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Selected Paper

One-Electron-Oxidized States of Dihedral-Angle-Controlled 2,2′-Bithiophenes with Terminal Ferrocenyl Groups

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Dihedral-angle-controlled 2,2′-bithiophenes with terminal ferrocenyl groups were designed and prepared as long π-conjugated systems. Electrochemical and spectroscopic studies were carried out to evaluate the one-electron-oxidized states of the diferrocenyl derivatives and the interaction between the two terminals. Oxidized diferrocenyl derivatives comprising a more flat bithiophene moiety showed electronic communication between both the terminal ferrocenyl moieties, while an oxidized diferrocenyl derivative comprising a distinctly twisted bithiophene moiety would exhibit only electrostatic communication (with no electronic communication). These results indicated that the interaction between the terminal ferrocene moieties is strongly affected by the twist in the π-conjugated system.

Organic materials with π-conjugated systems have attracted considerable attention because the π-conjugated materials exhibit interesting properties such as electric conductivity, electrochromism, optical nonlinearity, and so on. Among the π-conjugated materials, oligothiophene and its derivatives have been extensively studied due to excellent environmental stability in both neutral and oxidized states.[1] Furthermore, it clarifies the function of the π-conjugated systems in detail to introduce redox centers, such as ferrocene,[2] at termini of the systems. Some papers have reported the preparation and properties of multiple ferrocenyloligothiophenes and investigated the interaction, the electronic or electrostatic communication, between the terminal ferrocene groups.[3–13] The interaction has been reported to decay with increasing metal–metal distance.[3,13,14] We synthesized diferrocenyl-dimethoxyterthiophene[5] and diferrocenyldihexylterthiophene.[15] The comparison of their redox processes showed that the interaction between the terminal ferrocenyl groups is intensively affected by substituents on the π-conjugated system.[16] In addition, the torsion of the π-conjugated systems in differocenyl oligothiophenes would also influence the interaction. We reported the preparation and fundamental properties of dihedral-angle-controlled 2,2′-bithiophenes with terminal ferrocenyl groups, 4,4-diethyl-2,6-diferrocenylcyclopenta[2,1-*b*:3,4-*b*′]dithiophene (C1FF) and 2,9-diferrocenylcycloocta(2,1-b:3,4-b′)dithiophene (C4FF) in a preliminary paper[17] (Chart 1).

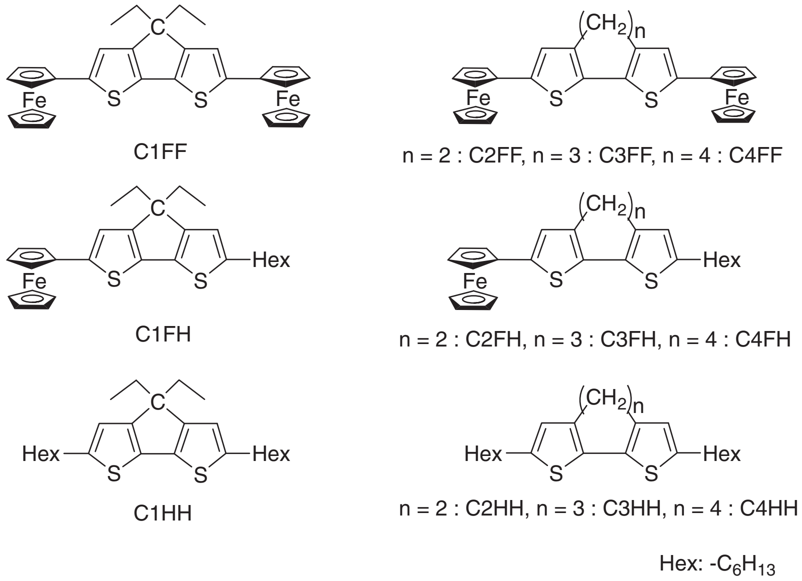
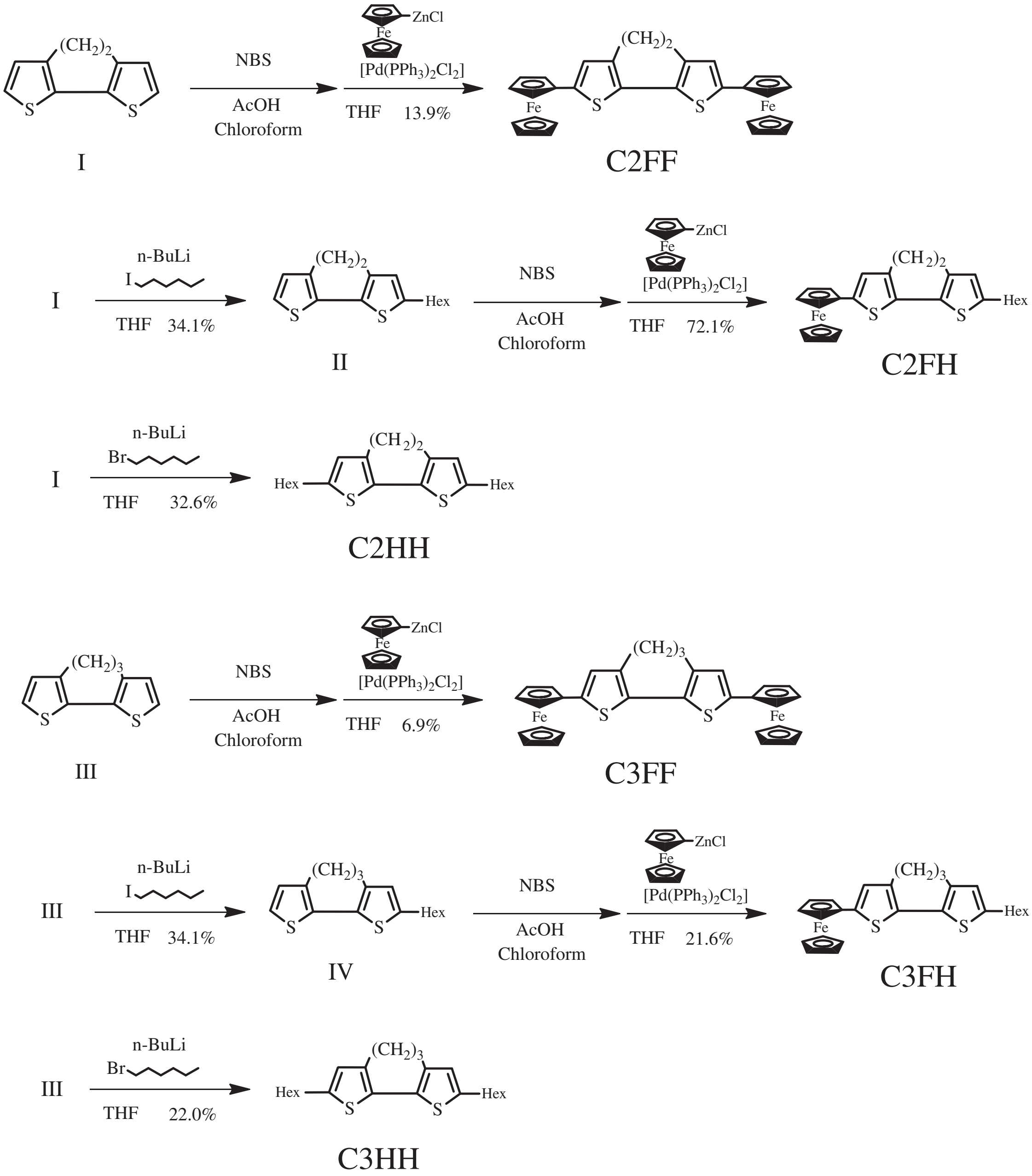


Chart 1. Dihedral-angle-controlled 2,2′-bithiophene derivatives.

In this paper, novel dihedral-angle-controlled 2,2′-bithiophenes with terminal ferrocenyl groups, 2,7-diferrocenylcyclohexa[2,1-*b*:3,4-*b*′]dithiophene (C2FF) and 2,8-diferrocenylcyclohepta[2,1-*b*:3,4-*b*′]dithiophene (C3FF) were prepared, and their electrochemical and optical properties were examined (Chart 1). The 2,2′-bithiophene moiety in C1FF is linked with a methylene bridge between 3- and 3′-carbons, being almost planer, whereas the moiety in C2FF, C3FF, and C4FF is bridged with α,ω-alkane, deviating from planarity. In addition to the diferrocenyl derivatives, monoferrocenyl derivatives; 4,4-diethyl-2-ferrocenyl-6-hexylcyclopenta[2,1-*b*:3,4-*b*′]dithiophene (C1FH), 2-ferrocenyl-7-hexylcyclohexa[2,1-*b*:3,4-*b*′]-dithiophene (C2FH), 2-ferrocenyl-8-hexylcyclohepta[2,1-*b*:3,4-*b*′]dithiophene (C3FH), and 2-ferrocenyl-9-hexylcycloocta[2,1-*b*:3,4-*b*′]dithiophene (C4FH), and non-ferrocenyl derivatives; 4,4-diethyl-2,6-dihexylcyclopenta[2,1-*b*:3,4-*b*′]-dithiophene (C1HH), 2,7-dihexylcyclohexa[2,1-*b*:3,4-*b*′]dithiophene (C2HH), 2,8-dihexylcyclohepta[2,1-*b*:3,4-*b*′]dithiophene (C3HH), and 2,9-dihexylcycloocta[2,1-*b*:3,4-*b*′]dithiophene (C4HH), were investigated as reference compounds for detailed discussion (Chart 1).

Results and Discussion

Synthesis and Characterization. The synthesis methods of the series of C1 (C1FF, C1FH, and C1HH) and C4 (C4FF, C4FH, and C4HH) were previously reported in the Supporting Information of Ref. 17. Cyclohexa[2,1-*b*:3,4-*b*′]dithiophene, the bithiophene moiety of the C2 series, and cyclohepta[2,1-*b*:3,4-*b*′]dithiophene, that of the C3 series, were synthesized according to the methods reported by Sannicolb et al.[18] and



Scheme 1. Synthesis of dihedral-angle-controlled bithiophene derivatives.

Table 1. Calculated Dihedral Angles of Diferrocenyl Derivatives

Compound	Angle a)/°
C1FF	0.23
C2FF	12.43
C3FF	7.71
C4FF	50.03

a) The values show the dihedral angles between the thiophene rings.

Table 2. Electrochemical Data of Ferrocene and Dihedral-Angle-Controlled 2,2′-Bithiophene Derivatives

Compound	E^{1}_{ox} a) /V	n^{1}_{ox} b) /F mol^{-1}	E^{2}_{ox} a) /V	n^{2}_{ox} b) /F mol^{-1}	ΔE c) /V	K_{c} d)
Ferrocene	0.00	1.1	—	—	—	—
C1FF	−0.08	1.2	0.09	1.2	0.17	750
C1FH	−0.04	1.2	—	—	—	—
C1HH	0.36	—	—	—	—	—
C2FF	−0.05	1.1	0.10	1.2	0.15	510
C2FH	−0.03	1.2	—	—	—	—
C2HH	0.41	—	—	—	—	—
C3FF	−0.05	1.1	0.08	0.9	0.13	110
C3FH	−0.01	1.2	—	—	—	—
C3HH	0.49	—	—	—	—	—
C4FF	0.00 e)	—	0.08 e)	2.4	0.08	22
C4FH	0.00	1.1	—	—	—	—
C4HH	0.66	—	—	—	—	—

a) E^{n}_{ox}'s are n-th oxidization potentials. b) n^{n}_{ox}'s are coulometric n-value for the n-th oxidization. c) ΔE's are potential differences between the two ferrocenyl-related oxidization processes ($E^{2}_{\mathrm{ox}} - E^{1}_{\mathrm{ox}}$). d) Comproportionation constants. e) Each value was obtained by curve-fitting.

Zimmer et al.,[19] respectively. The obtained cycloalkadithiophenes were converted to the final products analogously to the syntheses of ferrocenyl- or hexyloligothiophenes[20] (Scheme 1). Cyclohexa[2,1-*b*:3,4-*b*′]dithiophenyl and cyclohepta[2,1-*b*:3,4-*b*′]dithiophenyl bromides were extremely unstable, thus used in the next step reaction, ferrocenylation, without complete purification. The yields of the ferrocenylation in the C2 and C3 series were different from each other depending on the stabilities of the corresponding bromides. The molecular conformations of the diferrocenyl derivatives were calculated using Gaussian 09.[21] Geometry optimization was performed using B3LYP/6-31G(d) integrated the polarizable continuum model, which was assumed for dichloromethane. The dihedral angles between the thiophene rings in the obtained calculation results are summarized in Table 1, and the optimized structures are described in Supporting Information. The π-conjugated system of the bithiophene moiety in C1FF has an almost flat conformation; the dihedral angle between the thiophene rings is 0.23°, those in C2FF and C3FF have slightly twisted conformations; the dihedral angles are about 10°, and that in C4FF has a distinctly twisted conformation; the dihedral angle is 50.03°. The longer alkylene bridging group possesses a higher degree of freedom of the conformation. Consequently, one can expect that the dihedral angle between the thiophene rings increases with the number of carbon atoms in the alkylene bridging group in the diferrocenyl derivatives. In the present calculation results, the relation of between C2FF and C3FF runs counter to the prediction. The conformation shown by the calculation is the most stable conformation. Taking account of the variation in the conformation, the most stable conformation is not necessary the statistically average conformation of the respective molecule. In the above discussions, we should recognize that the dihedral angle between the thiophene rings roughly increases with the length of the bridging alkylene group in diferrocenyl derivatives, and the dihedral angle in C4FF is considerable.

Electrochemistry. Oxidation of the series of Cn and ferrocene 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}) and the Coulometric n-values (n_{ox}), are summarized in Table 2.

Ferrocene and the dihexyl derivatives (C1HH, C2HH, C3HH, and C4HH) have one E_{ox} at 0.00 V and at remarkably high potentials from 0.36 to 0.66 V in electrolysis windows, respectively. When the cyclic voltammograms of the Cn series were applied more positive than ca. 0.5 V, the voltammograms showed irreversible processes, probably attributable to the decomposition and/or reaction of the substances. In the ferrocenyl derivatives, the ferrocene moieties would be more readily oxidizable than the bithiophene moieties. The ferrocenyl derivatives have one E_{ox} or two E_{ox}'s, the potentials being around 0.0 V. In addition, each total n_{ox} for their oxidation agrees with the number of terminal ferrocene moiety; ca. 1 F mol^{-1} for the monoferrocenyl derivatives and ca. 2 F mol^{-1} for the diferrocenyl derivatives. These results imply that the observable and reversible oxidation waves in the mono- and diferrocenyl derivatives are assigned to the oxidation of ferrocenyl moieties.

C1FF, C2FF, and C3FF in the diferrocenyl derivatives revealed two redox waves due to the terminal ferrocenyl moieties (Figure 1). The oxidation waves of C4FF were apparently observed as only one wave, however, the peak separation using the curve fitting for the wave revealed two peaks at 0.00 and 0.08 V, which correspond to each E_{ox} of two terminal ferrocene moieties (Figure 1). On the other hand, the same procedure for the oxidation waves of the monoferrocenyl derivatives, dihexyl derivatives and ferrocene show no peak separation. The oxidation of the two terminal ferrocene moieties in all the diferrocenyl derivatives shows two-stepwise process and the redox splittings are interpreted in terms of the interaction between the terminal ferrocene moieties in the oxidation. The redox splittings for C1FF, C2FF, and C3FF are obvious ($\Delta E = E^{1} - E^{2}$, ≥ 0.15 V), while the splitting for C4FF is smaller ($\Delta E < 0.10$ V). From the separated potential values (ΔE), the comproportionation constants (K_{c}) were determined using the formula $RT(\ln K_{\mathrm{c}}) = \Delta EF$, shown in Table 2.[22] According to Robin–Day classification for mixed-valence compounds such as diferrocenyl compounds, the K_{c}'s indicate that C1FF, C2FF, and C3FF are Class II, those in

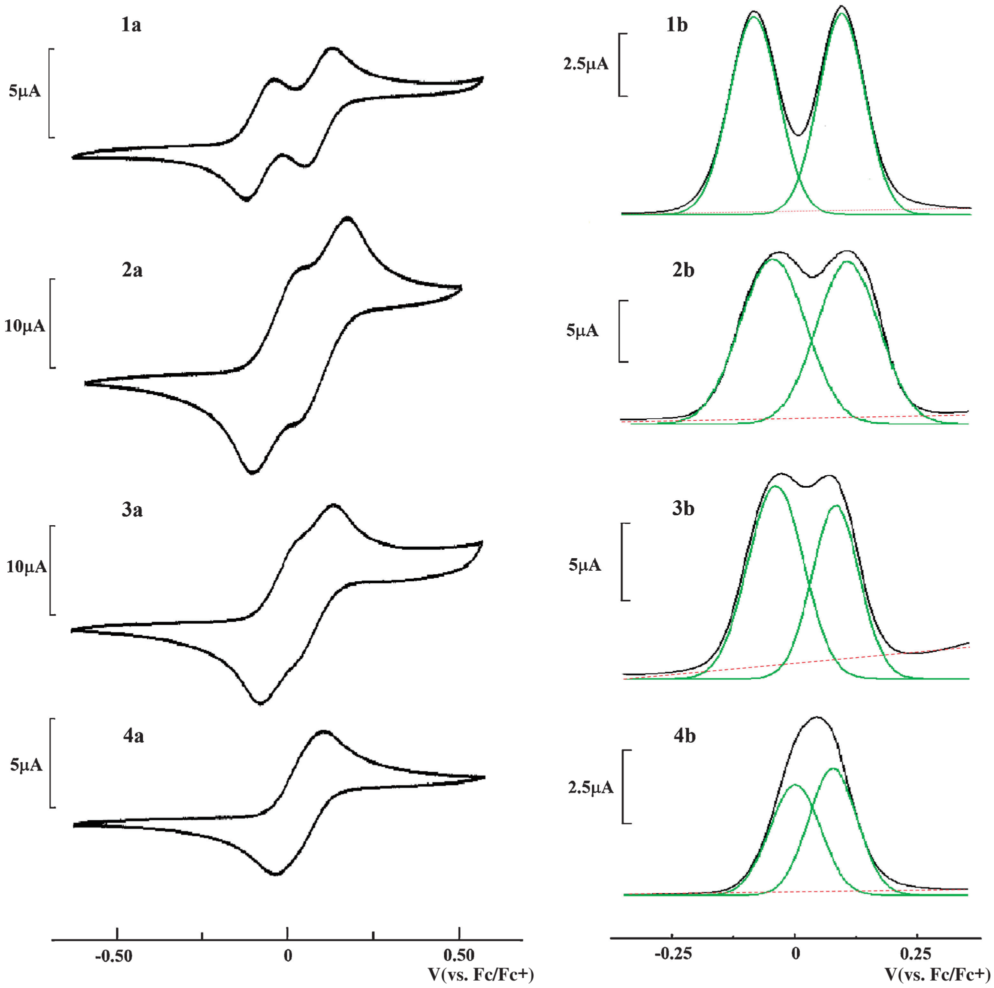


Figure 1. Cyclic voltammograms (left: a) and square wave voltammograms (right: b) of C1FF (1a, 1b), C2FF (2a, 2b), C3FF (3a, 3b), and C4FF (4a, 4b). The baselines represented as red dotted lines would be attributable to the oxidation or decomposition of water as an impurity. The waves at higher potentials were ascertained in blank tests. The green lines denote the Gaussian fit of the square wave voltammograms.

which the charge is partially delocalized between the ferrocene moieties, and C4FF is Class I, that in which the charge is localized on one of two ferrocene moieties.[23,24]

The first E_{ox}'s of the ferrocenyl derivatives of the C4 series (C4FH and C4FF) are 0.00 V, the same as that of ferrocene ($E_{ox} = 0.00$ V). In contrast, the first E_{ox}'s of the ferrocenyl derivatives of the C1, C2, and C3 series are negative, less than ferrocene. Each E_{ox} of C1FF, C2FF, and C3FF is significantly less than that of the monoferrocenyl derivative in the same series and then the E_{ox} in the ferrocenyl derivatives shows an increasing trend with the length of the alkylene bridging groups, C1 < C2 ≤ C3. Considering the strong relationship between the electronic structure and the E_{ox}, these results indicate that the ferrocene moieties in the ferrocenyl derivatives of C4 series are electronically independent or have negligible interaction with the other moieties in the first one-electron oxidation, from the neutral state to the one-electron-oxidized state, while the ferrocene moieties in those of the C1, C2, and C3 series definitely electronically interact with the adjacent bithiophene moieties, and then the ferrocene moieties of C1FF, C2FF, and C3FF are done with the other ferrocene moieties. These observations support the conclusion that C4FF is Class I, while C1FF, C2FF, and C3FF are Class II, as mentioned in the last paragraph. Additionally, the interaction in C1FF, which shows the smallest dihedral angle between the thiophene rings, is highest in the diferrocenyl derivatives and the interaction in C4FF, having a distinct dihedral angle, is none or negligible in the first one-electron oxidation.

Electronic Absorption Spectroscopy. Electronic absorption spectra analysis was performed for the Cn series and ferrocene to elucidate neutral and one-electron-oxidized states. Chemical oxidation was achieved by stoichiometric addition of $FeCl_3$ to the 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. Neutral C1HH, C2HH, C3HH, and C4HH have a π–π* transition band at 3.7, 3.7, 3.8, and 4.2 eV, respectively (Figure 2). The absorption energy of C4HH is apparently higher than those of C1HH, C2HH, and C3HH, implying that the dihedral angle between the thiophene rings in C4HH would be larger in comparison with those in the other

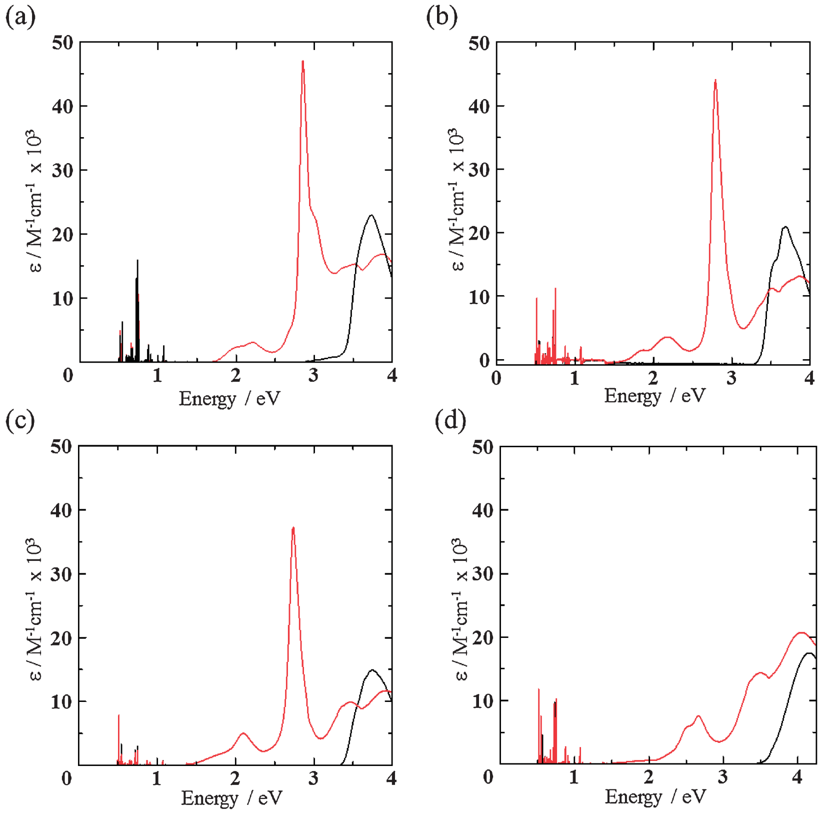


Figure 2. Electronic absorption spectra of neutral and one-electron-oxidized (a) C1HH, (b) C2HH, (c) C3HH, and (d) C4HH; neutral (black line), one-electron-oxidized (red line).

dihexyl derivatives. The spectrum of the each neutral monoferrocenyl derivative shows a strong π–π* transition band at lower energy (3.3 eV for C1FH, 3.3 eV for C2FH, 3.4 eV for C3FH, and 3.8 eV for C4FH) than that of the corresponding dihexyl derivative, and then a d–d* transition band at about 2.7 eV, which is assigned to the ferrocene moiety and is weak due to the forbidden nature (Figure 3). Moreover, the spectrum of the each neutral diferrocenyl derivative exhibits a strong π–π* transition band at further lower energy (3.1 eV for C1FF, 3.1 eV for C2FF, 3.2 eV for C3FF, and 3.5 eV for C4FF) than those of the corresponding dihexyl and monoferrocenyl derivatives, and a d–d* transition band at about 2.7 eV with a higher optical density than the corresponding monoferrocenyl derivative (Figure 4). Theses results suggest that the bithiophene moieties are conjugated with the linking terminal ferrocene moieties in the neutral monoferrocenyl and diferrocenyl derivatives, which have longer effective conjugation lengths than the dihexyl derivatives, the bithiophenes ($n = 2$).

The one-electron oxidation of C1HH, C2HH, and C3HH results in the appearance of a strong and sharp absorption band in the range from 2.5 to 3.0 eV, and then a weak band about 2.0 eV, whereas the oxidation of C4HH results in no strong band, but a weak band about 2.6 eV (Figure 2). The two bands observed in one-electron-oxidized C1HH, C2HH, and C3HH are specific to oxidized oligothiophenes.[20,25–27] Longer oligothiophenes showed the bathochromic shift of the specific two bands, reported in the previous papers.[25,27] For example, the energy of the two bands decreased from 1.9 and 1.2–1.1 eV for one-electron-oxidized quaterthiophene ($n = 4$) to 1.6 and 0.8 eV for one-electron-oxidized sexithiophene ($n = 6$). The bands above 3.0 eV (3.4 and 4.0 eV) would be mainly attributable to iron(III) chloride and related substances, such as iron(II) chloride.

The one-electron oxidation of C4FH and C4FF results in the appearance of two broad, weak bands (at 2.2 and 1.0 eV for C4FH and at 2.1 and 0.8 eV for C4FF) (Figures 3 and 4). Further, the absorption pattern of two-electron-oxidized C4FF is similar to that of one-electron-oxidized one (Figure S2). Given the classification of C4FF (CLASS I), as described in the section of electrochemistry, these two absorption bands above 2.0 and below 1.0 eV are assigned to Cp → $\mathrm{Fe^{III}}$ and bithiophene → $\mathrm{Fe^{III}}$ ligand to metal charge transfer (LMCT) transitions, respectively, as previously reported at similar energies in related compounds.[28] The spectra of the one-electron-oxidized monoferrocenyl derivatives of C1FH, C2FH, and C3FH are similar to those of one-electron-oxidized C4FH, mainly due to LMCT transitions. However, it is different in that they show the sharp absorption about 1.9 eV (below 2.0 eV) and the π–π* transition bands distinctly reduce by one-electron oxidation, implying that oxidized species would spread to the bithiophene moieties from the ferrocene moieties. (Figure 3) When the diferrocenyl derivatives of C1FF, C2FF, and C3FF are one-electron-oxidized, the π–π* transition bands reduce and two absorption bands appear below 3.0 eV: one band with a maximum below 2.0 eV in a wide range from 1.5 to 3.0 eV and the other band below 1.0 eV. The spectra of C1FF, C2FF, and C3FF show a sharp peak or shoulder about 1.6 eV and the bathochromic shift of the band below 1.0 eV in comparison

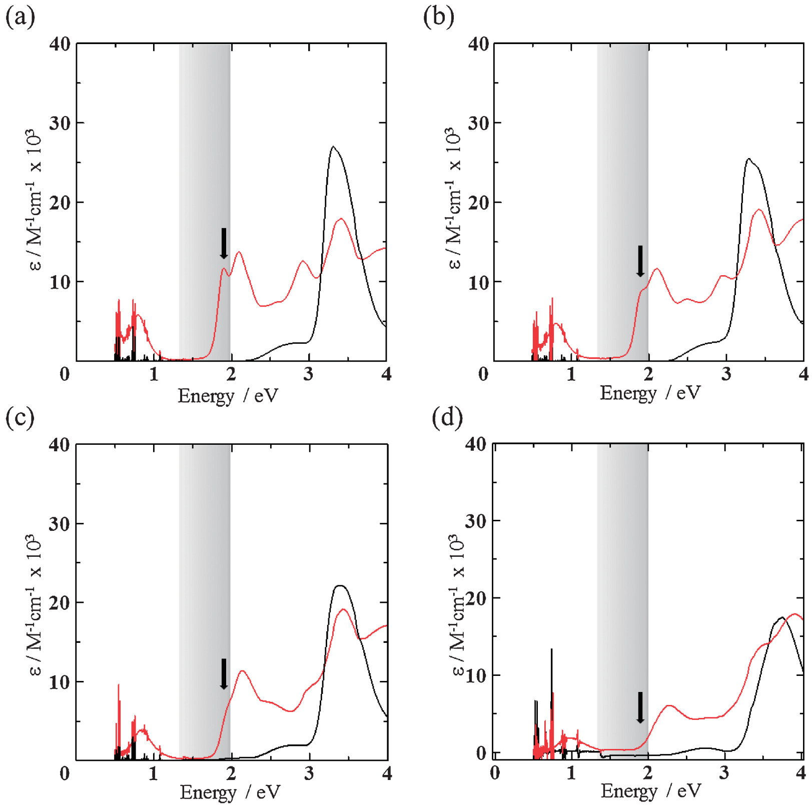


Figure 3. Electronic absorption spectra of neutral and one-electron-oxidized (a) C1FH, (b) C2FH, (c) C3FH, and (d) C4FH; neutral (black line), one-electron-oxidized (red line).

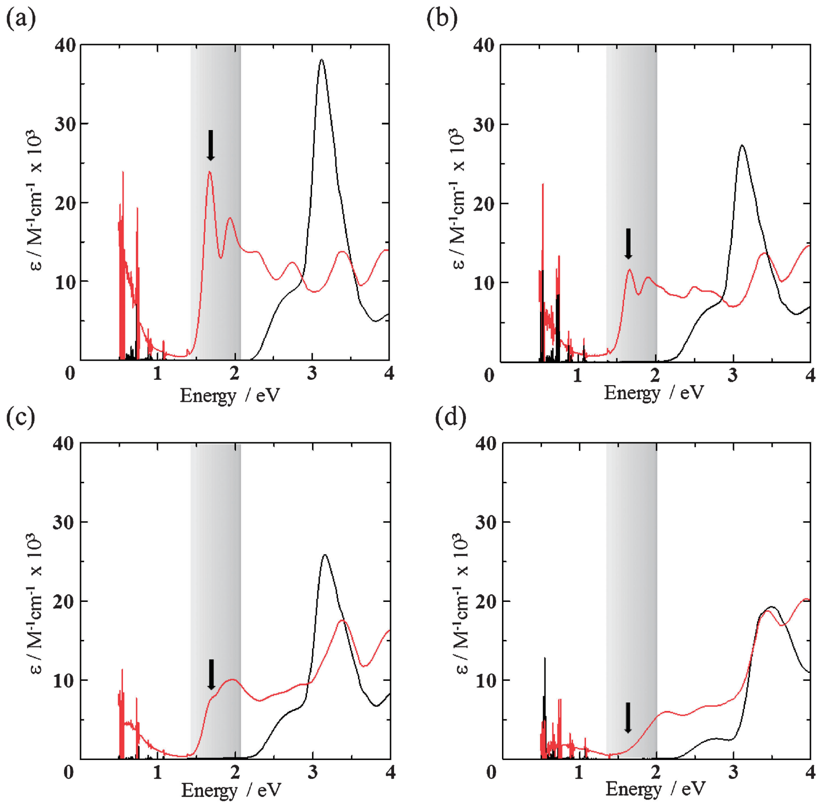


Figure 4. Electronic absorption spectra of neutral and one-electron-oxidized (a) C1FF, (b) C2FF, (c) C3FF, and (d) C4FF; neutral (black line), one-electron-oxidized (red line).

with that of the corresponding monoferrocenyl derivative. Moreover, the sharp absorption peaks observed for one-electron-oxidized C1FF, C2FF, and C3FF disappear in two-electron-oxidized states. (Figure S2) These spectral changes indicate that the oxidizing species would not localized in the ferrocene moieties but spread to the bithiophene moieties in one-electron-oxidized C1FF, C2FF, and C3FF, further the spread of the oxidizing species would be larger than the corresponding monoferrocenyl derivatives. In this research, it is impossible to assign the bands in the near-IR region (below 1.0 eV) to intervalence charge transfer (IVCT) and/or LMCT because of no peak in the limited measuring region.

Conclusion

We designed and prepared dihedral-angle-controlled 2,2′-bithiophenes with terminal ferrocenyl groups, C1FF, and C2FF, C3FF, and C4FF. Their electrochemical and optical properties were compared with those of the bithiophenes with one or no ferrocenyl group. All the one-electron-oxidized diferrocenyl derivatives show the interaction between the terminal ferrocene moieties; C1FF, C2FF, and C3FF belong to Class II, and then C4FF does to Class I in the Robin–Day classification. The first oxidation potentials of the ferrocenyl derivatives reveal that each ferrocene moiety in C1FF, C2FF, and C3FF perturbs not only the adjacent bithiophene moiety but also the other ferrocene moiety. These data lead us to conclude that the terminal ferrocene moieties in C1FF, C2FF, and C3FF would communicate electronically, and then those in C4FF would interact electrostatically. The interaction between the terminal ferrocene moieties is strongest in C1FF, with almost a flat bithiophene moiety, among the diferrocenyl derivatives, CnFF's. The electronic absorption spectra of C4FF and C4FH show two broad and weak absorption bands, which would be attributable to the LMCT transition. On the other hand, those of the diferrocenyl and monoferrocenyl derivatives in the C1, C2, and C3 series indicate the presence of oxidized species in the bithiophene moieties, consistent with the electrochemical results. These results demonstrate the distinct effectiveness of the intramolecular torsion in π-conjugation systems for controlling the charge transfer in the system.

Experimantal

General. ^{1}H NMR experiments were performed using VARIAN UNITY500 (500 MHz) 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. For the measurement of HRMS spectra, a THERMO FISHER SCIENTIFIC LTQ Orbitrap Discovery spectrometer was used. Cyclic voltammograms and chronoamperograms were measured with a BAS 100A electrochemical analyzer. An 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.[5]

Materials. Cyclohexa[2,1-*b*:3,4-*b*′]dithiophene (**I**), cyclohepta[2,1-*b*:3,4-*b*′]dithiophene (**III**), ferrocenylzinc chloride were synthesized according to previously reported methods.[4,18,19] Ether and tetrahydrofuran (THF) were distilled under nitrogen over sodium-benzophenone, respectively. Unless stated otherwise, all reagents were purchased from commercial sources and used without purification.

2-Hexylcyclohexa[2,1-*b*:3,4-*b*′]dithiophene (II). To a solution of **I** (0.235 g, 1.21 mmol) in anhydrous THF (30 mL) was added n-butyllithium (0.960 ml, 1.6M in hexane) under nitrogen in a salt/ice bath. After stirring for 0.5 h, n-hexyl iodide (0.394 g, 1.86 mmol) was added. The mixture was stirred overnight at room temperature. After quenching with water, the mixture was extracted with ether and the extract was washed with water, and dried over $MgSO_4$. The solvent was removed by rotary evaporation. The residue was treated with flash chromatography on silica gel (hexane) to obtain 120 mg (51.1%) of **II** as colorless viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.00 (d, $J = 4.7$ Hz, 1H), 6.88 (d, $J = 4.7$ Hz, 1H), 6.58 (s, 1H), 2.85 (d, $J = 7.7$ Hz, 2H), 2.82 (d, $J = 7.7$ Hz, 2H), 2.75 (t, $J = 7.7$ Hz, 2H), 1.65 (tt, 7.7 and 7.7 Hz, 2H), 1.40–1.28 (m, 6H), 0.89 (t, $J = 6.6$ Hz, 3H). IR (thin layer): ν 3106, 3064, 2999, 2913, 2827, 1286, 883, 711, 673, 626 cm^{-1}.

2,7-Dihexylcyclohexa[2,1-*b*:3,4-*b*′]dithiophene (C2HH). This dihexyl derivative was prepared from **I** in a similar manner as described for the synthesis of **II**. The obtained crude product was purified by flash chromatography on silica gel (hexane) to yield C2HH as colorless viscous oil. (32.6%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.54 (s, 2H), 2.77 (s, 4H), 2.75 (t, $J = 7.5$ Hz, 4H), 1.65 (tt, $J = 7.5$ and 7.5 Hz, 4H), 1.37 (tt, $J = 7.5$ and 7.5 Hz, 4H), 1.32–1.28 (m, 8H), 0.89 (t, $J = 6.9$ Hz, 6H). IR (thin layer): ν 3046, 2954, 2927, 2869, 2854, 1542, 1463, 1436, 1295, 836 cm^{-1}. HRMS-ESI m/z Calcd (MH+): 361.2024 ; Found: 361.2018. Anal. Calcd for $C_{22}H_{32}S_2$: C, 73.27; H, 8.94%. Found: C, 73.16; H, 9.22%.

2-Ferrocenyl-7-hexylcyclohexa[2,1-*b*:3,4-*b*′]dithiophene (C2FH). **II** (0.149 g, 0.410 mmol) was dissolved in a solvent mixture of chloroform and acetic acid (1:1 v/v, 40 mL). To the solution was added NBS (0.073 g, 0.410 mmol) in small portion. The resulting solution was poured into water and extracted with ether. The organic layer was washed with a 10% NaOH aqueous solution and water, dried over $MgSO_4$, and evaporated the solvent to obtain a yellow viscous oil. These procedures were done within 1 h, due to instability of the bromide. The residue was used immediately in the next procedure.

To a solution of ferrocenyllithium (prepared from ferrocene (0.651 g, 3.50 mmol) and *t*-butyllithium (2.33 mL of a 1.65 M pentane solution) in THF (10 mL)) was added a suspension of anhydrous $ZnCl_2$ (0.520 g, 3.85 mmol) 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 dichlorobis(triphenylphosphine)palladium(II) (0.137 g, 0.190 mmol) and then a solution of the crude bromide in THF (15 mL). The mixture was stirred at room temperature overnight and then heated at 50 °C for 1 h before being poured into 2 M hydrochloric acid. The aqueous layer was extracted with benzene. The organic extract was washed with 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 then recrystallized from a mixture of benzene/hexane to provide C2FH (0.056 g, 25.1%) as dark red crystals. Mp. 48.5–49.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ

6.77 (s, 1H), 6.57 (s, 1H), 4.53 (dd, $J = 1.7$ and 1.4 Hz, 2H), 4.26 (dd, $J = 1.7$ and 1.4 Hz, 2H), 4.10 (s, 5H), 2.81 (m, 4H), 2.77 (t, $J = 7.6$ Hz, 2H), 1.67 (tt, $J = 7.6$ and 7.2 Hz, 2H), 1.38 (tt, $J = 7.2$ and 6.3 Hz, 2H), 1.32–1.29 (m, 4H), 0.90 (t, $J = 6.4$ Hz, 3H). IR (thin layer): ν 3095, 2960, 2929, 2886, 2857, 1105, 1027, 1000, 835, 821 cm^{-1}. HRMS-ESI m/z Calcd (M+): 460.0982 ; Found: 460.0987. Anal. Calcd for $C_{26}H_{28}Fe_{1}S_{2}$: C, 67.82; H, 6.31%. Found: C, 67.80; H, 6.21%.

2,7-Diferrocenylcyclohexa[2,1-*b*:3,4-*b*′]dithiophene (C2FF). This diferrocenyl derivative was prepared from **I** in a similar manner as described for the synthesis of C2FH. The obtained crude product was purified by flash chromatography on silica gel (benzene/hexane), and then recrystallized from a mixture of benzene/hexane to provide C2FF as dark red needles. (13.9%) Decomp. 227 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.79 (s, 2H), 4.55 (dd, $J = 1.9$ and 1.4 Hz, 4H), 4.28 (dd, $J = 1.9$ and 1.4 Hz, 4H), 4.12 (s, 10H), 2.84 (s, 4H). IR (KBr): ν 3091, 3079, 2929, 2884, 2829, 1438, 1409, 1103, 1027, 1002 cm^{-1}. HRMS-ESI m/z Calcd (M+): 560.0018 ; Found: 559.9999. Anal. Calcd for $C_{30}H_{24}S_{2}Fe_{2}$: C, 64.31; H, 4.32%. Found: C, 64.33; H, 4.50%.

2-Hexylcyclohepta[2,1-*b*:3,4-*b*′]dithiophene (IV). This monohexyl derivative was prepared from **III** in a similar manner as described for the synthesis of **II**. The obtained crude product was purified by flash chromatography on silica gel (hexane) to yield **IV** as colorless viscous oil. (34.1%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.02 (d, $J = 5.5$ Hz, 1H), 6.74 (d, $J = 5.5$ Hz, 1H), 6.44 (s, 1H), 2.94 (t, $J = 5.5$ Hz, 2H), 2.90 (t, $J = 5.5$ Hz, 2H), 2.69 (t, $J = 7.4$ Hz, 2H), 2.03–1.99 (m, 2H), 1.65 (tt, $J = 7.3$ and 7.3 Hz, 2H), 1.40–1.28 (m, 6H), 0.89 (t, $J = 6.9$ Hz, 3H). IR (thin layer): ν 3102, 3070, 2927, 2854, 1465, 1438, 1292, 846, 711, 680 cm^{-1}.

2,8-Dihexylcyclohepta[2,1-*b*:3,4-*b*′]dithiophene (C3HH). This dihexyl derivative was prepared from **III** in a similar manner as described for the synthesis of **II**. The obtained crude product was purified by flash chromatography on silica gel (hexane) to yield **IV** as colorless viscous oil. (22.0%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.35 (s, 2H), 2.80 (t, $J = 5.6$ Hz, 4H), 2.61 (t, $J = 7.2$ Hz, 4H), 1.92 (quin, $J = 5.6$ Hz, 2H), 1.56 (tt, $J = 7.2$ and 7.0 Hz, 4H), 1.32–1.21 (m, 12H), 0.81 (t, $J = 6.8$ Hz, 6H). IR (thin layer): ν 3050, 2954, 2927, 2854, 1465, 1442, 1303, 1052, 842, 730 cm^{-1}. HRMS-ESI m/z Calcd (M+): 374.2102 (MH+): 375.2180 ; Found: 374.2095. Anal. Calcd for $C_{23}H_{34}S_{2}$: C, 73.74; H, 9.15%. Found: C, 73.51; H, 9.28%.

2-Ferrocenyl-8-hexylcyclohepta[2,1-*b*:3,4-*b*′]dithiophene (C3FH). This monoferrocenyl derivative was prepared from **III** in a similar manner as described for the synthesis of C2FH. The obtained crude product was purified by flash chromatography on silica gel (benzene/hexane), and then recrystallized from a mixture of benzene/hexane to provide C3FH as dark viscous oil. (21.6%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.65 (s, 1H), 6.45 (s, 1H), 4.51 (dd, $J = 1.7$ and 1.4 Hz, 2H), 4.25 (dd, $J = 1.7$ and 1.4 Hz, 2H), 4.11 (s, 5H), 2.90 (m, 4H), 2.70 (t, $J = 7.5$ Hz, 2H), 2.02 (bs, 2H), 1.65 (tt, $J = 7.5$ and 7.1 Hz, 2H), 1.38 (tt, $J = 7.1$ and 6.6 Hz, 2H), 1.41–1.30 (m, 6H), 0.90 (t, $J = 6.6$ Hz, 3H). IR (KBr): ν 3091, 3079, 2929, 2884, 2829, 1438, 1409, 1103, 1027, 864 cm^{-1}. HRMS-ESI m/z Calcd (M+): 474.1138 ; Found: 474.1124. Anal. Calcd for $C_{27}H_{30}Fe_{1}S_{2}$: C, 68.34; H, 6.37%. Found: C, 68.18; H, 6.36%.

2,8-Diferrocenylcyclohepta[2,1-*b*:3,4-*b*′]dithiophene (C3FF). This diferrocenyl derivative was prepared from **III** in a similar manner as described for the synthesis of C2FH. The obtained crude product was purified by flash chromatography on silica gel (benzene/hexane), and then recrystallized from a mixture of benzene/hexane to provide C3FF as dark needles. (6.9%). Decomp. 231 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.67 (s, 2H), 4.54 (dd, $J = 1.8$ and 1.4 Hz, 4H), 4.28 (dd, $J = 1.8$ and 1.4 Hz, 4H), 4.14 (s, 10H), 2.94 (t, $J = 5.6$ Hz, 4H), 2.05 (quin, $J = 5.6$ Hz, 2H). IR (KBr): ν 3093, 3052, 2919, 2857, 1105, 1056, 1024, 1000, 927, 815 cm^{-1}. HRMS-ESI m/z Calcd (M+): 574.0175 ; Found: 574.0143. Anal. Calcd for $C_{31}H_{26}Fe_{2}S_{2}$: C, 64.83; H, 4.56%. Found: C, 64.92; H, 4.59%.

Supporting Information

The optimized structures of CnFF's are described in Figure S1 and the electronic absorption spectra of one- and two-electron-oxidized CnFF's is shown in Figure S2. This material is available free of charge on J-STAGE.

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