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Oxidation States of Unsymmetrically Substituted Quaterthiophenes with Two Terminal Ferrocenyl Groups

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Unsymmetrically substituted quaterthiophenes with two terminal ferrocenyl groups were prepared as long π-conjugated systems. Anisotropy of the chemical structures of the π-conjugated systems was introduced by substitution of methoxy and hexyl groups. Electrochemical and spectroscopic studies were carried out to evaluate the oxidation states of the diferrocenylquaterthiophenes and the interaction between the two terminals. The one-electron oxidation of one diferrocenylquaterthiophene adequately substituted with two methoxy and one hexyl group occurs at one ferrocene moiety specified due to the unsymmetry of the quaterthiophene moiety. The one-electron oxidizing species extends into the quaterthiophene moiety and apparently interacts with the other terminal ferrocene moiety.

Long π-conjugated systems are of both fundamental and applicable interest for their electronic and redox properties during recent years. In order to clarify and modify the properties, the introduction of redox-active terminals into the systems is effective. Furthermore, multiple introduction enables investigate of the interaction between the terminals via the conjugated systems.[1–3] Ferrocene is well known as a highly stable compound in both the oxidized and the neutral states and thus appropriate for the terminals. Several researchers have prepared diferrocenylpolyenes,[4] diferrocenylarenes,[5–8] diferrocenylcumulenes,[9] and diferrocenylarylenevinylenes,[10] which should be regarded as π-conjugated systems with two terminals. The compounds are symmetric in structure and the two terminals are entirely equivalent. Groups substituted on π-conjugated systems significantly affect their chemical structures, suggesting that one can control the oxidation processes and states of diferrocenyl-conjugated systems. We reported the preparations and fundamental properties of an unsymmetrically substituted quaterthiophene with two terminal ferrocenyl groups; 5,5‴-diferrocenyl-3-hexyl-4′,3‴-dimethoxy-2,2′:5′,2″:5″,2‴-quaterthiophene (**FHMMF**), and quaterthiophenes with one or no terminal ferrocenyl group; 5-ferrocenyl-3-hexyl-4′,3‴-dimethoxy-5‴-methyl-2,2′:5′,2″:5″,2‴-quaterthiophene (**FHMM**), 5‴-ferrocenyl-3-hexyl-4′,3‴-dimethoxy-5-methyl-2,2′:5′,2″:5″,2‴-quaterthiophene (**HMMF**), 3-hexyl-4′,3‴-dimethoxy-5,5‴-dimethyl-2,2′:5′,2″:5″,2‴-quaterthiophene (**HMM**).[11] In this paper, we prepared a new diferrocenylquaterthiophene; 5,5‴-diferrocenyl-3,3″-dihexyl-3‴-methoxy-2,2′:5′,2″:5″,2‴-quaterthiophene (**FHHMF**), and the corresponding dimethylquaterthiophene; 3,3″-dihexyl-3‴-methoxy-5,5‴-dimethyl-2,2′:5′,2″:5″,2‴-quaterthiophene (**HHM**), and investigate the oxidation processes and states for a series of the quaterthiophene derivatives by comparing their electrochemical and spectroscopic properties in one-electron oxidation. The two terminal ferrocenyl groups of **FHMMF** and **FHHMF** are nonequivalent because of linkage with the unsymmetrically substituted quaterthiophene moiety (Chart 1).

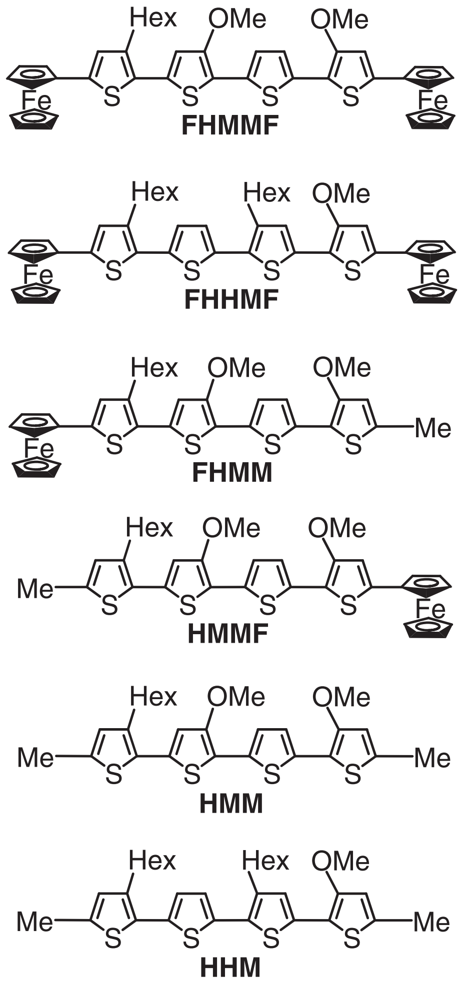

Chart 1. Unsymmetrically substituted quaterthiophene derivatives.

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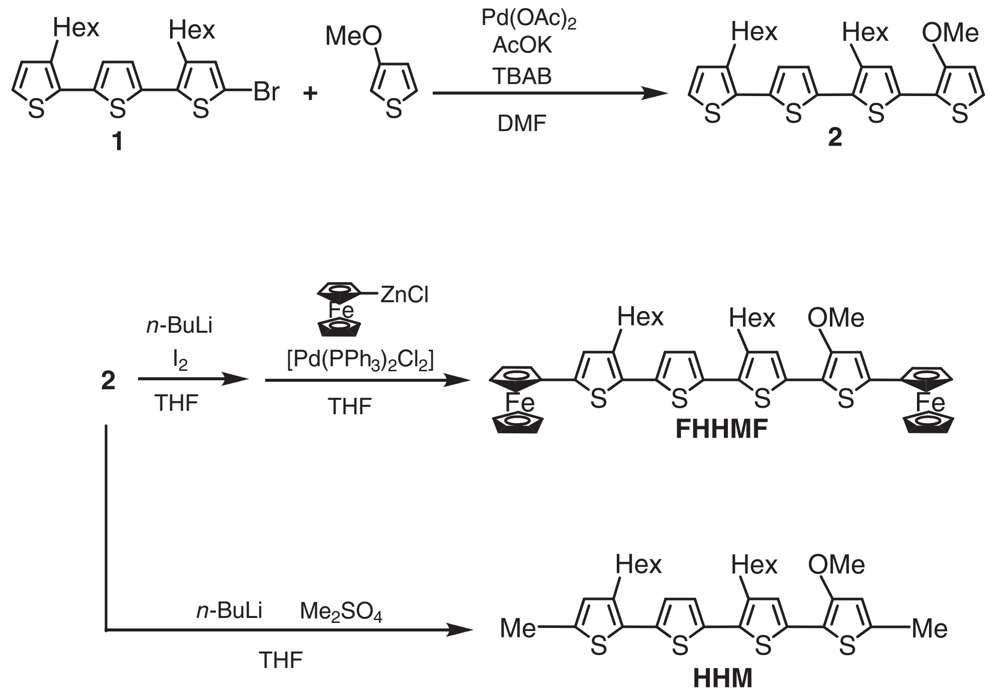

Scheme 1. Synthesis of **FHHMF** and **HHM**.

Results and Discussion

Preparation. **FHMMF**, **FHMM**, **HMMF**, and **HMM** were prepared using methods reported in the Supporting Information of Ref.[11] The synthetic routes for **FHHMF** and **HHM** are depicted in Scheme 1. The precursor of **FHHMF** and **HHM**, the dihexylmethoxyquaterthiophenes **2**, was prepared by coupling of bromodihexylterthiophene **1** with methoxythiophene under Heck-type experimental conditions.[12] Then, the obtained quaterthiophene **2** was lithiated with *n*-butyllithium at the free α-positions, and the lithiated compound was subjected to reaction with iodine. The resulting iodide was not stable enough to be purified by chromatography, and thus the crude iodide was used for Negishi coupling with ferrocenylzinc chloride to yield desired **FHHMF**. Both end-capping of **2** with methyl groups was accomplished with *n*-butyllithium followed by dimethyl sulfate to gain **HHM**.

Electrochemistry. Oxidation of the quaterthiophene derivatives was investigated by cyclic voltammetry, square wave voltammetry, and controlled potential coulometry. The 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 and the square wave voltammograms, the potentials were swept at rates of 100 and 60 mV s^{-1}, respectively.

The electrochemical data, the oxidation potentials (E_{ox}s) and the coulometric *n*-values (n_{a}s), are summarized in Table 1. The cyclic voltammograms of ferrocene and the dimethylquaterthiophenes **HMM** and **HHM** revealed one and two reversible redox waves, respectively. The dimethylquaterthiophenes formed successively cation radicals and then dications in this measurement range, as reported for long oligothiophenes.[13–17] The cyclic voltammograms of the monoferrocenylquaterthiophenes **FHMM** and **HMMF** and one diferrocenylquaterthiophene **FHHMF** showed three reversible redox waves, whereas the other diferrocenylquaterthiophene **FHMMF** gave four redox waves, shown in Figure 1.

Table 1. Electrochemical Data of Ferrocene and Quaterthiophene Derivatives

Compound	E^{1}_{ox} a) /V	n^{1}_{a} b) /F mol^{-1}	E^{2}_{ox} a) /V	n^{2}_{a} b) /F mol^{-1}	E^{3}_{ox} a) /V	E^{4}_{ox} a) /V
Ferrocene	0.00	1.0	—	—	—	—
FHMMF	−0.05	— c)	0.05	2.3	0.27	0.59
FHHMF	0.01	2.2	0.40	—	0.66	—
FHMM	−0.01	1.2	0.14	2.2	0.47	—
HMMF	−0.05	1.1	0.14	2.2	0.54	—
HMM	0.06	—	0.38	—	—	—
HHM	0.21	—	0.48	—	—	—

a) E^{n}_{ox}s are the *n*-th oxidation potentials. b) n^{1}_{a} and n^{2}_{a} are coulometric *n*-values for the first and second oxidation, respectively. c) The value is uncertain on account of overlapping of waves.

The E_{ox} of ferrocene was 0.00 V and lower than the first of the dimethylquaterthiophenes (0.06 V for **HMM** and 0.21 V for **HHM**), indicating that in the ferrocenylquaterthiophenes the ferrocene moieties are more oxidizable than the quaterthiophene moieties. In the diferrocenylquaterthiophenes, the n_{a}s up to the second oxidation of **FHMMF** and up to the first oxidation of **FHHMF** were 2.3 and 2.2 F mol^{-1} (two-electron oxidation), respectively. These results demonstrate that the two lower redox waves of **FHMMF** (E_{ox}s $= -0.05$ and 0.05 V) and the lowest redox wave of **FHHMF** (E_{ox}s $= 0.01$ V) are assignable to the oxidation of the two ferrocene moieties, and the remaining two higher waves to the oxidation of the quaterthiophene moieties. Splitting of the redox waves for the

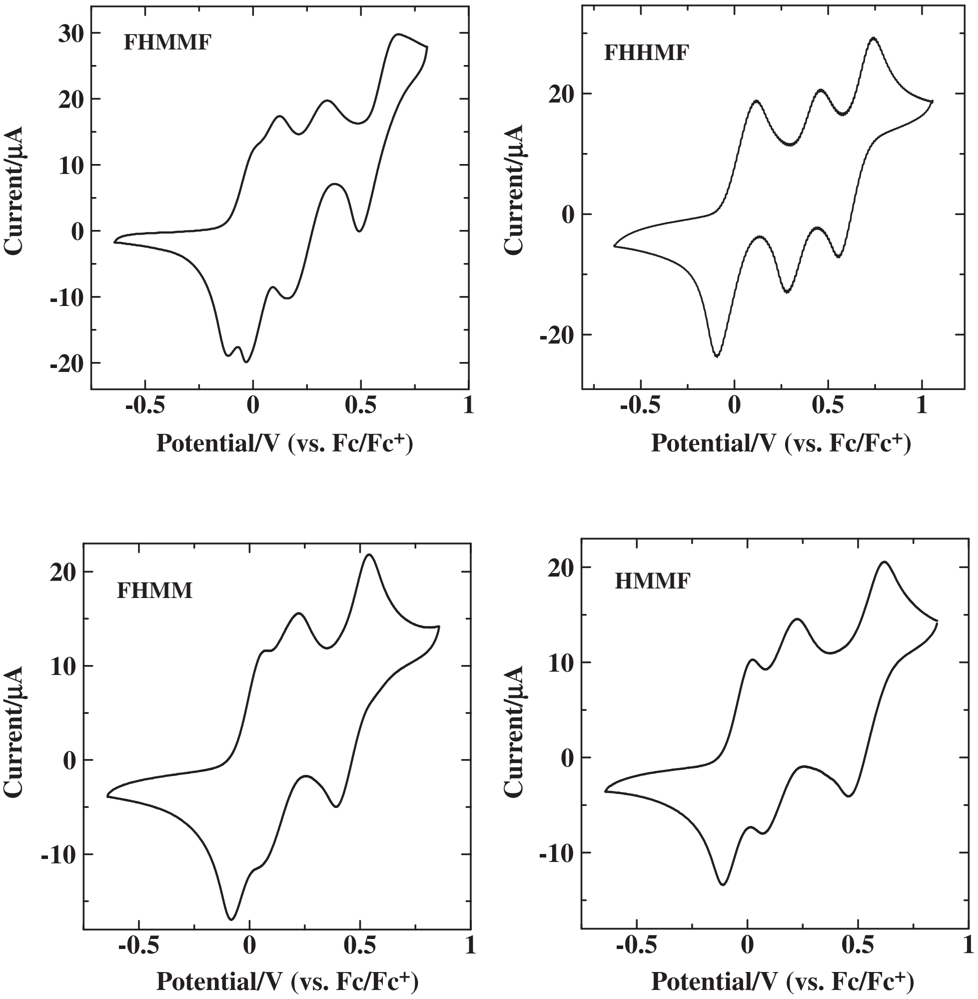

Figure 1. Cyclic voltammograms of ferrocenylquaterthiophenes.

ferrocene moieties was observed for **FHMMF** while no splitting was observed for **FHHMF**. The splitting is a consequence of the different chemical structure of the linking moieties between the two ferrocene moieties, the quaterthiophene moieties.

Figure 2 displays the square wave voltammograms of **FHMMF**, **FHMM**, and **HMMF** in the voltage range from −0.20 to 0.20 V. Waves attributable to the oxidation of the ferrocene moieties in **FHMM** and **HMMF** were observed at −0.01 and −0.05 V, respectively. Both the peak potentials are shifted from the E_{ox} of ferrocene, 0.00 V, and the degrees of the shifts are apparently different. This demonstrates that the intensity of the interaction between the two neighboring moieties, the ferrocene moiety and the quaterthiophene moiety, would depend on the linked position of the ferrocenyl group on the unsymmetric quaterthiophene moiety; the α-position of the end hexylthiophene ring for **FHMM** and the α-position of the end methoxythiophene ring for **HMMF**. The voltammogram of **FHMMF** shows two waves at −0.05 and 0.05 V assignable to the oxidations of the two ferrocene moieties. The peak potential of the one wave (at −0.05 V) agrees with that of the wave due to the ferrocene moiety in **HMMF**, however, the peak potential of the other (at 0.05 V) is clearly higher than that of the wave due to the ferrocene moiety in **FHMM** (at −0.01 V). That is, the two peak potentials, the E_{ox}s, of the ferrocene moieties in **FHMMF** are not completely consistent with the combination of the peak potentials, the E_{ox}s, of the ferrocene moieties in **FHMM** and

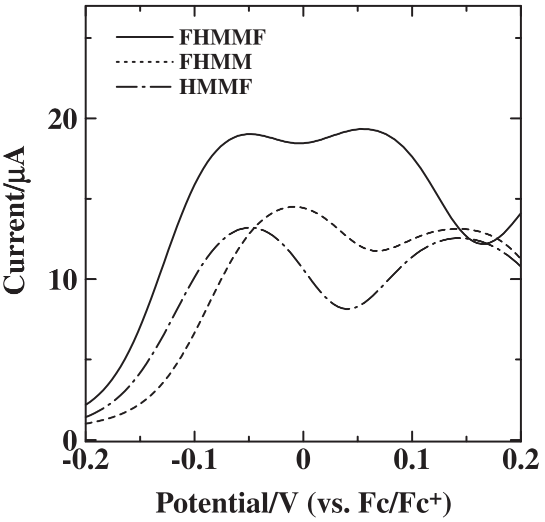

Figure 2. Square wave voltammograms of **FHMMF**, **FHMM**, and **HMMF**.

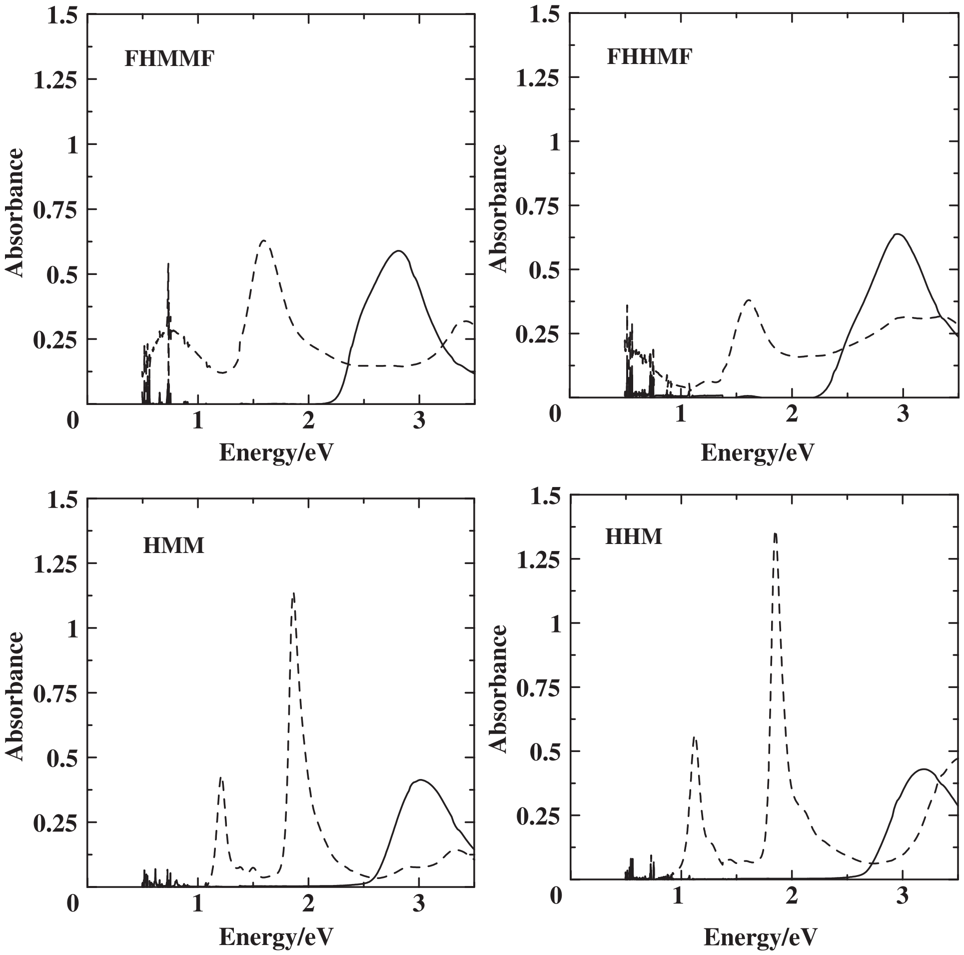

Figure 3. Electronic absorption spectra of diferrocenylquaterthiophenes and dimethylquaterthiophenes: neutral (solid line) and chemically one-electron-oxidized (dashed line).

HMMF. The inconsistence of the potentials leads us to infer that the two terminal ferrocenyl groups in **FHMMF** interact with each other. Further, the agreement of the first E_{ox} of the ferrocene moiety in **FHMMF** and the E_{ox} of the ferrocene moiety in **HMMF** implies that the one-electron oxidation of **FHMMF** occurs at one ferrocene moiety that is linked to the α-position of the end methoxythiophene ring and the interaction between the ferrocene moieties in **FHMMF** does not take place in the neutral state but in the one-electron-oxidized state.

Electronic Absorption Spectroscopy. Electronic absorption spectra analysis was performed for ferrocene, the dimethylquaterthiophenes **HMM** and **HHM**, and the diferrocenyls **FHHMF** and **FHMMF** to elucidate the one-electron-oxidized state. Chemical oxidation was achieved by stoichiometric addition of $FeCl_3$ to a dichloromethane solution containing 2.8×10^{-5} M of each compound. The electronic absorption spectra of neutral and one-electron-oxidized ferrocene demonstrated no distinct band because of their small optical densities. Figure 3 shows the electronic absorption spectra of the dimethyls and the diferrocenyls. Each quaterthiophene derivative in a neutral state has one strong π–π^* transition band and the energies of the band maxima for the diferrocenyls are lower than those for the corresponding dimethyls by about 0.2 eV (**HMM**; 3.00 eV, **HHM**; 3.09 eV, **FHMMF**; 2.80 eV, and **FHHMF**; 2.95 eV). These band shifts indicate that the ferrocenyls possess longer effective conjugation lengths by the interaction between the quaterthiophene and the ferrocene moieties in a neutral state. The one-electron oxidation of the dimethyls resulted in the remarkable decrease of the π–π^* transition bands and the appearance of the two strong absorption bands below 2.0 eV (**HMM**; 1.86 and 1.21 eV, and **HHM**; 1.85 and 1.13 eV). These spectral changes during one-electron oxidation resemble those of previously reported oligothiophenes with a relatively less conjugated system, e.g., ter-, quater-, and quinquethiophenes.[14–16] When the diferrocenyls are one-electron oxidized, the π–π^* transition bands decrease and two broad absorption bands appear below 2.0 eV (**FHMMF**; 1.6 and 0.7 eV, and **FHHMF**; 1.6 and less than 0.6 eV). The absorption patterns are similar to those of one-electron-oxidized oligothiophenes with a more conjugated system, and even poly(3-alkylthiophenes) oxidized in solution.[16,17] The spectral changes of previously reported oligothiophenes and poly(3-alkylthiophenes) have been interpreted by the generation of a cation radical (polaron). Therefore, these results lead us to confirm that one-electron-oxidizing species, such as a cation radical, is present in the quaterthiophene moieties of not only the dimethyls synthesized in this paper but the diferrocenyls. In previous reports,[16,17] it has been shown that the greater the conjugation of the oligothiophenes, the broader the additional absorption peaks observed in one-electron oxidation. On the basis of this, observation of the broader additional bands of the one-electron-oxidized diferrocenyls in this paper imply that the oxidizing species are not localized in the quaterthiophene moieties but spread in the more conjugation systems, consisting of the ferrocene and the quaterthiophene moieties. In addition, the two additional bands of one-electron-oxidized **FHHMF** are apparently weaker than those of **FHMMF** and the π–π^* transition band of **FHHMF** slightly remains in one-electron oxidation, suggesting that the extent of the oxidizing species in the quaterthiophene moiety would be limited and/or the intensity of the species lower.

Thus, assuming that a similar oxidation state occurs by both electrochemical and chemical oxidation, we can say that the interaction between the terminal ferrocene moieties for one-electron-oxidized **FHMMF** is mediated by the oxidizing species of the quaterthiophene moiety, and then the extent and/or the intensity of the oxidizing species in the quaterthiophene moiety is important for the interaction.

Conclusion

We prepared unsymmetrically substituted quaterthiophenes with two terminal ferrocenyl groups, **FHMMF** and **FHHMF**, as long π-conjugated systems. Their electrochemical and optical properties were compared with those of a series of quaterthiophenes with one or no terminal ferrocenyl group. One-electron-oxidized **FHMMF** shows the interaction between the terminal ferrocene moieties, whereas such interaction for **FHHMF** was not observed. The interaction could be mediated by the linking quaterthiophene moiety and affected by the extent and/or the intensity of the oxidizing species generated in the quaterthiophene moiety. Because of the unsymmetrical substitution in **FHMMF**, the one-electron oxidation of **FHMMF** would occur at one ferrocene moiety attached to the end methoxythiophene ring. This paper shows that adequate substitution for π-conjugated systems enables control of the oxidation state and process.

Experimental

General. Ferrocenylzinc chloride, 3-methoxythiophene, 5-bromo-3,3″-dihexyl-2,2′:5′,2″-terthiophene (**1**), **FHMMF**, **FHMM**, **HMMF**, and **HMM** were synthesized according to previously reported methods.[5,11,13,18,19] Ether and tetrahydrofuran (THF) were distilled under nitrogen over $LiAlH_4$ and calcium hydride, respectively. *N*-Methylpyrrolidone (NMP) was dried over 4A molecular sieves and distilled under reduced pressure.

^{1}H NMR experiments were performed using VARIAN UNITY400 spectrometers 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. The electrochemical properties were measured by cyclic voltammetry (CV), square wave voltammetry (SWV), and controlled potential coulometry (CPC), using a three-electrode one-component cell equipped with a platinum working electrode ($S = 0.024\,cm^2$) and platinum counter-electrode for CV and SWV, and a three-electrode two-component cell equipped with a platinum gauge working electrode and platinum counter-electrode for CPC. A Ag/Ag^+ reference electrode was used and the measurements were referenced against ferrocenium/ferrocene (Fc^+/Fc) as the internal standard. The spectroscopic and electrochemical methods have been previously reported as well.[20]

3,3″-Dihexyl-3‴-methoxy-2,2′:5′,2″:5″,2‴-quaterthiophene (2). A flask was charged with **1** (1.50 g, 3.03 mmol), 3-methoxythiophene (350 mg, 3.03 mmol), tetrabutylammonium bromide (980 mg, 3.03 mmol), potassium acetate (1.78 g, 18.2 mmol), palladium(II) acetate (68.0 mg, 0.303 mmol), and DMF (20 mL). The reaction mixture was heated to 80 °C under nitrogen and stirred for 1 h. The resulting mixture was allowed to cool to room temperature, and then quenched with water. The aqueous solution was extracted with CH_2Cl_2. The organic extract was washed with brine and dried over $MgSO_4$. The solvent was removed by rotary evaporation. The residue was purified with flash chromatography on silica gel (benzene/hexane) to provide 1.10 g (69%) of the title product as viscous red-orange oil.

IR (thin layer): 3107, 3064, 2927, 2854, 1460, 1387, 1254, 1070, 928, 829, 712 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.88 (t, $J = 5.8$ Hz, 6H), 1.30–1.39 (m, 12H), 1.61–1.68 (m, 4H), 2.76 (t, $J = 9.1$ Hz, 2H), 2.78 (t, $J = 9.1$ Hz, 2H), 3.95 (s, 3H), 6.86 (d, $J = 5.7$ Hz, 1H), 6.93 (d, $J = 5.0$ Hz, 1H), 7.04–7.07 (m, 4H), 7.15 (d, $J = 5.0$ Hz, 1H); Anal. Calcd for $C_{29}H_{36}OS_4$: C, 65.86; H, 6.86%. Found: C, 65.91; H, 7.07%.

5,5‴-Diferrocenyl-3,3″-dihexyl-3‴-methoxy-2,2′:5′,2″:5″,2‴-quaterthiophene (FHHMF). To a solution of **2** (300 mg, 0.567 mmol) in THF (30.0 mL) was added dropwise *n*-butyllithium (1.44 mL, 2.30 mmol, 1.6 M in hexane) at −78 °C. The reaction mixture was stirred at 0 °C for 40 min before being cooled back to −78 °C. To that solution, iodine (583 mg, 2.30 mmol) in THF (5.0 mL) was added dropwise and stirred at room temperature for 30 min. The mixture and dichlorobis(triphenylphosphine)palladium(II) (150 mg, 0.214 mmol) was added to a solution of ferrocenylzinc chloride [prepared from ferrocene (1.07 g, 5.75 mmol), *t*-butyllithium (3.99 mL, 6.34 mmol, 1.59 M in pentane), and zinc chloride (862 mg, 6.33 mmol) in THF (30.0 mL)][5] at 0 °C. The resulting black mixture was gradually warmed to room temperature and then refluxed for 2 h before being poured into 2 M hydrochloric acid. The aqueous layer was extracted with benzene. The organic extract was washed with a sodium thiosulfate solution, brine and dried over $MgSO_4$. The solvent was removed by rotary evaporation. The residue was treated with flash chromatography on silica gel (benzene/hexane) and recrystallized from a mixture of benzene/hexane to provide 120 mg (23.4%) of the title product as red crystals. Mp 186.0–187.5 °C. IR (KBr): 3083, 2925, 2852, 1568, 1458, 1381, 1221, 1092, 1026, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.90 (m, 6H), 1.26–1.42 (m, 12H), 1.68 (m, 4H), 2.78 (m, 4H), 3.99 (s, 3H), 4.13 (s, 5H), 4.14 (s, 5H), 4.29 (m, 2H), 4.32 (m, 2H), 4.56 (m, 2H), 4.58 (m, 2H), 6.78 (s, 1H), 6.84 (s, 1H), 7.01 (s, 1H), 7.06 (d, $J = 3.5$ Hz, 1H), 7.07 (d, $J = 3.5$ Hz, 1H); Anal. Calcd for $C_{49}H_{52}Fe_2OS_4$: C, 65.61; H, 5.84%. Found: C, 65.53; H, 5.70%.

3,3″-Dihexyl-3‴-methoxy-5,5‴-dimethyl-2,2′:5′,2″:5″,2‴-quaterthiophene (HHM). To a solution of **2** (200 mg, 0.378 mmol) in THF (30 mL) at −78 °C was added dropwise *n*-butyllithium (0.96 mL, 1.53 mmol, 1.6 M in hexane). The reaction mixture was warmed to 0 °C and kept stirring for 1 h before being recooled back to −78 °C, and dimethyl sulfate (193 mg, 1.53 mmol) was added. The mixture was stirred overnight at room temperature, and then poured into water. The aqueous layer was extracted with benzene two times, and the combined organic layer was dried over $MgSO_4$. the solvent was removed by rotary evaporation, and then the residue was purified by flash chromatography on silica gel with a graduated solvent of hexane–benzene to yield 180 mg (85.9%) of the title product as viscous red-orange oil. IR (KBr): 3064, 2925, 2854, 1726, 1572, 1460, 1379, 1219, 1092, 931 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.89 (t, $J = 6.3$ Hz, 6H), 1.31–1.40 (m, 12H), 1.59–1.68 (m, 4H), 2.42 (s, 3H), 2.43 (s, 3H), 2.71 (t, $J = 7.6$ Hz, 2H), 2.75 (t, $J = 7.9$ Hz, 2H), 3.90 (s, 3H), 6.56 (s, 1H), 6.59 (s, 1H), 6.94 (s, 1H), 6.98 (d, $J = 3.8$ Hz, 1H), 7.03 (d, $J = 3.8$ Hz, 1H); Anal. Calcd for $C_{31}H_{40}OS_4$: C, 66.85; H, 7.24%. Found: C, 66.56; H, 7.38%.

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