidation of **M6M**, the π–π* transition band disappears and two strong absorption bands at 0.8 and 1.6 eV with a shoulder on the high-energy side appear. This spectral change is similar to that of **M3M**, and can be explained by the generation of a cation radical (polaron) during the one-electron oxidation of **M3M**.

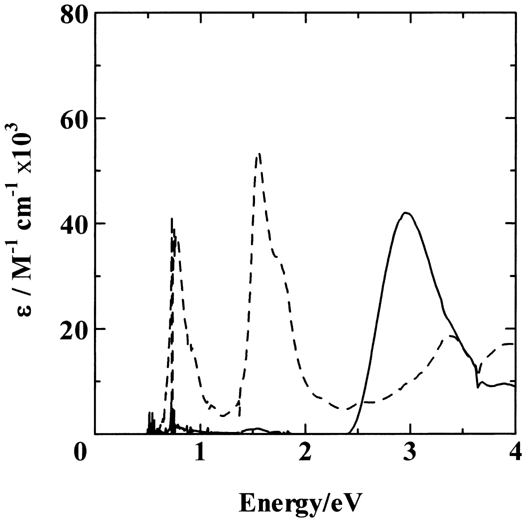

Fig. 5. Electronic absorption spectra neutral and oxidized **M6M**; neutral one (solid line), one-electron oxidized one (dashed line).

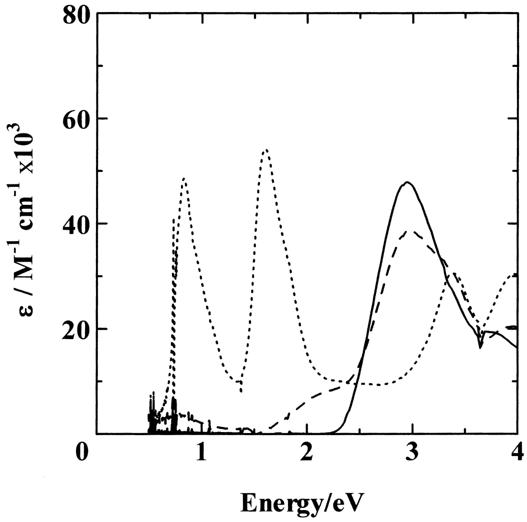

Fig. 6. Electronic absorption spectra neutral and oxidized **F6M**; neutral one (solid line), one-electron oxidized one (dashed line), two-electron oxidized one (dotted line).

The spectra of neutral and oxidized **F6M** and **F6F** are shown in Figs. 6 and 7, respectively. The neutral ferrocenyl-sexithiophenes have a π–π* transition band at 2.9 eV. When **F6M** is one-electron oxidized or **F6F** is two-electron oxidized, the π–π* transition bands reduce and two broad bands at about 0.8 and 2.2 eV appear below 3.0 eV. These additional bands show considerable optical densities ($\varepsilon_{\max}$ 3500 at 0.8 eV, $\varepsilon_{\max}$ 8200 at 2.2 eV) for one-electron oxidized **F6M** and ($\varepsilon_{\max}$ 9500 at 0.8 eV, $\varepsilon_{\max}$ 21000 at 2.2 eV) for two-electron oxidized **F6F**. The intensity is remarkably higher than that of the absorption band for isolated ferricinium ions, and the spectral feature is different from that of one-electron oxidized **M6M**. The electrochemical measurements show that the first oxidation of the ferrocenyl-sexithiophenes, which means the one-electron oxidation of **F6M** and the two-electron oxidation of **F6F**, occurs in the ferrocene moiety, as described in "*Oxidation process*". Therefore, the reduction of the π–π* transition band and the high intensity of the additional bands imply that the bands are attributable to a seeping of the oxidized states from the ferricinium ion moiety into the sexithiophene moiety. Furthermore, in the oxidation of **F6F** the intensity of the additional bands below 3.0 eV constantly increases along with the oxidation until the two-electron oxidation of **F6F** proceeds. This change shows an isolation of the oxidized species produced in both ferrocene moieties, in contrast to **F3F**. It can therefore be presumed that the spread of the oxidized species from the ferricinium ion moiety is less than four thiophene rings of the terthiophene moiety.

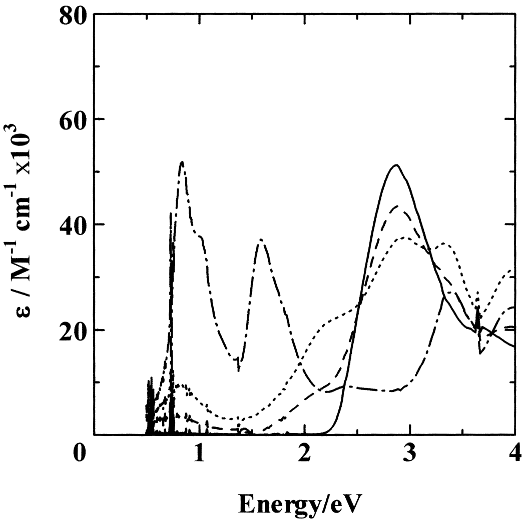

Fig. 7. Electronic absorption spectra neutral and oxidized **F6F**; neutral one (solid line), one-electron oxidized one (dashed line), two-electron oxidized one (dotted line), three-electron oxidation (dot-dashed line).

With further oxidation of the ferrocenyl-sexithiophenes, the π–π* transition bands disappear and two new bands grow at 0.8 and 1.6 eV. The absorption spectra of two-electron oxidized **F6M** and three-electron oxidized **F6F** is similar to those of one-electron oxidized **M6M** and other sexithiophene derivatives.[9,10,12] The additional bands would be ascribed to a cation radical on the sexithiophene moiety.

Conclusion

We prepared novel model compounds for a molecular wire, diferrocenyl-terthiophene and diferrocenyl-sexithiophene derivatives. The electrochemical measurements of the model compounds show that the first oxidation takes place in the ferrocene moieties (terminals). The charge, the oxidized species, produced on both the ferrocene moieties (terminals) seeps into the terthiophenes moiety or the sexithiophene moiety (wire). The spread of the charge ranges over 2 or 3 thiophene rings of the oligothiophene moiety linked to the ferrocene moiety. The further oxidation would generate a cation radical on the sexithiophene moiety.

Experimental

General Procedures. 3,3″-dihexyl-2,2′:5′,2″-terthiophene, 3,3″,4‴,3‴″-tetrahexyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2‴″-sexithiophene, and the corresponding dibromides were synthesized according to previously reported methods.[13–16] Tetrahydrofuran (THF) and ether were distilled under nitrogen over calcium hydride and $LiAlH_4$, respectively. *N*,*N*-dimethylformamide (DMF) was dried over type 4 Å molecular sieves and distilled under reduced pressure.

^{1}H NMR experiments were performed using a HITACHI R-1500 spectrometer in the pulse Fourier-transform mode. Infrared spectra were obtained using a JASCO FT-IR-230 spectrometer and electronic absorption spectra were recorded on a JASCO V-570 spectrometer. Cyclic voltammograms and chronoamperograms[17] were measured with a BAS 100A, using a three-electrode one-compartment cell equipped with a platinum working electrode (s = 0.024 cm^2) and a platinum counter-electrode, and a three-electrode two-compartment cell with a platinum gauze disk anode and cathode, respectively. An Ag/Ag$^+$ reference electrode was used.

5,5″-Diferrocenyl-3,3″-dihexyl-2,2′:5′,2″-terthiophene (F3F). To a solution of ferrocenyllithium (prepared from ferrocene (1.4 g, 17.7 mmol) and *t*-butyllithium (5.2 mL of a 1.7 M pentane solution) in THF (7.0 mL)) was added a suspension of anhydrous zinc chloride (1.3 g, 9.1 mmol) in THF (12 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 0.5 h. To the resultant ferrocenylzinc chloride mixture was added a suspension of dichlorobis(triphenylphosphine)palladium(II) (170 mg, 0.25 mmol) in THF (5.0 mL) and then a solution of 5,5″-dibromo-3,3″-dihexyl-2,2′:5′,2″- terthiophene (800 mg, 2.2 mmol) in THF (3.0 mL). The mixture was stirred at room temperature for 2 h and then refluxed for 10 h before being poured into 2 M hydrochloric acid. The aqueous layer was extracted with benzene. The organic extracts were washed with brine and dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporation. The residue was treated with flash chromatography on silica gel (benzene/hexane), and then recrystallized from a mixture of benzene/hexane to provide 560 mg (32%) of the title product as dark red needles; mp 92–93 °C; IR (KBr) 3087, 2954, 2925, 2856, 1458, 1105, 1059, 1028, 1001, 823, 669, 646 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.06 (s, 2H), 6.82 (s, 2H), 4.55 (t, *J* = 1.7 Hz, 4H), 4.27 (t, *J* = 1.7 Hz, 4H), 4.11 (s, 10H), 2.77 (t, *J* = 7.4 Hz, 4H), 1.37 (m, 16H), 0.90 (t, *J* = 4.4 Hz, 6H); Anal. Calcd for $C_{44}H_{48}Fe_2S_3$: C, 67.34; H, 6.17%. Found: C, 67.30; H, 6.09%.

5,5‴″-Diferrocenyl-3,3″,4‴,3‴″-tetrahexyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2‴″-sexithiophene (F6F). Analogously to the preparation of DFTT, the title compound **F6F** was obtained from 5,5‴″-dibromo-3,3″,4‴,3‴″-tetrahexyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2‴″-sexithiophene. Purification by recrystallization of the crude product gave dark-red needles; mp 154–156 °C; IR (KBr) 3080, 2954, 2854, 2925, 1560, 1457, 1105, 1058, 1027, 1000, 821 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.05 (s, 4H), 7.00 (s, 2H), 6.81 (s, 2H), 4.57 (m, 4H), 4.31 (m, 4H), 4.13 (s, 10H), 2.72 (t, *J* = 7.6 Hz, 8H), 1.31 (m, 32H), 0.90 (m, 12H); Anal. Calcd for $C_{68}H_{78}Fe_2S_6$: C, 68.09; H, 6.55%. Found: C, 67.98; H, 6.49%.

3,3″-Dihexyl-5,5″-dimethyl-2,2′:5′,2″-terthiophene (M3M). To a mixture of 5,5″-dibromo-3,3″-dihexyl-2,2′:5′,2″-terthiophene (2.0 g, 5.0 mmol), dichlorobis(triphenylphosphine)nickel(II) (46 mg, 70 mmol), and ether (20 mL) was added a solution of methylmagnesium iodide (prepared from magnesium (390 mg, 16 mmol) and methyl iodide (1.0 mL, 15 mmol) in ether (20 mL)) at room temperature. The resulting black homogeneous mixture was stirred overnight at room temperature and hydrolyzed with 3 M hydrochloric acid. The organic layer and extracts from the aqueous layer were combined, washed with brine, a saturated sodium hydrogencarbonate solution, and brine, and then dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was purified by flash chromatography on silica gel (hexane) to give 1.24 g (56%) of the title product as yellow viscous oil; IR (thin layer) 3062, 2954, 2925, 2856, 1457, 1377, 1136, 829, 725, 679 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.94 (s, 2H), 6.58 (s, 2H), 2.69 (t, *J* = 7.5 Hz, 4H), 2.42 (s, 6H), 1.33 (m, 16H), 0.87 (t, *J* = 3.9 Hz, 6H); Anal. Calcd for $C_{26}H_{36}S_3$: C, 70.21; H, 8.16%. Found: C, 70.12; H, 8.12%.

3,3″,4‴,3‴″-Tetrahexyl-5,5‴″-dimethyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2‴″-sexithiophene (M6M). Analogously to the preparation of **M3M**, the title compound **M6M** was obtained from

5,5′′′′′-dibromo-3,3′′,4′′′,3′′′′′-tetrahexyl-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′:5′′′′,2′′′′′-sexithiophene. **M6M** was purified by flash chromatography on silica gel (hexane), affording orange needles (53%); mp 98–96 °C; IR (KBr) 3070, 2954, 2923, 2852, 1508, 1465, 1135, 1062, 829, 794 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.96 (s, 8H), 6.56 (s, 2H), 2.71 (t, $J = 6.6$ Hz, 4H), 2.40 (s, 6H), 1.34 (m, 32H), 0.88 (t, $J = 4.4$ Hz, 12H); Anal. Calcd for $C_{50}H_{66}S_6$: C, 69.87; H, 7.74%. Found: C, 69.78; H, 7.64%.

5-Ferrocenyl-3,3′′-dihexyl-5′′-methyl-2,2′:5′,2′′-terthiophene (F3M). 3,3′′-dihexyl-2,2′:5′,2′′-terthiophene was monobrominated with an equimolar amount of N-bromosuccinimide in DMF. The mono-bromide was reacted with methylmagnesium iodide, similarly to the preparation of **M3M**, to give the hexyl-methyl-terthiophene derivative. Further, the derivative was brominated again with *N*-bromosuccinimide, and then coupled with ferrocenylzinc chloride, similarly to the preparation **F3F**, to obtain a dark-red viscous oil (49%); IR (thin layer) 3093, 2925, 2856, 1525, 1458, 1377, 1136, 1107, 1059, 1026, 1001, 820, 725, 677 cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.98 (s, 2H), 6.78 (s, 1H), 6.58 (s, 1H), 4.55 (m, 2H), 4.28 (m, 2H), 4.12 (s, 5H), 2.72 (t, $J = 6.9$ Hz, 4H), 2.43 (s, 3H), 1.35 (m, 16H), 0.86 (m, 4H); Anal. Calcd for $C_{35}H_{42}FeS_3$: C, 68.38; H, 6.89%. Found: C, 68.53; H, 6.88%.

5-Ferrocenyl-3,3′′,4′′′,3′′′′′-tetrahexyl-5′′′′′-methyl-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′:5′′′′,2′′′′′-sexithiophene (F6M). Analogously to the preparation of **F3M**, the title compound **F6M** was obtained from 3,3′′,4′′′,3′′′′′-tetrahexyl-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′:5′′′′,2′′′′′-sexithiophene via two-step reactions. Purification by flash chromatography on silica gel (hexane/benzene) gave a dark-red viscous oil; IR (thin layer): 3100, 2060, 2952, 2925, 2854, 1509, 1457, 1376, 1107, 793, 669 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.05 (s, 2H), 6.99 (s, 2H), 6.82 (s, 1H), 6.59 (s, 1H), 4.55 (t, $J = 1.7$ Hz, 2H), 4.28 (t, $J = 1.7$ Hz, 2H), 4.12 (s, 5H), 2.76 (m, 8H), 2.44 (s, 3H), 1.35 (m, 32H), 0.89 (t, $J = 4.4$ Hz, 12H); Anal. Calcd for $C_{59}H_{72}FeS_6$: C, 68.84; H, 7.05%. Found: C, 68.66; H, 7.16%.

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