Design of reversible multi-electron redox systems using benzochalcogenophenes containing aryl and/or ferrocenyl fragments

Satoshi Ogawa *, Hiroki Muraoka, Kenji Kikuta, Fumihito Saito, Ryu Sato *

Department of Chemical Engineering, Faculty of Engineering, Iwate University, 4-3-5 Ueda, Morioka 020-8551 Iwate, Japan

Abstract

2,3-Disubstituted benzo[*b*]thiophenes, 1,3-disubstituted benzo[*c*]thiophenes, and 1,3-disubstituted benzo[*c*]selenophene have been systematically and selectively synthesized from benzo[*b*]thiophene or phthaloyl dichloride as a starting material, respectively. Characterization of the molecules was performed by physical and spectroscopic means and X-ray crystallographic analyses. The cyclic voltammograms of the chalcogenophene derivatives containing aryl fragments showed well-defined reversible both anodic and cathodic steps derived from the unusually stable 5π chalcogenophene radical cations and 7π chalcogenophene radical anions. The cyclic voltammograms of the novel chalcogenophene derivatives containing ferrocenyl fragments showed a well-defined reversible cathodic step derived from the unusually stable 7π chalcogenophene radical anions and two distinct reversible anodic steps derived from ferrocenium cations separated from each other by a thiophene-heterocycle. The radical character of several novel 7π chalcogenophene radical anions was measured by ESR spectroscopy.
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1. Introduction

In recent years, the study of molecules comprising multiple reduction–oxidation (redox) centers have attracted considerable research interest in the field of material science due to the preparation of new π-conjugated materials with application in material science [1]. Moreover, this kind of molecule having more than two redox-active metal centers is a fundamentally attractive target for the study of multielectron transfer processes via the mixed-valence state derived from these multi-metallic systems [2]. On the other hand, interest in the design of novel redox-active organic centers by the use of a 5π- and 7π-electron framework [3] containing group 16 elements has led us to explore the synthesis of new five-membered heterocycles containing sulfur and/or selenium atom(s). This time our studies are aimed at

the design of reversible multi-steps redox systems using simple molecules with both organic and organometallic electron transfer fragments. Although the synthesis and characterization of substituted benzochalcogenophenes have been reported [4], there is no report concerning benzannulated thiophene and selenophene containing a ferrocene fragment on the five-membered heterocyclic unit, which are of structural and redox-characteristic interest. Recently, we reported a new type of multi-steps reversible redox systems using organic–organometallic hybrid molecules, 1-ferrocenyl- and 1,9-diferrocenyl-thianthrenes [5]. Therefore, we have designed 2,3-disubstituted benzo[*b*]thiophene and 1,3-disubstituted benzo[*c*]chalcogenophene as both cathodic and anodic multiple-redox active organic–organometallic hybrid molecules. In this paper, we provide the details on the synthesis, structural characterization, and electrochemical properties of 2,3-disubstituted benzo[*b*]thiophenes, 1,3-disubstituted benzo[*c*]thiophenes, and 1,3-disubstituted benzo[*c*]selenophenes.

* Corresponding authors. Tel./fax.: +81 19 621 6934.
 *E-mail address:* ogawa@iwate-u.ac.jp (S. Ogawa).

2. Results and discussion

2.1. Synthesis of 2,3-disubstituted benzo[b]thiophenes (2a–d)

Upon treatment of 2,3-dibromobenzo[b]thiophene, which was prepared by general bromination of benzo[b]thiophene with bromine [6], with ferrocenylzinc chloride in the presence of a catalytic amount of tetrakis(triphenylphophine)palladium $(PPh_3)_4Pd$, in tetrahydrofuran (THF) under reflux condition by the modified methods previously reported [7] 3-bromo-2-ferrocenylbenzo[b]thiophene (**1**)

was obtained in moderate yield. Then, compound **1** was reacted with arylboronic acids by Suzuki-coupling [8] in the presence of a catalytic amount of $(PPh_3)_4Pd$ in dimethylformamide (DMF) at 100 °C to give 3-aryl-2-ferrocenylbenzo[b]thiophene (**2a–c**) in good yields. The synthesis of 2,3-diferrocenylbenzo[b]thiophene (**2d**) was achieved through a single step transition metal-catalyzed cross-coupling reaction of **1** with ferrocenylzinc chloride in the presence of a catalytic amount of bis(triphenylphophine)palladium(II) dichloride $(PPh_3)_2PdCl_2$, in tetrahydrofuran (THF) under reflux condition in moderate yield (Scheme 1).
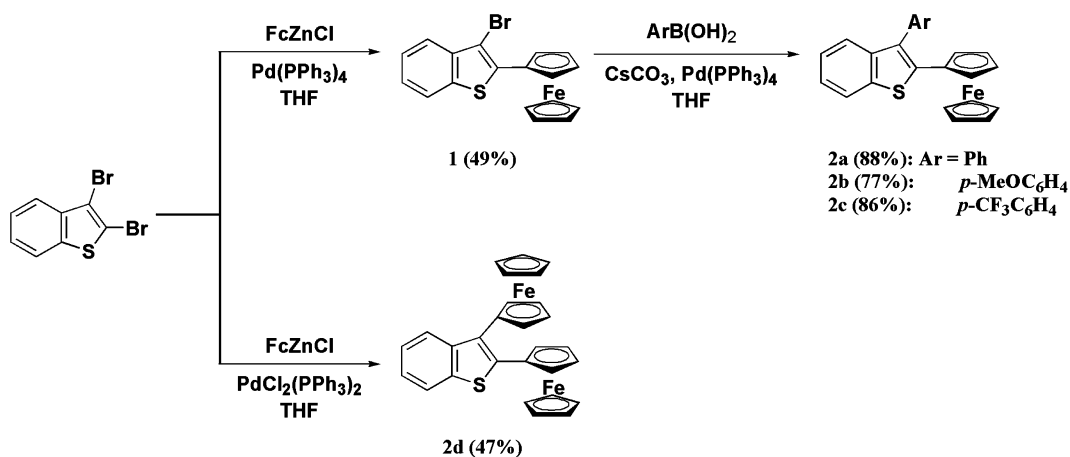
Scheme 1.
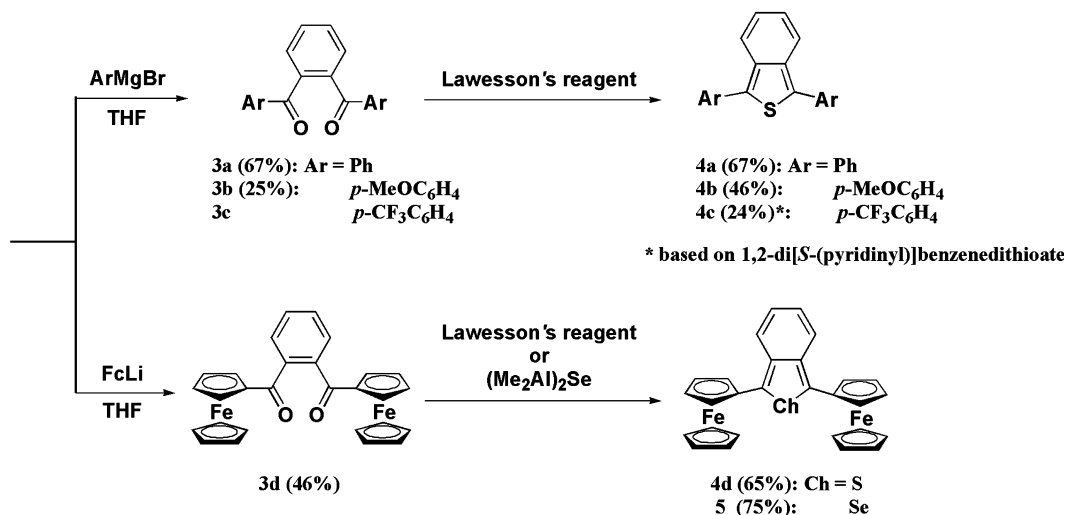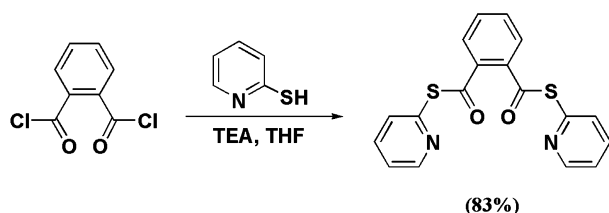
Scheme 2.

2.2. Synthesis of 1,3-disubstituted benzo[c]thiophenes (4a–d), and benzo[c]selenophenes (5)

We employed phthaloyl dichloride as a starting material for the synthesis of 1,3-disubstituted benzo[c]thiophene (4a–d). However, two acid chlorides in the *ortho* position are too reactive toward nucleophilic substitution by the use of Grignard or organolithium reagents even at low temperature. Therefore, we synthesized 1,2-di[S-(2-pyridinyl)]benzenedithioate which has two functional groups with lower reactivity as compared with phthaloyl dichloride by the modified method previously reported [9]. Since we obtained 1,2-di[S-(2-pyridinyl)]benzenedithioate, the next step consisted of performing the reaction with aryl Grignard reagents or a ferrocenyllithium reagent. The aryl Grignard reagents were slowly added at 0 °C to 1,2-di[S-(2-pyridinyl)]benzenedithioate in a solution of THF. The mixture was stirred at 0 °C for 15 min and finally quenched by addition of 2 mol dm^{-3} HCl aqueous solution. After usual work-up *ortho* diaroylbenzenes (3a–c) were obtained in moderate yield. In the case of introduction of a ferrocenyl substituent, the ferrocenyllithium, which was prepared from ferrocene with *t*-butyllithium, was slowly added at −60 °C to 1,2-di[S-(2-pyridinyl)]benzenedithioate in a solution of THF. The mixture was stirred at −60 °C for 30 min and finally quenched by addition of HCl aqueous solution (2 mol dm^{-3}). After usual work-up *ortho* diferrocenoylbenzene (3d) was obtained in moderate yield. Finally, the isothianaphthene core was formed through ring closure of 3a–d by means of Lawesson's reagent to give 1,3-disubstituted benzo[c]thiophene (4a–d) in moderate yield (Scheme 2). In the case of the synthesis of 1,3-diferrocenylbenzo[c]selenophene (5) the final ring-closure reaction was performed by the use of bis(dimethylaluminium) selenide developed by Segi and Zingaro [10] as a selenating reagent.

3. X-ray crystallographic analysis

The molecular structures of benzo[b]thiophene 2d, benzo[c]thiophene 4d, and benzo[c]selenophene 5 were confirmed by X-ray crystallographic analyses (Fig. 1 and Table 1). The data revealed that two ferrocene fragments were located in anti-conformation, respectively, having the dihedral angles between the chalcogenophene ring and the bonded cyclopentadienyl ring of 34.3(5)° and 42.3(4)° for 2d, −23.7(2)° and +30.0(2)° for 4d, −21.9(5)° and +30.1(5)° for 5. The anti-geometry of two fragments in 2d implies the presence of repulsion of each bulky substituent. On the other hand, the anti-geometry of 4d and 5 could be explained by the crystal packing. The C–C bond distances between the ferrocenyl carbon and the carbon(s) next to the chalcogen atom are 1.458(4) Å for 2d, 1.461(2) and 1.461(2) Å for 4d, 1.451(6) and 1.447(5) Å for 5 and are similar to the corresponding bond distance (1.464(7) Å) of 2,5-diferrocenylthiophene previously reported [11]. These results suggest a double bond character reflected a conjugation effect [4h,12] between
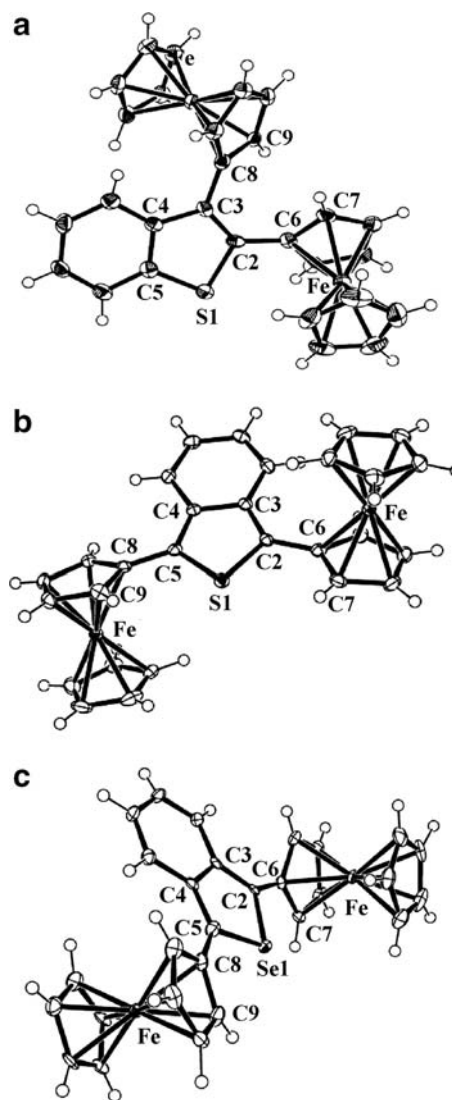

Fig. 1. ORTEP drawing of (a) 2d · CH$_2$Cl$_2$ (dichloromethane molecule is omitted for clarity), (b) 4d, and (c) 5. Thermal ellipsoids are drawn at 50% probability.

the chalcogenophene ring and the cyclopentadienyl ring of the ferrocene because the bond lengths were significantly shorter than that of the sp^2–sp^2 single bond (1.516 Å) [13].

4. Electrochemical studies

The solution redox properties of the benzochalcogenophenes 2a–d, 4a–d, and 5 were studied by cyclic volammetry technique, since little has been known about the electrochemically stepwise multi-electron transfer behavior of organic–organometallic hybrid molecules by the use of a chalcogenophene framework as an organic redox unit. The data are collected in Table 2 and typical cyclic voltammograms (CV) of 2d, 4d, and 5 are shown in Fig. 2.

The CV of 2a–c at concentrations 2.0 mmol dm^{-3} in THF/0.1 mol dm^{-3} *n*-Bu$_4$NPF$_6$ showed reversible oxidation couples, $E_{1/2} = +0.28$ V for 2a; +0.27 V for 2b; +0.28 V for 2c; *vs.* Ag/Ag$^+$, derived from the formation

Table 1
Selected bond lengths (Å), bond angles (°), and torsion angles (°)

Benzo[b]thiophene 2d		Benzo[c]thiophene 4d		Benzo[c]selenophene 5	
Bond lengths					
S1–C2	1.760(4)	S1–C2	1.720(2)	Se1–C2	1.867(4)
C2–C3	1.355(4)	C2–C3	1.393(2)	C2–C3	1.381(5)
C3–C4	1.451(5)	C3–C4	1.443(2)	C3–C4	1.456(5)
C4–C5	1.404(5)	C4–C5	1.390(2)	C4–C5	1.386(5)
C5–S1	1.735(3)	C5–S1	1.714(2)	C5–Se1	1.862(4)
C2–C6	1.458(4)	C2–C6	1.461(2)	C2–C6	1.447(5)
C3–C8	1.490(5)	C5–C8	1.461(2)	C5–C8	1.451(6)
Bond angles					
S1–C2–C3	112.5(3)	S1–C2–C3	110.2(1)	Se1–C2–C3	109.9(3)
C2–C3–C4	113.0(3)	C2–C3–C4	112.4(2)	C2–C3–C4	115.3(3)
C3–C4–C5	111.3(2)	C3–C4–C5	112.9(1)	C3–C4–C5	115.0(3)
C4–C5–S1	112.2(2)	C4–C5–S1	110.3(1)	C4–C5–Se1	110.0(3)
C5–S1–C2	91.0(2)	C5–S1–C2	94.16(8)	C5–Se1–C2	89.8(2)
C8–C3–C2	122.3(3)				
C6–C2–C3	130.3(3)				
Torsion angles					
C7–C6–C2–C3	34.3(5)	S1–C2–C6–C7	−23.7(2)	C9–C8–C5–Se1	−21.9(5)
C2–C3–C8–C9	42.3(4)	C9–C8–C5–S1	30.0(2)	Se1–C2–C6–C7	30.1(5)
C6–C2–C3–C8	4.8(5)				

Table 2
Redox potentials [V *vs.* Ag/Ag$^+$][a]

	Neutral/7π radical anion			Ferrocene/ferrocenium cation						Neutral/5π radical cation		
				First			Second					
	E_{pa}	E_{pc}	$E_{1/2}$	E_{pa}	E_{pc}	$E_{1/2}$	E_{pa}	E_{pc}	$E_{1/2}$	E_{pa}	E_{pc}	$E_{1/2}$
Benzo[b]thiophene												
2a	−2.70[b]	−2.92[b]	–	+0.38	+0.17	+0.28						
2b	−2.71	−2.94	−2.83	+0.38	+0.16	+0.27						
2c[c]	–	–	–	+0.37	+0.18	+0.28						
2d	−2.71	−3.02	−2.87	+0.38	+0.06	+0.22	+0.56	+0.25	+0.41			
Benzo[c]thiophene												
4a	−2.06	−2.25	−2.16							+0.93	+0.74	+0.84
4b	−2.30	−2.11	−2.21							+0.80	+0.63	+0.72
4c	−1.77	−1.93	−1.85							+1.10	+0.94	+1.02
4d	−2.31	−2.45	−2.38	+0.21	+0.07	+0.14	+0.41	+0.27	+0.34			
Benzo[c]selenophene												
5	−2.19	−2.42	−2.31	+0.27	+0.02	+0.15	+0.51	+0.26	+0.39			

[a] Conditions: concentration, 2 mmol dm^{-3} sample in 0.1 mol dm^{-3} *n*-Bu$_4$NPF$_6$/THF solution; working electrode, glassy-carbon; reference electrode, Ag/0.01 mol dm^{-3} AgNO$_3$ in 0.1 mol dm^{-3} *n*-Bu$_4$NPF$_6$/CH$_3$CN solution; counter electrode, Pt; temperature, 223–233 K for **2a–d**, 293 K for **4a–d**, 233 K for **5**; scan rate, 200 mV s^{-1} for **2a–d**, 100 mV s^{-1} for **4a–d** and **5**.
[b] Quasi-reversible.
[c] Reduction peak was not observed.

of the ferrocenium cation. At negative scan, one-electron reduction waves derived from 7π thiophene radical anions were observed, $E_{pc} = -2.92$ V for **2a**; −2.94 V for **2b**. The reduction wave involving decomposition for **2c** was observed in this condition, but the clear reduction peak could not be assigned. Interestingly, the reduction potentials for **2a** and **2b** were almost the same, while the electrochemical reversibility was different; quasi-reversible for **2a**; reversible for **2b**. Therefore, although aryl substituents of the 3-position of the benzo[b]thiophene framework serve for stability of the 7π thiophene radical anions, those have

little influence on the reduction potential of the thiophene moiety and oxidation potential of the ferrocene moiety.

The CV of **4a–c** under the same conditions showed well-defined reversible two one-electron redox couples, $E_{1/2} = -2.16$, +0.84 V for **4a**; − 2.21, +0.72 V for **4b**; − 1.85, +1.02 V for **4c**; derived from the formation of the 7π thiophene radical anions and 5π thiophene radical cations. The oxidation and reduction half-potentials indicate that the HOMO level elevates in the order of **4c** < **4a** < **4b**, and the LUMO level elevates in the order of **4b** > **4a** > **4c**. These results indicate that electron-donating or -withdraw-
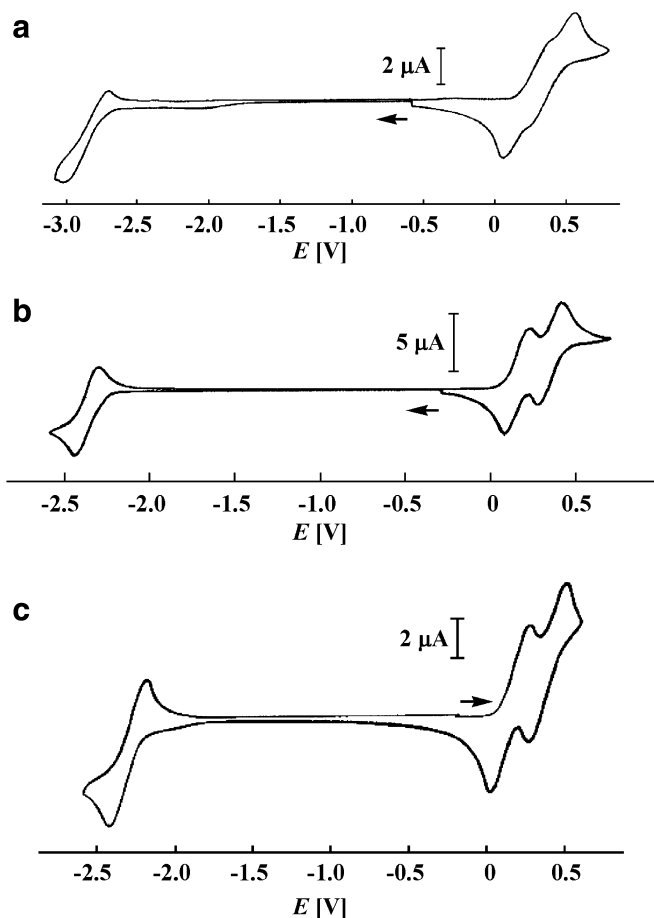
Fig. 2. Cyclic voltammograms of (a) **2d**, (b) **4d**, and (c) **5** in THF (0.1 mol dm^{-3} n-Bu$_4$NPF$_6$). The measurements were carried out at 223 K for **2d**, 293 K for **4d**, 233 K for **5** with scan rate 100–200 mV s^{-1}.

ing effects of the aryl groups at 1,3-positions influence both the reduction and oxidation potentials.

On the other hand, the dominant feature of CV scans of benzochalcogenophenes containing two ferrocene units at the same conditions is three one-electron redox couples, $E_{1/2} = -2.87, +0.22, +0.41$ V for **2d**; $-2.38, +0.14, +0.34$ V for **4d**; $-2.31, +0.15, +0.39$ V for **5**; vs. Ag/Ag$^+$, respectively, that is well-defined reversibility. At negative

scan, the reduction of **2d**, **4d**, and **5** is chemically reversible and a cathodic product wave appears, assigned to formation of the corresponding 7π chalcogenophene radical anions. On the other hand, at positive scan, the oxidation of **2d**, **4d**, and **5** is also chemically reversible and two anodic product waves appear, assigned to stepwise formation of the corresponding mono- and bis-(ferrocenium cation).

By CV and differential pulse voltammograms (DPV) measurements of **2d**, **4d**, and **5** employing dichloromethane (CH$_2$Cl$_2$) as a solvent, the oxidation waves derived from the ferrocene fragments showed good separated and well-defined reversible one-electron redox couples (Fig. 3 and Table 3). These results suggest that the dielectric constant of the solvent has a significant effect on the electrostatic contributions to the two oxidation processes of the intra-molecular ferrocene fragments [14]. The differences between the first and second half-potentials ($\Delta E_{1/2} = E_{1/2}^1 - E_{1/2}^2$) for the Fe(II)–Fe(III) and Fe(III)–Fe(III) couples of **2d**, **4d**, and **5** were 192, 280, and 305 mV, respectively (Table 3). These results suggest that the structural difference between diferrocenylbenzothiophene **2d** and **4d** based on the annulation mode and the substituent position should cause the differences in their redox behavior and thermodynamic stability in mixed-valence intermediates. The comproportionation constants (K_c) [15] for the Fe(II)–Fe(III) mixed-valence state estimated from $\Delta E_{1/2}$ were 1.1×10^5 for **4d** and 3.0×10^5 for **5**. Therefore, the electronic interaction between the metal center of ferrocene and the ferrocenium cation in the mixed-valence state of **4d**

Table 3
Redox potentials [V vs. Ag/Ag$^+$][a]

	$E_{1/2}^1$ (V)	$E_{1/2}^2$ (V)	$\Delta E_{1/2}$[b] (mV)
2d	+0.21	+0.40	+192
4d	+0.13	+0.41	+280
5	+0.12	+0.42	+305

[a] Conditions: concentration, 1 mmol dm^{-3} sample in 0.1 mol dm^{-3} n-Bu$_4$NPF$_6$/CH$_2$Cl$_2$ solution; temperature, 281 K; working electrode, glassy-carbon; reference electrode, Ag/0.01 mol dm^{-3} AgNO$_3$ in 0.1 mol dm^{-3} n-Bu$_4$NPF$_6$/CH$_3$CN solution; counter electrode, Pt; scan rate, 100 mV s^{-1}.
[b] $\Delta E_{1/2} = E_{1/2}^2 - E_{1/2}^1$.

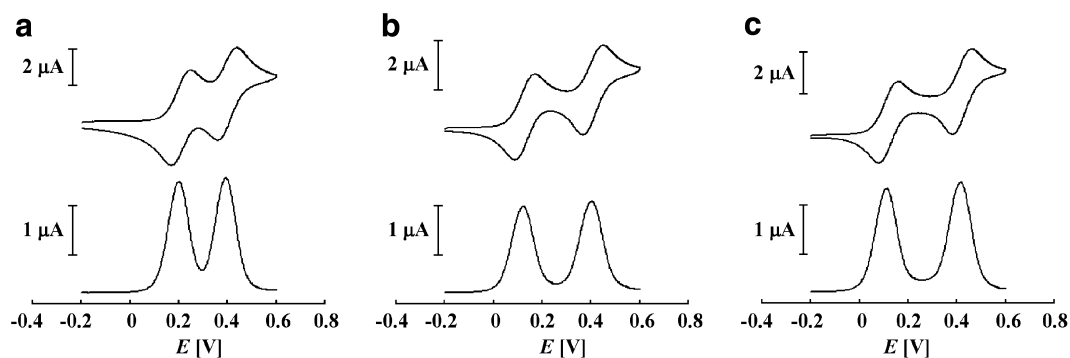Fig. 3. Cyclic (top) and differential pulse (bottom) voltammograms of (a) **1**, (b) **2** and (c) **3** in CH$_2$Cl$_2$ (0.1 mol dm^{-3} n-Bu$_4$NPF$_6$). The measurements were carried out at 281 K with scan rate 100 mV s^{-1}.
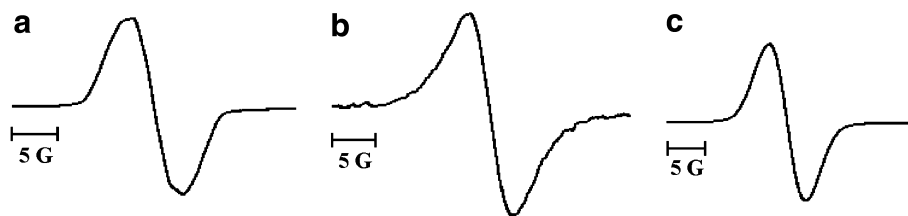
Fig. 4. ESR spectra of (a) **2d**$^{\cdot-}$, (b) **4d**$^{\cdot-}$, and (c) **5**$^{\cdot-}$ in THF.

and **5** can be expected to be strong because of potential through-bond and/or through-space interactions. In the case of compound **2d**, it is difficult to discuss the comproportionation constant K_c, because it has essentially different oxidation potential based on the position of ferrocenes.

5. 7π Radical anions and ESR spectra

In contrast to the studies on oxidation of chalcogenophenes [16], there are few reports for the formation of 7π chalcogenophene radical anions [16a,16d,16f,17] by reduction. The results of the reversibility observed in CV described above clearly indicate that the several benzochalcogenophenes generate stable 7π radical anions even at room temperature. Several novel benzochalcogenophene radical anions, **2d**$^{\cdot-}$, **4d**$^{\cdot-}$, and **5**$^{\cdot-}$, were readily generated in the one-electron reduction of benzochalcogenophenes, **2d**, **4d**, and **5**, in THF with metal potassium under an argon atmosphere. The ESR spectra of the dark blue or green solution of showed the presence of broad singlet peaks, $g = 2.00474$ for **2d**$^{\cdot-}$; 2.00895 for **4d**$^{\cdot-}$; 2.01343 for **5**$^{\cdot-}$; attributable to the corresponding 7π radical anions (Fig. 4). Unfortunately, hyper-fine splitting of each radical anion could not be observed under our measurement conditions.

6. Conclusions

We have synthesized and characterized novel benzochalcogenophenes containing aryl and/or ferrocenyl units. The electrochemical properties showed reversible multi-electron transfer phenomena assigned to the chalcogenophene (organic) and ferrocene (organometallic) fragments owing to good stability of the negative-charged reduction products (radical anions) and positive-charged oxidation products (radical cations, and mono- or bis-ferrocenium cations). Therefore, we succeeded in establishing a new type of multi-steps reversible redox systems using neutral organic–organometallic hybrid molecules.

7. Experimental

7.1. General

Melting and decomposition points were determined on a Mel-Temp capillary tube apparatus, and were uncorrected. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra were measured on a Bruker AC-400 spectrometer using chloro-

form-*d* as a solvent with Me_4Si as the internal standard. ^{77}Se (76 MHz) NMR spectra used Me_2Se as the external standard. IR spectra were recorded on a JASCO FT-7300 spectrometer. Mass spectra were determined on a Hitach M-2000 spectrometer operating at 70 eV in the EI mode. Elemental analyses were carried out by using a Yanagimoto MT-5 CHN corder and determined in the Division of Elemental Analysis in Iwate University. Cyclic voltammetry was carried out by using a Cypress Systems CS-1090 galvanostat/potentiostat or a Hokuto Denko function generator HB-104 and galvanostat/potentiostat HA-303. A three-electrode system was used, consisting of a glassy-carbon working electrode, a platinum wire auxiliary electrode and an Ag/0.01 mol dm^{-3} AgNO$_3$ reference electrode. The measurements were carried out in THF or dichloromethane solution containing 0.1 mol dm^{-3} *n*-Bu$_4$NPF$_6$ as a supporting electrolyte with scan rates in a range of 100–200 mV s^{-1} under an Ar atmosphere. ESR data were taken in a JEOL JES-FA 100 spectrometer working in the X-band as THF solution with Mn^{2+} on MgO as field marker. All solvents used in the reactions were purified by the general methods. All reactions were carried out under a nitrogen or an argon atmosphere. Silica-gel column chromatography was performed with a Wakogel C-200.

7.2. Synthesis of 3-bromo-2-ferrocenylbenzo[b]thiophene (**1**)

To a stirred solution of ferrocene (1.552 g, 8.342 mmol) in THF (10 mL) was added *t*-butyllithium (5.5 mL of a 1.53 M pentane solution, 8.3 mmol) at 0 °C under an N$_2$ atmosphere. After stirring at 0 °C for 1 h, a solution of zinc chloride (1.137 g, 8.343 mmol) in THF (20 mL) was added to the mixture, and the resulting mixture stirred at room temperature for 2 h. To the mixture was added a solution of 2,3-dibromobenzo[b]thiophene (1.740 g, 5.959 mmol) and tetrakis(triphenylphosphine)palladium (0.413 g, 0.358 mmol) in THF (20 mL). After stirring under reflux for 24 h, it was cooled to room temperature. The reaction mixture was acidified with aqueous hydrochloric acid, and extracted with chloroform. The organic layer was dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane) to give 3-bromo-2-ferrocenylbenzo[b]thiophene (**1**, 1.164 g, 2.932 mmol, 49%): orange plate; mp 125.5–126.6 °C; ^1H NMR (400 MHz, CDCl$_3$) δ 4.19 (s, 5H, *free*-Cp), 4.41 (t,

$J = 1.9$ Hz, 2H, C_5H_4), 4.99 (t, $J = 1.9$ Hz, 2H, C_5H_4), 7.34 (td, $J = 0.8$, 8.0 Hz, 1H, ArH), 7.41 (td, $J = 0.8$, 8.0 Hz, 1H, ArH), 7.72 (d, $J = 8.0$ Hz, 1H, ArH), 7.76 (dd, $J = 0.8$, 8.0 Hz, 1H, ArH); ^{13}C NMR (101 MHz, CDCl$_3$) δ 69.3 (2C), 70.1, 77.6, 103.4, 121.8, 122.6, 124.9, 125.1, 136.7, 138.5, 139.5; IR (KBr) ν 3457, 3094, 1542, 1445, 1422, 1258, 1000, 808, 493 cm^{-1}; MS (70 eV) m/z 398 (M$^+$); Anal. Calc. for $C_{18}H_{13}BrFeS$: C, 54.44; H, 3.30. Found: C, 54.58; H, 3.30%.

7.3. General procedure for the synthesis of 3-aryl-2-ferrocenylbenzo[b]thiophene (2a–2c)

A solution of 3-bromo-2-ferrocenylbenzo[b]thiophene (**1**, 0.397 g, 1.000 mmol), phenylboronic acid (0.134 g, 1.10 mmol), cesium carbonate (0.492 g, 1.51 mmol), and tetrakis(triphenylphosphine)palladium (0.023 g, 0.020 mmol) in DMF (12 mL)/water (2 mL) was stirred for 24 h at 100 °C under an N$_2$ atmosphere. After cooling to room temperature, the reaction mixture was acidified with aqueous hydrochloric acid, and extracted with chloroform. The organic layer was dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, chloroform:hexane = 1:4) to give 2-ferrocenyl-3-phenylbenzo[b]thiophene (**2a**, 0.346 g, 0.877 mmol, 88%): brown plate; mp 161.2–161.9 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.08 (s, 5H, *free*-Cp), 4.18 (t, $J = 1.9$ Hz, 2H, C_5H_4), 4.23 (t, $J = 1.9$ Hz, 2H, C_5H_4), 7.22–7.36 (m, 5H, ArH), 7.40–7.49 (m, 3H, ArH), 7.78 (d, $J = 7.3$ Hz, 1H, ArH); ^{13}C NMR (101 MHz, CDCl$_3$) δ 68.8, 69.0, 70.0, 78.8, 121.7, 122.4, 123.9, 124.3, 127.5, 128.6, 130.3, 132.2, 136.2, 138.1, 139.4, 141.5; IR (KBr) ν 3062, 1425, 1055, 1001, 812, 758, 730, 609, 497 cm^{-1}, MS (70 eV) m/z 394 (M$^+$); Anal. Calc. for $C_{24}H_{18}FeS$: C, 73.10; H, 4.60. Found: C, 72.96; H, 4.84%.

7.4. 2-Ferrocenyl-3-(p-methoxyphenyl)benzo[b]thiophene (2b)

Dark brown plate; mp 185.2–186.0 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.08 (s, 5H, *free*-Cp), 4.19 (t, $J = 1.9$ Hz, 2H, C_5H_4), 4.26 (t, $J = 1.9$ Hz, 2H, C_5H_4), 7.01 (d, $J = 8.6$ Hz, 2H, ArH), 7.23–7.35 (m, 5H, ArH), 7.76–7.78 (m, 1H, ArH); ^{13}C NMR (101 MHz, CDCl$_3$) δ 55.3, 68.7, 69.0, 70.0, 78.9, 114.0, 121.7, 122.4, 123.9, 124.2, 128.3, 131.4, 131.8, 138.0, 139.2, 141.7, 159.0; IR (KBr) ν 2833, 1609, 1508, 1456, 1286, 1242, 1105, 1032, 820, 763, 578, 532, 496 cm^{-1}; MS (70 eV) m/z 424 (M$^+$); Anal. Calc. for $C_{25}H_{20}FeOS$: C, 70.76; H, 4.75. Found: C, 70.68; H, 4.80%.

7.5. 2-Ferrocenyl-3-(p-trifluoromethylphenyl)benzo[b]-thiophene (2c)

Dark brown plate; mp 239.1–240.7 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.11 (s, 5H, *free*-Cp), 4.216 (br t, 2H, C_5H_4), 4.219 (br t, 2H, C_5H_4), 7.27–7.35 (m, 3H, ArH), 7.48 (d, $J = 8.0$ Hz, 2H, ArH), 7.73 (d, $J = 8.0$ Hz, 2H, ArH), 7.80 (d, $J = 7.6$ Hz, ArH); ^{13}C NMR (101 MHz, CDCl$_3$) δ 69.1, 69.3, 70.2, 78.4, 121.9, 122.1, 124.28, 124.34 (q, $J_{13\ C-19F} = 272.2$ Hz), 124.6, 125.6 (q, $J_{13C-19F} = 3.6$ Hz), 129.8 (q, $J_{13C-19F} = 32.2$ Hz), 130.7, 130.8, 138.3, 140.3, 140.7, 140.9; IR (KBr) ν 3059, 1930, 1616, 1403, 1067, 918, 840, 765, 622 cm^{-1}; MS (70 eV) m/z 462 (M$^+$); Anal. Calc. for $C_{25}H_{17}F_3FeS$: C, 64.95; H, 3.71. Found: C, 64.71; H, 4.04%.

7.6. Synthesis of 2,3-diferrocenylbenzo[b]thiophene (2d)

To a stirred solution of ferrocene (2.989 g, 16.07 mmol) in THF (20 mL) was added *t*-butyllithium (11.0 mL of a 1.45 M pentane solution, 16.0 mmol) at 0 °C under an Ar atmosphere. After stirring at 0 °C for 1 h, a solution of zinc chloride (2.177 g, 15.97 mmol) in THF (30 mL) was added to the mixture, and the resulting mixture was stirred at room temperature for 2 h. To the mixture was added a solution of 2,3-dibromobenzo[b]thiophene (1.177 g, 4.031 mmol) and bis(triphenylphosphine)palladium dichloride (0.168 g, 0.239 mmol) in THF (30 mL). After stirring under reflux for 18 h, it was cooled to room temperature. The reaction mixture was acidified with aqueous hydrochloric acid, and extracted with chloroform. The organic layer was dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane, and then chloroform:hexane = 1:5) to give 2,3-diferrocenylbenzo[b]thiophene (**2d**, 0.825 g, 1.64 mmol, 58%): brown crystals; mp 175.9–176.3 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.06 (s, 5H, *free*-Cp), 4.15 (s, 5H, *free*-Cp), 4.25 (t, $J = 1.9$ Hz, 2H, C_5H_4), 4.26 (t, $J = 1.9$ Hz, 2H, C_5H_4), 4.32 (t, $J = 1.9$ Hz, 2H, C_5H_4), 4.36 (t, $J = 1.9$ Hz, 2H, C_5H_4), 7.35 (td, $J = 1.3$, 8.0 Hz, 1H, ArH), 7.44 (td, $J = 1.3$, 8.0 Hz, 1H, ArH), 7.78 (d, $J = 8.0$ Hz, 1H, ArH), 8.57 (d, $J = 8.0$ Hz, 1H, ArH); ^{13}C NMR (101 MHz, CDCl$_3$) δ 68.3, 68.1, 69.2, 69.6, 70.0, 70.6, 80.5, 80.8, 121.7, 123.5, 123.8, 124.1, 128.9, 138.7, 138.9, 140.0; IR (KBr) ν 3100, 2362, 1412, 1320, 1107, 1000, 820, 733, 490 cm^{-1}; MS (70 eV) m/z 502 (M$^+$); Anal. Calc. for $C_{28}H_{22}Fe_2S$: C, 66.96; H, 4.42. Found: C, 67.28; H, 4.65%.

7.7. Synthesis of 1,2-di[S-(pyridinyl)]benzenedithioate

To a stirred solution of 2-mercaptopyridine (1.1 g, 9.9 mmol) in THF (20 mL) was added triethylamine (1.67 mL) at 0 °C under an N$_2$ atmosphere. After stirring for 15 min at 0 °C, phthaloylchloride (0.73 mL, 5.1 mmol) was added to the mixture. Immediately the reaction was quenched by the addition of aqueous hydrochloric acid. After the resulting mixture was extracted with dichloromethane, the organic layer was washed with saturated sodium hydrogencarbonate solution and dried over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure, and the residue was purified by

recrystallization from dichloromethane/ether to give 1,2-di[S-(pyridinyl)]benzenedithioate (1.476 g, 4.188 mmol, 83%): colorless crystals; mp 114.3–115.1 °C (lit. [9b], 109.7 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.30 (t, $J = 5.7$ Hz, ArH), 7.65 (dd, $J = 3.4$, 5.6 Hz, 2H, ArH), 7.31–7.79 (m, 4H, ArH), 7.88 (dd, $J = 3.4$, 5.6 Hz, 2H, ArH), 8.63 (d, $J = 4.8$ Hz, 2H, ArH); ^{13}C NMR (101 MHz, CDCl$_3$) δ 123.7, 128.5, 130.4, 132.0, 136.7, 137.3, 150.3, 151.2, 190.1.

7.8. General procedure for the synthesis of o-aroylbenzene (3a–3c)

A solution of bromobenzene (4.003 g, 25.49 mmol) in THF (20 mL) was added to activated magnesium (0.744 g, 30.5 mmol) in THF (20 mL). After stirring for 3.5 h at room temperature, the solution was added to a solution of 1,2-di[S-(pyridinyl)]benzenedithioate (4.492 g, 12.75 mmol) in THF (70 mL) at 0 °C. After the mixture was stirred for 15 min at 0 °C under an N$_2$ atmosphere, it was acidified with aqueous hydrochloric acid (2 mol dm^{-3}). The resulting mixture was extracted with ether. Then, the organic layer was washed with aqueous sodium hydroxide (1 mol dm^{-3}), saturated sodium hydrogencarbonate solution, and brine, and dried over anhydrous magnesium sulfate. After the solvent was evaporated under reduced pressure, the residue was purified by column chromatography (silica gel, ethyl acetate:hexane = 1:5) to give o-dibenzoyllbenzene (3a, 2.431 g, 8.49 mmol, 67%): pale yellow crystals; mp 147.0–147.6 °C (lit. [4d], 144–148 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36 (t, $J = 7.5$ Hz, 4H, ArH), 7.51 (t, $J = 7.5$ Hz, 2H, ArH), 7.61 (s, 4H, ArH), 7.69–7.71 (m, 4H, ArH).

7.9. o-Bis(p-methoxyphenoyl)benzene (3b)

Pale yellow crystals, mp 157.3–158.1 °C (lit. [4d], 153–156 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.84 (s, 6H, OCH$_3$), 6.85 (d, $J = 8.9$ Hz, 4H, ArH), 7.58 (s, 4H, ArH), 7.67 (d, $J = 8.9$ Hz, 4H, ArH); ^{13}C NMR (101 MHz, CDCl$_3$) δ 55.4, 113.5, 129.2, 129.9, 130.2, 132.1, 140.1, 163.4, 195.3; IR (KBr) v 3069, 2838, 1655, 1596, 1510, 1315, 1263, 1173, 1150, 1032, 937, 840, 753, 599 cm^{-1}; MS (70 eV) m/z 346 (M$^+$); Anal. Calc. for C$_{22}$H$_{18}$O$_4$: C, 76.29; H, 5.24. Found: C, 76.55; H, 5.28%.

7.10. o-Bis(p-trifluoromethylphenoyl)benzene (3c)

This compound was difficult to obtain as a completely pure form by chromatographic technique. We employed the compound as a mixture of crude yellow oil to the next cyclization.

7.11. General procedure for the synthesis of 1,3-diarylbenzo[c]thiophene (4a–4c)

A mixture of o-dibenzoylbenzene (3a, 0.286 g, 0.999 mmol) and Lawesson's reagent (0.808 g, 2.00 mmol)

in chloroform (30 mL) was stirred under reflux for 12 h. After the solvent was evaporated under reduced pressure, the residue was dissolved in ethanol (30 mL) and the mixture was stirred under reflux for 12 h. After the resulting solution was cooled to room temperature, the solvent was evaporated under reduced pressure. The residue was dissolved in chloroform and was washed with sodium hydroxide solution (1 mol dm^{-3}). The organic layer was dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, chloroform:hexane = 1:1) to give 1,3-diphenylbenzo[c]thiophene (4a, 0.191 g, 0.667 mmol, 67%): yellow crystals; mp 117.6–117.9 °C (lit. [4d], 117–119 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.09 (dd, $J = 3.0$, 6.9 Hz, 2H, ArH), 7.38 (t, $J = 7.6$ Hz, 2H, ArH), 7.51 (t, $J = 7.6$ Hz, 4H, ArH), 7.69 (d, $J = 7.6$ Hz, 4H, ArH), 7.83 (dd, $J = 3.0$, 6.9 Hz, 2H, ArH).

7.12. 1,3-Bis(p-methoxyphenyl)benzo[c]thiophene (4b)

Yellow crystals; mp 143.1–144.2 °C (lit. [4d], 140–142 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.88 (s, 6H, OCH$_3$), 7.03 (d, $J = 8.8$ Hz, 4H, ArH), 7.04–7.06 (m, 2H, ArH), 7.60 (d, $J = 8.8$ Hz, 2H, ArH), 7.76 (dd, $J = 3.1$, 6.9 Hz, 2H, ArH), ^{13}C NMR (101 MHz, CDCl$_3$) δ 55.4, 114.4, 121.1, 123.8, 126.8, 130.3, 133.1, 134.7, 159.1; IR (KBr) v 3061, 1921, 1614, 1324, 1166, 1014, 755, 635, 443 cm^{-1}; MS (70 eV) m/z 346 (M$^+$); Anal. Calc. for C$_{22}$H$_{18}$O$_2$S: C, 76.27; H, 5.24. Found: C, 76.19; H, 5.27%.

7.13. 1,3-Bis(p-trifluoromethylphenyl)benzo[c]thiophene (4c)

Yellow crystals; mp 147.6–148.2 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.18 (dd, $J = 3.0$, 6.9 Hz, 2H, ArH), 7.76 (d, $J = 8.5$ Hz, 4H, ArH), 7.80 (d, $J = 8.5$ Hz, 4H, ArH), 7.83 (dd, $J = 3.0$, 6.9 Hz, 2H, ArH), ^{13}C NMR (101 MHz, CDCl$_3$) δ 120.8, 124.1 (q, $J_{13C-19F} = 272.0$ Hz), 125.2, 126.1 (q, $J_{13C-19F} = 3.7$ Hz), 129.3, 129.5 (q, $J_{13C-19F} = 32.7$ Hz), 133.5, 135.9, 137.5; IR (KBr) v 3061, 1614, 1408, 1325, 1165, 1113, 1068, 1014, 840, 600, 443 cm^{-1}; MS (70 eV) m/z 422 (M$^+$); Anal. Calc. for C$_{22}$H$_{12}$F$_6$S: C, 62.56; H, 2.86. Found: C, 62.36; H, 3.21%.

7.14. Synthesis of o-biferrocenoylbenzene (3d)

To a stirred solution of ferrocene (1.310 g, 7.041 mmol) in THF (15 mL) was added t-butyllithium (4.03 mL of a 1.40 M pentane solution, 5.64 mmol) at 0 °C under an N$_2$ atmosphere. After the mixture was stirred at 0 °C for 1 h, it was cooled to −60 °C. A solution of 1,2-di[S-(2-pyridinyl)]benzenedithioate (0.500 g, 1.41 mmol) in THF (10 mL) was added to the mixture, and the resulting mixture was stirred at −60°C for 30 min. The reaction mixture was acidified with aqueous hydrochloric acid, and extracted with ether. The organic layer was dried over

anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, ethyl acetate:hexane = 1:4) to give *o*-diferrocenoylbenzene (**3d**, 0.322 g, 6.41 mmol, 46%): red crystals; mp > 300 °C (decomp.); ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.21 (s, 10H, *free*-Cp), 4.48 (t, $J = 1.9$ Hz, 4H, C$_5$H$_4$), 4.68 (t, $J = 1.9$ Hz, 4H, C$_5$H$_4$), 7.58 (dd, $J = 3.3$, 5.6 Hz, 2H, ArH), 7.83 (dd, $J = 3.3$, 5.6 Hz, 2H, ArH); ^{13}C NMR (101 MHz, CDCl$_3$) δ 70.2, 71.0, 72.2, 79.2, 128.5, 129.7, 140.1, 200.1; IR (KBr) v 3089, 1711, 1644, 1445, 1374, 1286, 1026, 828, 506 cm^{-1}; MS (70 eV) m/z 502 (M$^+$); Anal. Calc. for C$_{28}$H$_{22}$Fe$_2$O$_2$: C, 66.97; H, 4.42. Found: C, 67.01; H, 4.43%.

7.15. Synthesis of 1,3-diferrocenylbenzo[c]thiophene (4d)

A mixture of *o*-diferrocenoylbenzene (**3d**, 0.629 g, 1.25 mmol) and Lawesson's reagent (1.012 g, 2.505 mmol) in dichloromethane (30 mL) was stirred for 12 h at room temperature. After evaporation of the dichloromethane under reduced pressure, the residue was dissolved in ethanol (30 mL) and the mixture was stirred under reflux for 12 h. After the resulting solution was cooled to room temperature, the solvent was evaporated under reduced pressure. The residue was dissolved in chloroform and was washed with aqueous sodium hydroxide (1 mol dm^{-3}). The organic layer was dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, chloroform:hexane = 1:1) and recrystallization from hexane to give 1,3-diferrocenylbenzo[c]thiophene (**4d**, 0.410 g, 0.816 mmol, 65%): purple crystals; mp 196.0 °C (decomp.); ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.18 (s, 10H, *free*-Cp), 4.39 (t, $J = 1.8$ Hz, 4H, C$_5$H$_4$), 4.74 (t, $J = 1.8$ Hz, 4H, C$_5$H$_4$), 7.00 (dd, $J = 3.1$, 6.9 Hz, 2H, ArH), 7.81 (dd, $J = 3.1$, 6.9 Hz, 2H, ArH); ^{13}C NMR (101 MHz, CDCl$_3$) δ 68.4, 68.6, 69.9, 80.2, 121.9, 123.0, 130.7, 135.2; IR (KBr) v 3093, 2927, 1741, 1644, 1464, 804, 740 cm^{-1}; MS (70 eV) m/z 502 (M$^+$); Anal. calcd for C$_{28}$H$_{22}$Fe$_2$S: C, 66.96, H, 4.42. Found: C, 66.80, H, 4.47%.

7.16. Synthesis of 1,3-diferrocenylbenzo[c]selenophene

To a stirred solution of bis(tributyltin) selenide (2.800 g, 4.248 mmol) in toluene (20 mL) was added trimethylalminium (8.1 mL of a 0.98 M THF solution, 7.9 mmol) at 0 °C under an N$_2$ atmosphere. After the mixture was stirred at 50 °C for 4 h, a solution of *o*-diferrocenoylbenzene (**3d**, 0.502 g, 1.00 mmol) in THF (70 mL) was added to the mixture. After stirring at 50 °C for 18 h, water was added. The resulting mixture was extracted with ether. The organic layer was washed with aqueous sodium hydroxide (1 mol dm^{-3}) and saturated sodium hydrogencarbonate solution. Then, it was dried over anhydrous magnesium sulfate and the solvent evaporated under reduced pressure. The residue was purified by column chromatography (silica

gel, chloroform:hexane = 1:1) to give 1,3-diferrocenylbenzo[c]selenophene (**5**, 0.414 g, 0.754 mmol, 75%): purple crystals; mp 196.0 °C (decomp.); ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.19 (s, 10H, *free*-Cp), 4.39 (t, $J = 1.8$ Hz, 4H, C$_5$H$_4$), 4.69 (t, $J = 1.8$ Hz, 4H, C$_5$H$_4$), 6.86 (dd, $J = 3.1$, 7.1 Hz, 2H, ArH), 7.67 (dd, $J = 3.1$, 7.1 Hz, 2H, ArH); ^{13}C NMR (101 MHz, CDCl$_3$) δ 68.7, 69.2, 70.2, 82.4, 122.5, 122.7, 137.6, 139.6; ^{77}Se NMR (76 MHz, CDCl$_3$) δ 687.8; IR (KBr) v 3090, 2346, 1655, 1410, 1314, 1104, 1000, 838, 819, 741, 478 cm^{-1}; MS (70 eV) m/z 550 (M$^+$); Anal. calcd for C$_{28}$H$_{22}$Fe$_2$Se: C, 61.24, H, 4.04. Found: C, 60.99, H, 4.34%.

7.17. X-ray crystal structure analyses of 2d, 4d, and 5

Diffraction data were collected on a Rigaku R-AXIS RAPID diffractometer employing Mo Kα ($\lambda = 0.71075$ Å) radiation. The structure was determined by direct methods (SIR 92 [18] or 97 [19]) and expanded using Fourier technique (DIRDIF99 [20]). All calculations were performed using the Crystal Structure 3.5.1 or 3.6.0 crystal structure analysis package of Rigaku and Rigaku/MSC.

Crystal data for **2d**·CH$_2$Cl$_2$: $M = 587.17$, C$_{29}$H$_{24}$Fe$_2$SCl$_2$, triclinic, space group $P\bar{1}$ (#2), $a = 10.429(2)$ Å, $b = 11.043(2)$ Å, $c = 11.191(2)$ Å, $\alpha = 83.94(2)°$, $\beta = 68.99(2)°$, $\gamma = 84.01(2)°$, $V = 1193.4(5)$ Å^3, $Z = 2$, $D_{calc} = 1.634$ g cm^{-3}, $T = 123 \pm 1$ K, λ(Mo Kα) = 0.71075 Å, 10,031 reflections measured, 4830 unique ($R_{int} = 0.045$). The final cycle of full-matrix least-squares refinement was based on 4405 observed reflections ($I > 2.00\sigma(I)$) and 403 variable parameters with $R_1 = 0.046$, $wR_2 = 0.112$ (all data).

Crystal data for **4d**: $M = 502.24$, C$_{28}$H$_{22}$Fe$_2$S, monoclinic, space group $P2_1/c$ (#14), $a = 11.9107(8)$ Å, $b = 14.1854(8)$ Å, $c = 12.218(1)$ Å, $\beta = 92.359(3)°$, $V = 2062.6(3)$ Å^3, $Z = 4$, $D_{calc} = 1.617$ g cm^{-3}, $T = 123 \pm 1$ K, λ(Mo Kα) = 0.71075 Å, 20,093 reflections measured, 4721 unique ($R_{int} = 0.033$). The final cycle of full-matrix least-squares refinement was based on 4721 observed reflections ($I > 2.00\sigma(I)$) and 368 variable parameters with $R_1 = 0.025$, $wR_2 = 0.031$ (all data).

Crystal data for **5**: $M = 549.14$, C$_{28}$H$_{22}$Fe$_2$Se, monoclinic, space group $P2_1/a$ (#14), $a = 12.139(4)$ Å, $b = 14.190(5)$ Å, $c = 12.083(4)$ Å, $\beta = 92.01(2)°$, $V = 2080(1)$ Å^3, $Z = 4$, $D_{calc} = 1.753$ g cm^{-3}, $T = 123 \pm 1$ K, λ(Mo Kα) = 0.71075 Å, 19,106 reflections measured, 4593 unique ($R_{int} = 0.089$). The final cycle of full-matrix least-squares refinement was based on 3783 observed reflections ($I > 2.00\sigma(I)$) and 369 variable parameters with $R_1 = 0.041$, $wR_2 = 0.114$ (all data).

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: Deposition number CCDC-299170 for compound No. **2d**, CCDC-299169 for compound No. **4d**, and CCDC-299168 for compound No. **5**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data

Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

References

[1] (a) D. Fichou, Handbook of Oligo- and Polythiophenes, VCH, Weinheim, 1999;
(b) P. Naguyen, P. Gómez-Elipe, I. Manners, Chem. Rev. 99 (1999) 1515;
(c) M. Iyoda, M. Hasegawa, Y. Miyake, Chem. Rev. 104 (2004) 5085.
[2] (a) S. Barlow, D. O'Hare, Chem. Rev. 97 (1997) 637;
(b) T.-Y. Dong, W.-Y. Lee, P.-T. Su, L.-S. Chang, K.-J. Lin, Organometallics 17 (1998) 3323;
(c) H. Nishihara, Bull. Chem. Soc. Jpn. 74 (2001) 19;
(d) T. Ito, T. Hamaguchi, H. Nagino, T. Yamaguchi, H. Kido, I.S. Zavarine, T. Richmond, J. Washington, C.P. Kubiak, J. Am. Chem. Soc. 121 (1999) 4625;
(e) T. Hamaguchi, H. Nagano, K. Hoki, H. Kido, T. Yamaguchi, B.K. Breedlove, T. Ito, Bull. Chem. Soc. Jpn. 78 (2005) 591.
[3] (a) D. Schröder, H. Schwarz, B. Löbrecht, W. Koch, S. Ogawa, Eur. J. Inorg. Chem. (1998) 983;
(b) S. Ogawa, M. Kikuchi, Y. Kawai, S. Niizuma, R. Sato, J. Chem. Soc., Chem. Commun. (1999) 1891;
(c) S. Ogawa, T. Ohmiya, T. Kikuchi, A. Kawaguchi, S. Saito, A. Sai, N. Ohyama, Y. Kawai, S. Niizuma, S. Nakajo, T. Kimura, R. Sato, J. Organomet. Chem. 611 (2000) 136;
(d) N. Nagahora, S. Ogawa, S. Yoshimura, Y. Kawai, R. Sato, Bull. Chem. Soc. Jpn. 76 (2003) 1043.
[4] (a) P.R. Buckland, N.P. Hacker, J.F.W. McOmie, J. Chem. Soc., Perkin Trans. 1 (1983) 1443;
(b) D.N. Nicolaides, K.E. Litinas, N.G. Argyropoulos, J. Chem. Soc., Perkin Trans. 1 (1986) 415;
(c) G.M. Brooke, S.D. Mawson, J. Chem. Soc., Perkin Trans. 1 (1990) 1919;
(d) W. Volz, J. Voß, Synthesis (1990) 670;
(e) A. Ishii, J. Nakayama, J. Kazami, Y. Ida, T. Nakamura, M. Hoshino, J. Org. Chem. 56 (1991) 78;
(f) Y. Okuda, M.V. Lakshmikantham, M.P. Cava, J. Org. Chem. 56 (1991) 6024;
(g) J.P. Selegue, K.A. Swarat, J. Am. Chem. Soc. 115 (1993) 6448;
(h) J. Roncali, Chem. Rev. 97 (1997) 173;
(i) E. Müller, R. Thomas, M. Sauerbier, E. Langer, D. Streichfuss, Tetrahedron Lett. 12 (1971) 521;
(j) L. Saris, M.P. Cava, J. Am. Chem. Soc. 98 (1976) 867;
(k) D.O. Cowan, A. Kini, L.Y. Chiang, K. Lerstrup, D.R. Talham, T.O. Poehler, A.N. Bloch, Mol. Cryst. Liq. Cryst. 86 (1982) 1;
(l) D. Lorcy, M.P. Cava, Adv. Mater. 4 (1992) 562;
(m) P. Bauerle, G. Gotz, P. Emerle, H. Port, Adv. Mater. 4 (1992) 564;
(n) S. Musinnanni, J.P. Ferraris, J. Chem. Soc., Chem. Commun. (1993) 172;
(o) A.K. Mohanakrishnan, P. Amaladass, Tetrahedron Lett. 46 (2005) 4225;
(p) A.K. Mohanakrishnan, P. Amaladass, Tetrahedron Lett. 46 (2005) 7201.
[5] S. Ogawa, H. Muraoka, R. Sato, Tetrahedron Lett. 47 (2006) 2479.
[6] A. Heynderickx, A. Samat, R. Guglielmetti, Synthesis 2 (2002) 213.
[7] (a) M. Iyoda, T. Kondo, T. Okabe, H. Matsuyama, S. Sasaki, Y. Kuwatani, Chem. Lett. (1997) 35;
(b) M. Iyoda, T. Okabe, M. Katada, Y. Kuwatani, J. Organomet. Chem. 569 (1998) 225;
(c) M. Iyoda, T. Takano, N. Otani, K. Ugawa, M. Yoshida, H. Matsuyama, Y. Kuwatani, Chem. Lett. (2001) 1310.
[8] (a) N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457;
(b) A.F. Littke, G.C. Fu, Angew. Chem., Int. Ed. 41 (2002) 4176;
(c) S. Kotha, K. Lahiri, D. Kashinath, Tetrahedron 58 (2002) 9633.
[9] (a) M. Araki, Bull. Chem. Soc. Jpn. 47 (1974) 1777;
(b) R.H.L. Kiebooms, P.J.A. Adriaensens, D.J.M. Vanderzande, J.M.J.V. Gelan, J. Org. Chem. 62 (1997) 1473.
[10] G.M. Li, R.A. Zingaro, M. Segi, J.H. Reibenspies, T. Nakajima, Organometallics 16 (1997) 756.
[11] P. Mathur, A.K. Singh, V.K. Singh, P. Singh, R. Rahul, S.M. Mobin, C. Thöne, Organometallics 24 (2005) 4793.
[12] Z. Hu, J.L. Atwood, M.P. Cava, J. Org. Chem. 59 (1994) 8071.
[13] C.D. Bryan, A.W. Cordes, R.C. Haddon, R.G. Hicks, R.T. Oakley, T.T.M. Palstra, A.J. Perel, J. Chem. Soc., Chem. Commun. (1994) 1447.
[14] J.M. Manriquez, M.D. Ward, W.M. Reiff, J.C. Calabrese, N.L. Jones, P.J. Carroll, E.E. Bunel, J.S. Miller, J. Am. Chem. Soc. 117 (1995) 6182.
[15] D.E. Richardson, H. Taube, Inorg. Chem. 20 (1981) 1278.
[16] (a) H. Bock, B. Roth, Phosphorus Sulfur 14 (1983) 211, and references cited therein;
(b) M. Shiotani, Y. Nagata, M. Tasaki, J. Sohama, J. Phys. Chem. 87 (1983) 1170;
(c) A.G. Davies, L. Julia, S.N. Yazdi, J. Chem. Soc., Chem. Commun. (1987) 929;
(d) A.G. Davies, L. Julia, S.N. Yazdi, J. Chem. Soc., Perkin Trans. 2 (1989) 239;
(e) A.G. Davies, C.H. Schiesser, J. Organomet. Chem. 389 (1990) 301;
(f) A. Alberti, L. Favaretto, G. Seconi, J. Chem. Soc., Perkin Trans. 2 (1990) 931;
(g) I. Tabakovic, T. Maki, L.L. Miller, Y. Yu, Chem. Commun. (1996) 1911;
(h) A. Wakamiya, T. Nishinaga, K. Komatsu, Chem. Commun. (2002) 1192;
(i) D. Yamazaki, T. Nishinaga, K. Komatsu, Org. Lett. 6 (2004) 4179.
[17] (a) R. Gerdil, E.A.C. Lucken, J. Am. Chem. Soc. 87 (1965) 213;
(b) P. Cavalieri d'Oro, A. Mangini, G.F. Pedulli, P. Spagnolo, M. Tiecco, Tetrahedoron Lett. 10 (1969) 4179;
(c) L. Lunazzi, G. Placucci, M. Tiecco, Tetrahedron Lett. 13 (1972) 3847.
[18] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. Burla, G. Polidori, M. Camalli, J. Appl. Crystallogr. 27 (1994) 435.
[19] A. Altomare, M. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 32 (1999) 115.
[20] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R. de Gelder, R. Israel, J.M.M. Smits, The DIRDIF-99 program system, University of Nijmegen, Netherlands, 1994.