Monatshefte für Chemie 133, 1055–1066 (2002)

Monatshefte für Chemie
Chemical Monthly

Printed in Austria

Synthesis of New Functionalized Compounds Related to π-Extended Tetrathiafulvalenes with Quinonoidal Structures Bearing a Ferrocene Moiety

Abd El-Wareth A. O. Sarhan*, **Makoto Murakami,** and **Taeko Izumi**

Department of Chemistry and Chemical Engineering, Faculty of Engineering,
Yamagata University, Yonezawa 992-8510, Japan

Summary. A number of π-extended conjugated tetrathiafulvalene (*TTF*) analogues were synthesized as new π-donors, and their structures and physical properties were determined. UV/Vis spectra and cyclic voltammetry of the π-extended ferrocenyl donors were studied in comparison with ferrocene, ferrocenylquinone, and the parent donor. A three-electron redox behaviour was observed. The absorption spectrum of the new donor **16** showed a slight red-shift and a slight increase in intensity relative to the compared compounds.

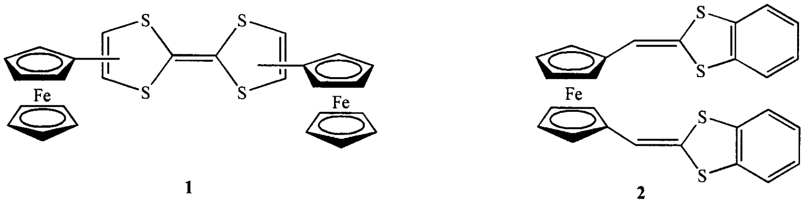
Keywords. Ferrocenyl quinone; Electrical properties; Cyclic voltammetry; Absorption intensity.

Introduction

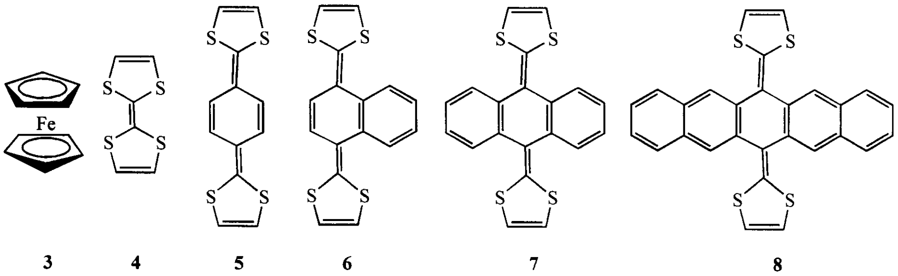
Recently, tetrathiafulvalenes *TTF*s have become an interesting topic of research due to their highly electrical conductivity and superconducting properties [1, 2]. It has also been reported that tetrathiafulvalenes show good π-donor properties [3]. The synthesis of two dithiole rings separated by a conjugated spacer has received great attention as a consequence of the potential of these compounds in the preparation of substances with nonlinear optical properties or as semiconductors. The synthesis of derivatives and analogues of dithiafulvalene (*DTF*) and tetrathiafulvalene (*TTF*) is of considerable interest [4, 5]. Due to the structural and electrochemical properties of ferrocene-containing tetrathiafulvalene derivatives, several ferrocene-tetrathiafulvalenes were constructed as donors for conducting charge transfer complexes. *Ueno et al.* have reported on the first compound belonging to this class of donor conducting materials [6]. A very similar type of donor molecules has recently been introduced by *Bryce* and co-workers [7]. Several charge transfer complexes of metal *bis*-arene compounds containing, among others, the familiar organic acceptor *TCNQ* have been also reported. Recently, *Togni et al.* have synthesized mono- and 1,1′-disubstituted ferrocene derivatives like **1** and **2** as novel donors for the preparation of charge transfer complexes which, structurally and

---

* Corresponding author. E-mail: sarhan@chem.yz.yamagata-u.ac.jp



Scheme 1



Scheme 2

electronically related to the *TTF*s, were conjugated with a ferrocene moiety [8] (Scheme 1). *Togni* has also mentioned that none of these materials has been shown to display physical properties superior to those of the metallocene systems [9] (Scheme 1).

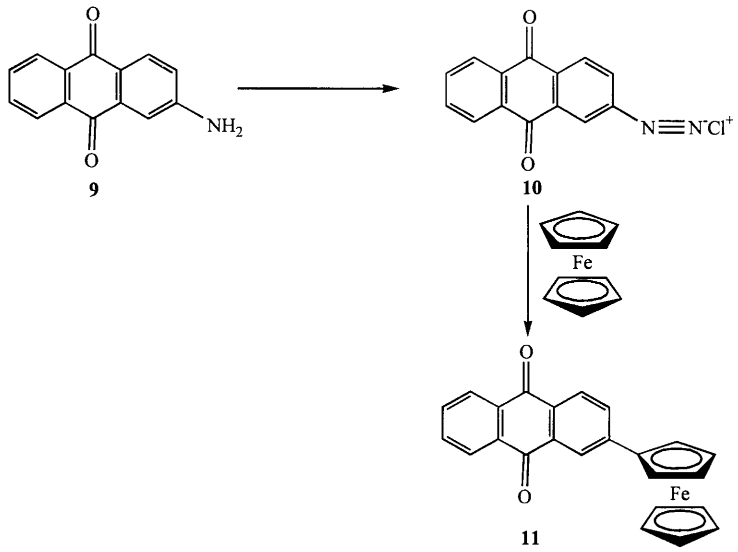
Extended *TTF* (**4**) derivatives like **5**–**8** having a *p*-quinodimethane structure have been used as strong electron donors. Due to their extended conjugation they exhibit a decrease of the intramolecular on-site *Coulomb* repulsion [10]. The formation of monostoichiometric complexes with acceptor molecules is due to their different sizes [11] (Scheme 2).

In contrast to **4** and its derivatives, the *p*-quinodimethane analogues of **4** form stable dication species which constitute CT complexes with interesting electrical and magnetic properties [11–13]. In spite of the importance of these π-extended *p*-quinodimethane analogues of **4** in the search for new opto-electronic properties, the synthesis of π-extended *p*-quinodimethanes connected directly to a ferrocene moiety (**3**) in addition to highly conjugated *TTF* units has not yet been described.

Results and Discussion

Synthesis

In this work we focused on the synthesis of novel donors based on ferrocene-tetrathiafulvalenes separated by conjugated spacers like *p*-benzoquinone or anthraquinone derivatives. We used new derivatives of quinones connected directly to the ferrocene moiety without a conjugated spacer between the quinodimethane and ferrocene moieties. Ferrocene is known to show only a single one-electron redox process at potentials near to the first oxidation step of *TTF* compounds [9]. Comparison of the electrochemical properties of the new π-donors with those of



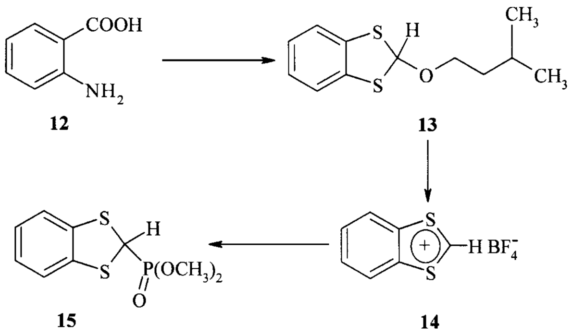
Scheme 3

ferrocene and tetrathiafulvalene homologues previously prepared is important for the molecular design of novel donor systems. We therefore synthesized and investigated the electronic interactions of a new π-extended donor in which the extended *TTF* is directly attached to the strong electron donor ferrocene without spacer. 2-Ferrocenylanthraquinone (**11**) was prepared in 21% yield *via* diazotation of 2-aminoanthraquinone (**9**) followed by coupling with ferrocene in acetic acid at 0°C (Scheme 3).

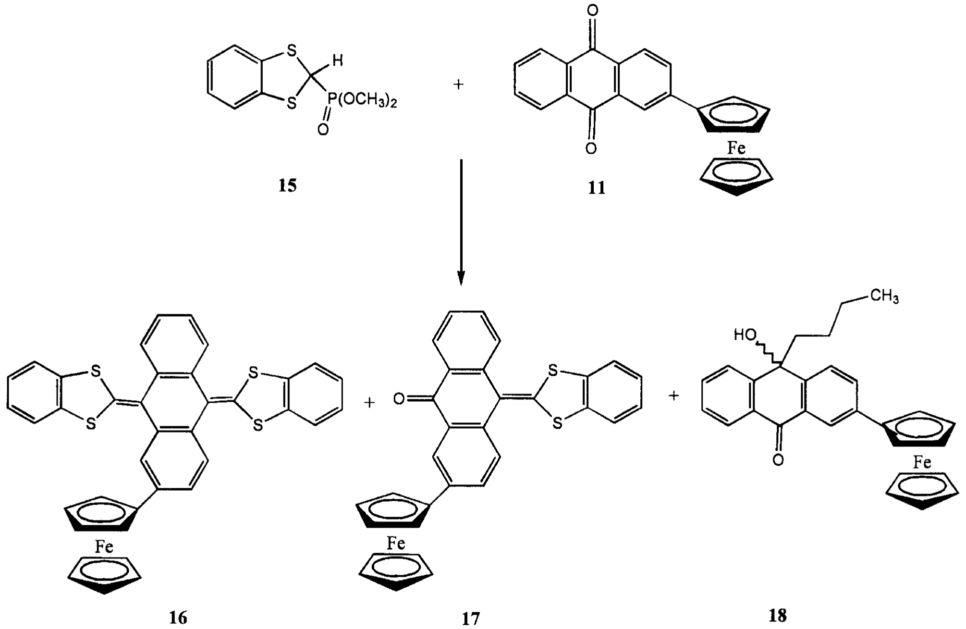
Compound **11** exhibited a deep violet color, and its UV/Vis spectrum in EtOH showed the presence of broad low-energy band at 598 nm which can be accounted as an intramolecular charge transfer band resulting from the strong electron donor ferrocene and the electron acceptor anthraquinone.

2-Dimethoxyphosphinyl-1,3-benzodithiole (**15**) was prepared following well-established procedures from anthranilic acid (**12**) [14]. Thus, 2-butoxy-1,3-benzodithiole (**13**) was obtained through four reaction steps. Aprotic diazotation of anthranilic acid (**12**) by alkyl nitrite gave the corresponding benzendiazonium-2-carboxylate. Its thermal decomposition to benzyne and reaction with carbon disulfide led to the 1,3-dithiole-2-carbene and subsequently to **13** by addition of 2-methylbutanol which either resulted from the diazotation of **12** by alkyl nitrite or was added prior to the reaction. **13** was reacted with HBF_4 in acetic anhydride to give 1,3-benzodithiolylium fluoroborate (**14**) in good yield. Refluxing of **14** with $P(OMe)_3$ in acetonitrile in presence of NaI gave 2-dimethoxyphosphinyl-1,3-benzdithiole (**15**) in high yield [14] (Scheme 4).

Synthesis of the target molecule **16** was carried out by *Wittig-Horner* olefination as shown in Scheme 5. The 2-ferrocenylquinone **11** was reacted with **15** in the presence of *n*-BuLi at −78°C in dry *THF*. **16** was obtained after chromatography as orange crystals in 28% yield; in addition, the starting compound **11** was isolated in very low yield. **17** could not be isolated in pure form and good yield; it was characterized by ^1H and ^{13}C NMR spectroscopy and by FAB mass spectra



Scheme 4



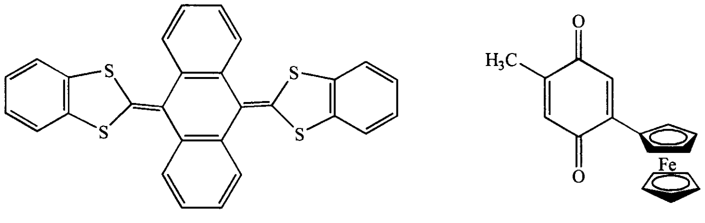
Scheme 5

(M$^+$: $m/z = 528$). In addition, the unexpected racemic anthrone derivative **18** was obtained as yellow orange crystals in 24% yield (Scheme 5).

The IR spectra of **16** lacked the carbonyl group of the 2-ferrocenylquinone (**11**) at 1666 cm^{-1}. The ^{13}C NMR spectrum also proved the absence of a CO group. Mass spectroscopic analysis gave the expected molecular ion peak at $m/z = 664$.

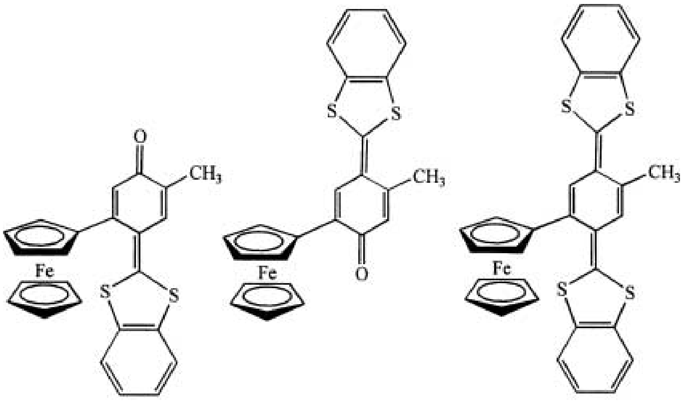
The structure of compound **18** was determined by spectroscopic analysis. The FAB mass spectra gave a molecular mass of 450, which agreed with the suggested structure. The ^{1}H NMR spectrum revealed 7 aromatic protons (besides ferrocene), butyl protons, and one hydroxy proton. The ^{13}C NMR spectrum showed only one carbonyl group at $\delta = 183.27$ ppm. The IR spectrum indicated the presence of a OH group ($\nu = 3467\,\mathrm{cm}^{-1}$) and a carbonyl group ($\nu = 1650\,\mathrm{cm}^{-1}$).

For comparison with the π-extended donor **16**, **19** was prepared by a *Wittig-Horner* reaction (n-BuLi/*THF*, −78°C) as yellow crystals in 97% yield [14c, 17] (Scheme 6).



19 **20**

Scheme 6



21 **22** **23**

Scheme 7

2-Ferrocenyl-5-methyl-*p*-benzoquinone (**20**) was obtained in 20% overall yield *via* several steps following the method reported by *Izumi et al.* [15]. Reaction of **20** with 2-dimethoxyphosphinyl-1,3-benzodithiole (**15**) using *n*-BuLi in *THF* at −78°C followed by stirring at room temperature overnight gave a mixture of unidentified products; neither the dithiafulvalenes **21** and **22** nor the tetrathiafulvalene **23** were formed. Several other attempts to synthesize the *TTF* **23** were also unsuccessful (Scheme 7).

Presently, attempts are made to synthesize 2-ferrocenyl-1,4-benzoquinone, 2-ferrocenyl-1,4-naphthoquinone, and 6-ferrocenyl-1,4-naphthoquinone and to react them with **15** to obtain different π-extended donors for electrochemical studies.

Electrochemical properties

The electrochemical properties of **16**, **19**, and **11** in comparison to ferrocene (**3**) were investigated by cyclic voltammetry in CH_2Cl_2 in the presence of 0.1 *M* tetra-*n*-butylammonium perchlorate (*TBAP*) as the supporting electrolyte using a Pt working electrode and a $Ag^+/AgCl$ reference electrode at ambient temperature. The donors **16** and **19** displayed one pair of redox waves corresponding to a one-electron transfer process; the redox potentials are summarized in Table 1.

Table 1. Formal electrode potentials for the redox changes in CH_2Cl_2; scan rate: $20\,mV \cdot s^{-1}$; supporting electrolyte: *TBAP* (0.1 *M*)

	Oxidation ($E^{1/2}$/V)	Reduction ($E^{1/2}$/V)
3	+0.51	+0.54
16	+0.58	+0.60
19	+0.67	–

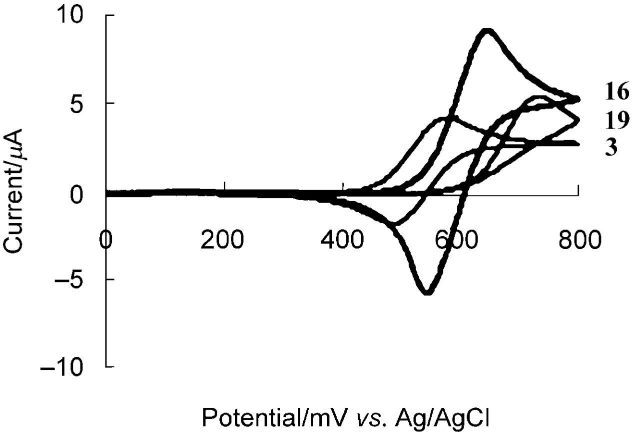


Fig. 1. Cyclic voltammograms of **3**, **16** and **19** in CH_2Cl_2 on a platinum electrode; $c = 1.0 \times 10^{-3}\,M$, scan rate: $20\,mV \cdot s^{-1}$, base electrolyte: *TBAP*, 0.1 *M*

Comparison of the redox potentials reveals that the oxidation potential of **16** is different from the oxidation potential of **19**: $E^{1/2}(\mathbf{19})-E^{1/2}(\mathbf{16}) = 0.09\,V$. $E^{1/2}(\mathbf{19})-E^{1/2}(\mathbf{16})$ is a measure of the on-site *Coulomb* repulsion and suggests the direct connection of the ferrocene to the π-extended donor **16**, thereby changing the electron donating ability of the donor. Considering all variables, **16** exhibited a single electrochemically reversible three-electron oxidation process at ambient temperature, whereas **19** showed a single electrochemically irreversible two-electron oxidation process under the same conditions (Fig. 1).

Increasing the scan rates gave the same peak pattern, but resulted in a significant increase of E_{pa} and a decrease of E_{pc}, indicative of a slow heterogeneous electron transfer process as shown in Fig. 2.

A striking feature of **16** is that this molecule undergoes a three-electron redox process observed as a single wave. The oxidation peaks could not be resolved by reducing the scan rate from 600 to $20\,mV \cdot s^{-1}$ (Fig. 2) or by using different solvents (Fig. 3). The redox wave of **16** is chemically reversible but electrochemically irreversible; the peak-to-peak potential varies from 190 to 100 mV depending on scan rate and solvent. The oxidation peak potential in CH_3CN/CH_2Cl_2 was lower than that in either CH_2Cl_2 or *THF* ($CH_3CN/CH_2Cl_2 < CH_2Cl_2 <$ *THF*) on the same electrodes at a scan rate of $20\,mV \cdot s^{-1}$ (Fig. 3).

The oxidation wave of ferrocene is reversible and occurs at the potential of the $Fe^{II/III}$ redox couple. The coalescence of the two different oxidation processes into one reveals the influence of the ferrocene moiety and the quinonoid structure

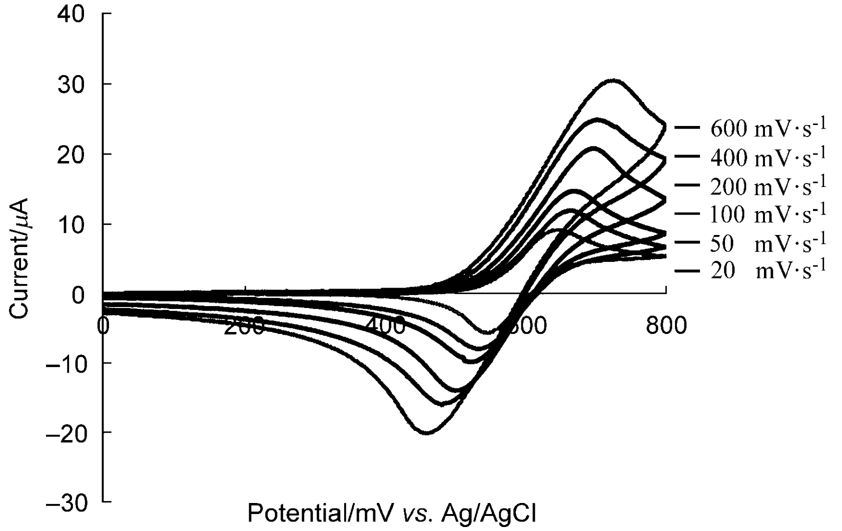


Fig. 2. Cyclic voltammograms of **16** in CH_2Cl_2 on a Pt electrode; $c = 1.0 \times 10^{-3}$ *M*, scan rate: 20–600 mV · s^{-1}, base electrolyte: *TBAP*, 0.1 *M*

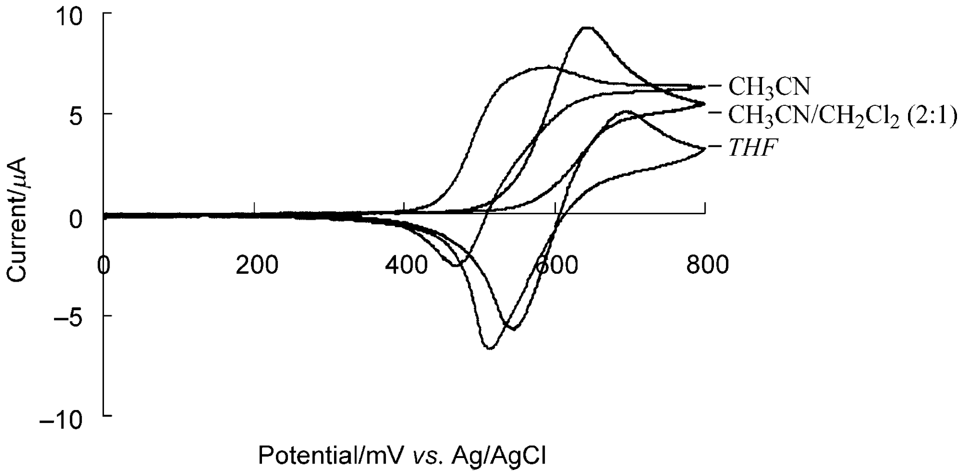


Fig. 3. Cyclic voltammograms of **16** in CH_2Cl_2, *THF* and CH_3CN/CH_2Cl_2 on a Pt electrode; $c = 1.0 \times 10^{-3}$ *M*, scan rate: 20 mV · s^{-1}, base electrolyte: *TBAP*, 0.1 *M*

between the two 1,3-dithiole rings. Three one-electron processes lead directly to the formation of a tricationic state Fc^{+}-ex*TTF*$^{2+}$ as described in the literature [9b]. The electrochemical data of **16** recorded in different solvents are shown in Fig. 3 and Table 2.

Bryce et al. [11] have reported that the X-ray analysis of the analogue of **19** was found to show a highly distorted geometry in the neutral state, whereas *Liu et al.* [10b] have suggested that this geometric distortion could be hold responsible for the coalescence of the oxidation wave of the anthracene moiety with that of the two 1,3-dithiole rings.

Table 2. Formal electrode potentials for the redox changes of the π-extended donor **16** on a Pt electrode; scan rate: $20\,\mathrm{mV} \cdot \mathrm{s}^{-1}$, base electrolyte: *TBAP* (0.1 *M*)

Solvent	Oxidation ($E^{1/2}$/V)	Reduction ($E^{1/2}$/V)
CH_3CN/CH_2Cl_2	+0.50	+0.53
THF	+0.63	+0.57
CH_2Cl_2	+0.58	+0.60

The coalescence behaviour of **16** indicated a planar aromatic hydrocarbon skeleton in the extended *TTF* moiety. It is known that these unstable radical cations easily form stable dications upon further oxidation in which the *Coulomb* repulsion is remarkably decreased [1, 10b, 12b].

Electronic spectroscopy

As shown in Fig. 4, the UV/Vis spectra of **16** and comparable compounds in ethanol are mainly dominated by the absorption of the ex*TTF* moiety in the region of 220–250 nm. Because of the weak intensity of the ferrocene spectrum, the $\log\varepsilon$ scale is used for comparison. The absorptions of **16** were observed at 241 ($\log\varepsilon = 4.78$), 352 ($\log\varepsilon = 4.32$), and 416 ($\log\varepsilon = 4.47$) nm. Upon comparison of the λ_{max} values of donors **16** and **19**, a slight red-shift and an increase of the absorption intensities were observed. This means that ground-state intramolecular electronic interactions are observed in the case of **16** (Table 3).

To account for the electrochemical observations, the molecular geometry of **16** was optimized using Win-MOPAC at the AM1 level. The minimum energy conformation of **16** is shown in Figure 5. The donor molecule adopts a butterfly shape with the central ring in a boat conformation, which is in good agreement with data

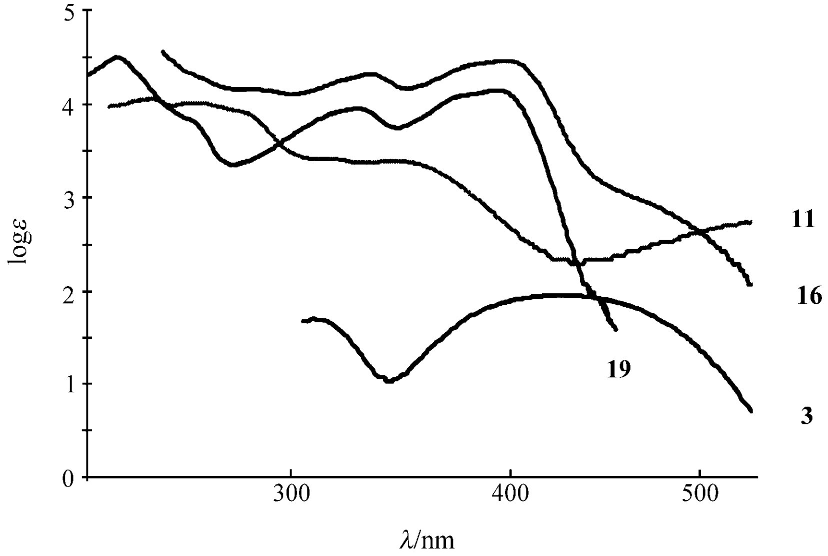


Fig. 4. UV/Vis spectra of **3**, **11**, **16**, and **19** in EtOH ($c = 4.05 \times 10^{-5}\,M$)

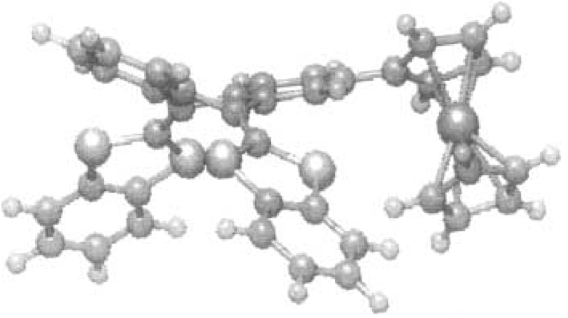


Fig. 5. AM1 optimized geometry of **16**

Table 3. Absorption maxima in the electronic spectra of quinones **11** and **20** and donors **16** and **19** in EtOH

	λ_{max}/nm (logε)
3	440 (2.01), 326 (1.77)
20	396 (2.82), 276 (4.01)
11	562 (2.77), 363 (3.4), 272 (4.01), 250 (4.06)
16	416 (4.47), 352 (4.32), 241 (4.78)
19	410 (4.15), 345 (3.95), 234 (4.32)

reported for analogues published recently [1, 8, 9a]. The conjugation between the donor and the ferrocene moiety ($\theta = 130.1°$) is rather pronounced.

Conclusions

The novel compound **16** was synthesized as a new π-donor, and its structure was confirmed by spectroscopic analyses. The electrochemical properties of **16** were studied using cyclic voltammetry at ambient temperatures on a Pt working electrode with *TBAP* as the supporting electrolyte. A three-electron redox behavior was observed as a single wave. The advantage of introducing ferrocene into the donor is that ferrocene has only a single one-electron redox process. Considering the fact that the π-extended donor **16** contains two different types of donor moieties, it was important to determine which is easier to oxidize by changing the solvent or using different scan rates. A single quasireversible three-electron oxidation process was observed in CH_2Cl_2, *THF*, or a mixture of CH_2Cl_2 and CH_3CN, whereas **19** exhibited a single electrochemically irreversible two-electron oxidation process under the same conditions. It is important to recognize that both ferrocene (**3**) and **16** showed typical electrochemically reversible redox processes with redox potentials. A comparison of the absorption bands of **16** and **19** showed a slight red-shift and a slight increase in the absorption intensities for **19**.

Experimental

Solvents were distilled before use. 2-Aminoanthraquinone is commercially available; ferrocene was prepared according to Ref. [19]. 2-Ferrocenyl-5-methyl-1,4-benzoquinone (**20**) was obtained according to a method previously described [15]. Melting points were recorded on a Gallencamp melting point apparatus and are uncorrected. IR spectra were measured on a Hitachi 260-10 spectrometer, ^{1}H and ^{13}C NMR spectra on a Varian Inova 500 MHz spectrometer at room temperature. Chemical shifts are given in δ units (ppm) relative to internal *TMS*; *J* values are given in Hz. $CDCl_3$ was used as solvent unless otherwise stated. Mass spectra were obtained using a Jeol JMS-AX505HA instrument. UV/Vis Spectra were detected using a Hitashi U-2010 spectrophotometer. Cyclic voltammetry was performed on a Lawrence Model CS-1090/Model CS-1087 system. Column chromatography was conducted on silica gel 60 (230–400 mesh ASTM).

2-Ferrocenylanthraquinone (**11**; $C_{24}H_{16}O_2Fe$)

A solution of 2.8 g (40 mmol) $NaNO_2$ in 40 cm^3 H_2O was added to a suspension of 8.0 g (36.0 mmol) 2-aminoanthraquinone (**9**) in 200 cm^3 conc. HCl at 0°C. The formed diazonium salt was added to a solution of 6.6 g (35.0 mmol) ferrocene in 200 cm^3 acetic acid under a stream of N_2 at 0°C. The reaction mixture was stirred at room temperature for 10 h and then left overnight. The precipitate was collected by filtration, washed with EtOH, and dried to give 10.5 g of a dark brown product. Chromatography on silica gel (benzene) afforded yellow crystals of anthraquinone in the early fractions, followed by deep-violet crystals of **11** (3.0 g (21%), m.p.: 141–143°C). The final fraction consisted of 0.4 g deep-gray crystals of 1,1′-dianthraquinonylferrocene (M^+: $m/z = 598$).

IR (KBr): $\nu = 3072$w, 2362m, 1666s, 1589s, 1448s, 1409m, 1328s, 1166m, 1105s, 711s, 669s cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz, δ): 8.3 (m, 3 aromatic H), 8.2 (d, $J = 8.5$ Hz, 1 aromatic H), 7.85 (m, 3 aromatic H), 4.86 (s, 2 ferrocene H), 4.50 (s, 2 ferrocene H), 4.08 (s, 5H, ferrocene H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz, δ): 183.64, 182.79 (2 CO), 147.60 (aromatic C), 134.15–123.71 (aromatic C), 82.13, 70.59, 70.04, 67.24 (ferrocene C) ppm; MS: m/z (%) = 392 (100).

2-(3-Methylbutoxy)-1,3-benzdithiol (**13**; $C_{12}H_{16}OS_2$)

The method previously reported by *J. Nakayama* [14a] was modified as described. A sample of 21 g anthranilic acid (**1**; 0.15 mol) was added portionwise over a period of 40 min to a stirred and gently refluxing solution of 21 g (0.18 mol) isoamyl nitrite, 26.5 g (0.3 mol) 3-methylbutanol, and 75 cm^3 CS_2 in 300 cm^3 1,2-dichloroethane:chloroform = 1:1. After the addition was completed, the mixture was refluxed for one further hour. The resulting red reaction mixture was evaporated under vacuum, and the residue was washed successively with H_2O (5x) and dried over Na_2SO_4. Solvent and excess reagents were removed under reduced pressure, and the red viscous oily residue was purified by column chromatography using hexane as eluent to give pale yellow oils of **13** in the first fractions (28.6 g, 77%). Increasing the polarity of the eluent by adding 30% $CHCl_3$ led to the isolation of unidentifiable polymeric material.

1,3-Benzodithiolium fluorborate (**14**; $C_7H_5S_2BF_4$)

To a stirred and ice-cooled solution of 3.93 g (16.0 mmol) **13** in 50 cm^3 Ac_2O, 7.0 g HBF_4 (79.7 mmol) was added dropwise over 20 min. After stirring at room temperature for 20 min, anhydrous diethyl ether (100 cm^3) was added to the mixture, and the resulting precipitate was collected by filtration and washed with 100 cm^3 anhydrous diethyl ether to give 2.0 g (51%) of **14** as colorless crystals. M.p.: 148–150°C (Ref. [14b]: 149–150°C (dec.)).

2-Dimethoxyphosphoryl-2-H-1,3-benzdithin (**15**; $C_9H_{11}PO_3S_2$)

A mixture of 0.935 cm^3 (8.0 mmol) $P(OCH_3)_3$ and 1.2 g (8.0 mmol) NaI were added successively to a stirred solution of 1.8 g (7.5 mmol) **14** in 60 cm^3 dry CH_3CN at room temperature under a stream of N_2. The mixture was stirred for further 2.5 h at room temperature, the solvent was removed under vacuum, and H_2O was added. The colorless crystals formed were filtered off and washed with H_2O (3x) to give 1.6 g (81.6%) of **15** as colorless crystals.

M.p.: 121–123°C (Ref. [14c]: 122–123°C); IR (KBr): $\nu = 3008$m, 2954s, 2898s, 2850s, 1625w, 1565w, 1442s, 1255s, 1207s, 1180s, 116s, 1027s, 759s, 740s cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz, δ): 7.20 (m, 2H, aromatic H), 7.03 (m, 2H, aromatic H), 4.88 (d, $J = 5$ Hz, CH$_2$), 3.8 (s, CH$_3$), 3.77 (s, CH$_3$); ^{13}C NMR (CDCl$_3$, 125 MHz, δ): 136.52 (aromatic C), 126.1 (aromatic CH), 122.22 (aromatic CH), 54.80 (CH$_2$), 44.58 (CH$_3$), 43.31 (CH$_3$); FAB-MS: m/z (%) = 262 (87).

2-Ferrocenyl-9,10-bis-(1,3-benzdithiol-2-ylidene)-9,10-dihydroanthracene (**16**; $C_{38}H_{24}S_4Fe$)

A sample of 286 mg (1.1 mmol) **15** was stirred in 40 cm^3 dry *THF* under a stream of N_2 at −78°C. 1.2 cm^3 *n*-BuLi solution (1.6 *M* in hexane) were added, and the mixture was stirred for 15 min. A solution of 203 mg (0.55 mmol) 2-ferrocenylanthraquinone (**11**) in 50 cm^3 dry *THF* was added portionwise. The temperature of the mixture was raised to room temperature, and it was kept overnight with stirring. The *THF* was removed under vacuum, and the residue was washed with H_2O and extracted with CHCl$_3$ and dried over Na$_2$SO$_4$. The crude oily product was chromatographed on silica gel using CHCl$_3$: hexane = 1 : 2 to give 40 mg of yellow crystals of an unknown compound in the early fractions, followed by 100 mg of yellow orange crystals of **16** (28%). With CHCl$_3$:hexane = 1:1, 108 mg of orange crystals of the racemic anthrone **18** were obtained (24%).

M.p.: 139–143°C; IR (KBr): $\nu = 3050$w, 2960m, 2923s, 1656m, 1567m, 1523s, 1446s, 1430s, 1261s, 1103s, 1027s, 806s, 736s cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz, δ): 7.87 (d, $J = 1.5$ Hz, 1 aromatic H), 7.77–7.75 (m, 2 aromatic H), 7.65 (d, $J = 8$ Hz, 1 aromatic H), 7.44 (dd, $J = 8$ Hz, $J = 1.5$ Hz, 1H, aromatic H), 7.38 (m, 2 aromatic H), 7.23–7.19 (m, 4 aromatic H), 7.08–7.06 (m, 4 aromatic H), 4.776–4.74 (dd, $J = 6$ Hz, $J = 1$ Hz, 2 ferrocene H), 4.38–4.36 (m, 2 ferrocene H), 4.15 (s, 5 ferrocene H) ppm; ^{13}C NMR (CDCl$_3$, 125 MHz, δ): 138.62–121.89 (aromatic C and CH), 85.90 (ferrocene C), 70.61, 70.10, 70.00, 67.92, 67.09 (ferrocene C) ppm; FAB-MS: m/z (%) = 664 (13).

18: M.p.: 151–152°C; IR (KBr): $\nu = 3467$s, 3093w, 3066w, 2954s, 2861s, 1650s, 1600s, 1455s, 1380s, 1326s, 1037s, 765s, 696s cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz, δ): 8.25 (d, $J = 7.5$ Hz, 1 aromatic H), 8.15 (dd, $J = 8$ Hz, $J = 1$ Hz, 1H, aromatic H), 7.97 (d, $J = 1.5$ Hz, 1 aromatic H), 7.92 (d, $J = 8$ Hz, 1 aromatic H), 7.68 (dt, $J = 1.5$ Hz, $J = 7.5$ Hz, 1 aromatic H), 7.55 (dd, $J = 2$ Hz, $J = 7.5$ Hz, 1 aromatic H), 7.50 (dt, $J = 1.5$ Hz, $J = 7.5$ Hz, 1 aromatic H), 4.83–4.79 (m, 2 ferrocene H), 4.45 (m, 2 ferrocene H), 4.04 (s, 5 ferrocene H), 2.45 (s, 1 OH), 2.06–2.03 (m, CH$_2$), 1.05–1.02 (m, CH$_2$), 0.72 (m, CH$_2$), 0.65–0.63 (t, $J = 7.5$ Hz, CH$_3$) ppm; ^{13}C NMR (CDCl$_3$, 125 MHz, δ): 183.27 (CO), 147.57, 147.31, 146.34, 133.48, 131.13 (aromatic C), 128.53, 128.03, 127.15, 126.74, 125.88, 125.48, 122.73 (aromatic CH), 83.15 (ferrocene C), 73.01, 70.20, 70.10, 69.94 (ferrocene CH), 48.44 (CH$_2$), 26.14 (CH$_2$), 22.47 (CH$_2$), 13.74 (CH$_3$) ppm; FAB-MS: m/z (%) = 450 (100).

9,10-Bis-(1,3-benzdithiol-2-ylidene)-9,10-dihydroanthracene (**19**; $C_{28}H_{16}S_4$)

According to the method described for synthesis of **16**, **19** was obtained in 98% yield.

IR (KBr): $\nu = 3052$w, 2919w, 1600w, 1567s, 1521s, 1446s, 1430s, 1282s, 1157m, 1122m, 754s, 674s cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz, δ): 7.74 (m, 4 aromatic H), 7.37 (m, 4 aromatic H), 7.27–7.16 (m, 4 aromatic H), 7.07 (m, 4 aromatic H) ppm; ^{13}C NMR (CDCl$_3$, 50 MHz, δ): 136.71, 135.61, 132.51 (aromatic C, anthracene ring), 126.80, 126.20, 126.14 (aromatic C, benzdithiole C), 124.23, 121.42 (C=C) ppm; FAB-MS: m/z (%) = 480 (23).

Acknowledgments

We are grateful to Fujitsu Co. Ltd. for an offer of ‘Win MOPAC’. This work was partially supported by a Grant-Aid for Scientific Research (No. 12650844) from the Ministry of Education, Sciences, Sports, and Culture (Japan).

References

[1] Martin N, Sanchez L, Seoane C, Orti E, Viruela PM, Veruela R (1998) J Org Chem **63**: 1268

[2] Yoshida Z, Kawase T, Awaji H, Sugimoto I, Sugimoto T, Yoneda S (1983) Tetrahedron Lett **24**: 3469

[3] Belyasmine A, Gorgues A, Jubault M (1991) Synthetic Metals **41–43**: 2323

[4] Moore AJ, Bryce MR (1991) Synthesis 26 and references cited therein

[5] Martin N, Sanchez L, Guldi DM (2000) Chem Commun 113

[6] Ueno Y, Sano H, Okawara M (1980) J Chem Soc Chem Commun 28

[7] Moore AJ, Skabara PJ, Bryce MR, Batsanov AS, Howard JAK, Daley STAK (1993) J Chem Soc Chem Commun 417

[8] Togni A, Hobi M, Rihs G, Rist G, Albinati A, Zanello P, Zech D, Keller H (1994) Organometallics **13**: 1224

[9] a) Togni A (1995) Ferrocene-Containing Charge Transfer Complexes. Conducting and Magnetic Materials. In: Togni A, Hayashi T (eds) Ferrocenes. VCH, Weinheim, p 434; b) Liu S, Perez I, Martin N, Echegoyen L (2000) J Org Chem **65**: 9092

[10] a) Martin N, Pérez I, Sanchèz L, Seoane C (1997) J Org Chem **62**: 870; b) Yamashita Y, Kobayashi Y, Migashi T (1989) Angew Chem Int Ed Engl **28**: 1052; c) Kitamura C, Tanaka S, Yamashita Y (1996) Adv Mater **8**: 570

[11] Bryce MR, Moore AJ, Hasan M, Ashwell GJ, Fraser AT, Clegg W, Hursthouse MB, Karaulov AI (1990) Angew Chem Int Ed Engl **29**: 1450

[12] a) Bryce MR, Moore AJ (1988) Synthetic Metals **25**: 203; b) Bryce MR, Coffin MA, Hursthouse MB, Karaulov AI, Müllen K, Scheich H (1991) Tetrahedron Lett **32**: 6029; c) Bryce MR, Moore AJ (1991) J Chem Soc Perkin Trans 1, 157

[13] a) Godbert N, Batsanov AS, Bryce MR, Howard JAK (2001) J Org Chem **66**: 713; b) Pérez I, Liu S, Martin N, Echegoyen L (2000) J Org Chem **65**: 3796; c) Lorcy D, Guerin D, Boubekeur K, Carlier R, Hascoat P, Tallee A, Robert A (2000) J Chem Soc Perkin Trans 1, 2719

[14] a) Nakayama J (1975) Synthesis 38; b) Nakayama J, Fujiwara K, Hoshino M (1975) Chem Lett 1099; c) Akiba K, Ishikawa K, Inamoto N (1978) Bull Chem Soc Jpn **51**: 2674

[15] Kasahara A, Izumi T, Ogata H, Tano S, Ito Y, Fujisawa T, Ogata T (1985) Bull Yamagata Univ (Eng) **18**: 125

[16] Benitez FM, Grunwell JR (1978) J Org Chem **43**: 2917

[17] Yamashita Y, Miashi T (1988) Chem Lett 661

[18] Bryce MR, Batsanov AS, Finn T, Hanse TK, Howard JAK, Kamenjicki M, Lednev IK, Asher SA (2000) Chem Commun 295

[19] Wilkinson G (1963) Org Synth **4**: 473

Received September 19, 2001. Accepted (revised) October 23, 2001