

# Synthesis and electrochemical properties of 1,1'-bis(benzo-1,3-dithiol-2-ylidene)ferrocene derivatives as novel electron donor compounds

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Dedicated to Prof. Dr. H.M.R. Hoffmann, Ph.D., D.Sc., to be professor emeritus at University of Hannover, Germany

## Abstract

A number of 1,1'-bis(benzo-1,3-dithiol-2-ylidene)ferrocene derivatives **7a–b** and **12–14** based on the strong electron donating ability of 1,3-dithiole and ferrocene moieties were synthesized as new  $\pi$ -donors. The structure and physical properties of these compounds were characterized both by experimental techniques and spectral analysis. These new classes of donor compounds were obtained in very high yields based on modification of the Wittig–Horner reaction and the 1,3-dithiole rings were separated by conjugated spacers including aryl–ferrocenyl–aryl. The electrochemical properties of the new compounds have been studied in comparison to DB-TTF **4** analogues, and the parent ferrocene donor by cyclic voltammetry (CV), using Pt electrode as the working electrode in  $\text{CH}_2\text{Cl}_2$  solutions at room temperature. Three subsequent oxidation processes are observed as three oxidation waves associated only with two reduction processes. Polycrystalline samples of **14a–b** are conducting  $\sigma_{\text{rt}}$  **14a** =  $0.2 \text{ S cm}^{-1}$  and  $\sigma_{\text{rt}}$  **14b** =  $4.8 \times 10^{-4} \text{ S cm}^{-1}$  respectively, while compounds **15** and **16** were found essentially as insulator ( $\sigma_{\text{rt}} < 10^{-10} \text{ S cm}^{-1}$ ).

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**Keywords:** Ferrocene-dialdehydes; Benzo-1,3-dithiole-2-ylidene moieties; Wittig–Horner reaction; Organic conductors; Electrochemical properties; Cyclic voltammetry

## 1. Introduction

Tetrathiafulvalene (TTF) and its analogues were prepared as strong electron-donor compounds for the development of electrically conducting materials. The first organic metal TTF-TCNQ was discovered after TTF was first synthesized by Wudl in 1970 [1]. While, the first organic molecule based superconductor was prepared from TTF analogue called tetramethyltetraselenafulvalene (TMTSF) in 1979 [2a]. The topics of organic metals have been reviewed by several authors during the last three decades [2]. After the discovery of metallic behavior of the TTF–TCNQ complex, various synthetic approaches to TTFs and tetraselenafulvalenes gained wide attention and charge-transfer from TTF to

tetracyanoquinodimethane (TCNQ) between adjacent stacks were extensively recognized [3]. Recently, Martin and Segura have reported that, the utility of TTF as building blocks in macromolecular and supramolecular structures, as well as molecule based ferromagnetic properties, as synthetic intermediates in organic chemistry, as a donor moiety in intramolecular donor–acceptor (D–A) systems in nonlinear optic (NLO) materials and in association with the fullerene core, as well as in the preparation of liquid crystalline materials and Langmuir–Blodgett (LB) films has made TTF one of the most extensively studied molecules [4].

Chemical modifications of the TTF framework have been added to improve their electrical conductive properties. Several TTFs like BEDT-TTF (**1**) and TTF (**2**) were previously prepared via one step reaction with different yields [5]. Bis-(ethylenedithio)tetrathiafulvalene (BEDT-TTF) (**1**) has been widely used for the preparation of different organic superconductors [6] (Chart 1). TTFs containing two or more fused or covalently

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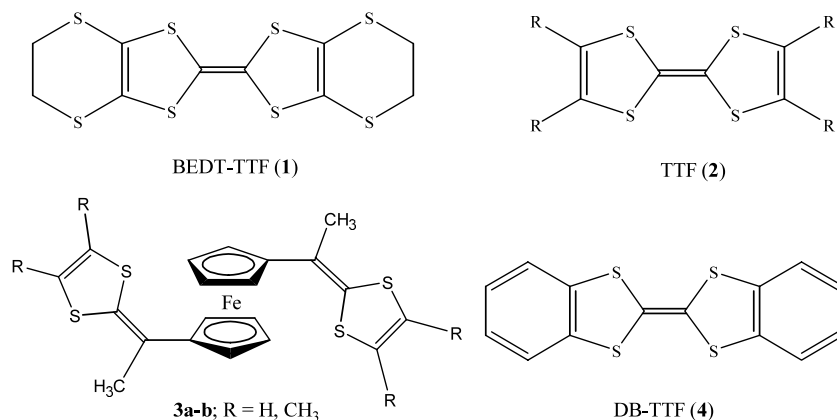


Chart 1.

attached TTFs units have been also used for preparing super conducting salts [7].

Since, Ueno et al. have prepared the first compound belonging to ferrocene-tetrathiafulvalenes (Fc-TTF) as a *cis/trans* isomeric mixture and was shown to form 1:1 CT complexes with both TCNQ and DDQ respectively [8]. A few reports have appeared dealing with the electrochemical properties and CT complexes of the dithiafulvalenes and tetrathiafulvalenes having ferrocene moiety [9]. Martin and Segura have reported recently that TTF is a molecule with unique electronic properties that challenges the creativity and inventiveness of chemists in areas such as organic, polymer and material chemistry and supramolecular chemistry [4]. These findings have prompted us to synthesize and investigate the electrochemical properties of novel TTF derivatives separated by insertion of a ferrocene moiety as conjugated spacer between the two 1,3-dithiole rings of the TTF (Chart 1).

## 2. Results and discussions

In this work we report a synthesis of novel TTF derivatives as new electron donors using the direct Wittig–Horner cross coupling reaction. 1,1'-Ferrocene dicarbonyl derivatives (**5a–b**) were synthesized cleanly and in high yields according to the reported methods [10]. The benzo-1,3-dithiole-2-phosphonate (**6**) was obtained in a relatively high yield as mentioned in the literature [11].

Reaction of ferrocene-1,1'-dicarboxaldehyde (**5a**) or 1,1'-diacetylferrocene (**5b**) with **6** in dry THF in the presence of *n*-BuLi at  $-78\text{ }^{\circ}\text{C}$  following to the Wittig–Horner reaction method afforded the corresponding 1,1'-bis[(benzo-1,3-dithiol-2-ylidene)methyl/ethyl]-ferrocenes (**7a–b**) in good yields as shown in Scheme 1. The donor **7a** was prepared following the procedures reported by Togni et al. as red crystals in good yield [12].

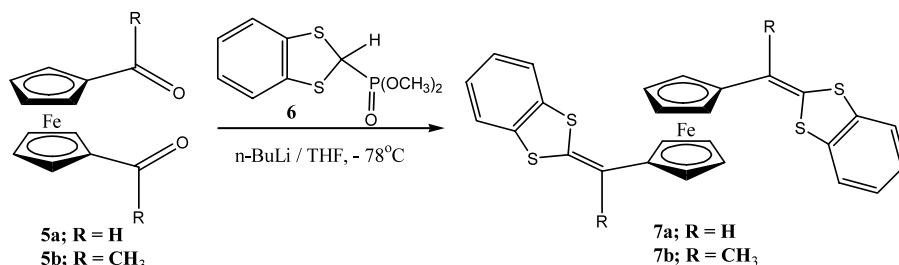
Following the methods previously described in literature [13], the 1-(*p*-formylphenyl)-1'-(4-formyl-1-naphthyl)ferrocene (**10**) and 1-(*m*-formylphenyl)-1'-(3-formyl-2-methoxyphenyl)ferrocene (**11**) intermediates were prepared. The synthesis of the dialdehydes **10** was carried out by Gomberg's arylation of *p*-(ethoxycarbonyl)ferrocene with diazonium salt derived from 4-ethoxycarbonyl-1-naphthylamine, followed by reduction with  $\text{LiAlH}_4$  and oxidation with activated  $\text{MnO}_2$  in dry  $\text{CHCl}_3$  (Scheme 2).

In the same manner the 1-(*m*-formylphenyl)-1'-(3-formyl-5-methoxyphenyl)ferrocene (**11**) was synthesized according to Gomberg's arylation of ferrocene with diazonium salt of the methyl 3-amino-2-methoxybenzoate to afford the corresponding 3-methoxycarbonyl-2-methoxyphenylferrocene which subjected to diazotization with diazonium salt derived from methyl 3-amino-benzoate, followed by reduction with  $\text{LiAlH}_4$  and oxidation with activated  $\text{MnO}_2$  in dry  $\text{CHCl}_3$  (Scheme 3).

Upon reaction of the dialdehyde **10** with the benzo-1,3-dithiole-2-phosphonate (**6**) using slight modification of the Wittig–Horner procedures, by virtue the reaction was carried out at  $-5$  to  $-20\text{ }^{\circ}\text{C}$  and afforded the expected donor **12** as red crystals in 80.5% yield as shown in Scheme 4.

In the same manner, reaction of the dialdehydes **11** with **6** gave the expected unsymmetric 1-[3-(benzo-1,3-dithiol-2-ylidene)methylphenyl]-1'-{5-methoxy-3-[(benzo-1,3-dithiol-2-ylidene)methyl]phenyl}ferrocene (**13**) as orange–red crystals in 97% yield (Scheme 5).

During this work we found that the addition of the ferrocene-dialdehydes to dithiolium salts at about  $-20$  to  $-5\text{ }^{\circ}\text{C}$  with continuous stirring efficiently uses the Wittig–Horner reaction, offering short reaction times and high yields. The structure of both compounds **12** and **13** were determined using IR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$  and FABMS spectral and elemental analyses. The  $^1\text{H-NMR}$  spectra of compound **12** revealed besides the aromatic protons (18H) and 2H, (2  $\text{CH}=\text{CS}_2$ ) another



Scheme 1.

8H as four sets at  $\delta$  4.65 (t,  $J = 1.5$  Hz, 2H), 4.56 (t,  $J = 1.5$  Hz, 2H), 4.35 (t,  $J = 1.5$  Hz, 2H), 4.28 (t,  $J = 1.5$  Hz, 2H) belongs to ferrocene-H; see Section 4 for full details. The DB-TTF **4** was prepared according to the method described in the literature [11a,14]; for comparison study of the electrochemical behavior using the CV with the synthesized compounds **7a–b** [12,15], **12** and **13**.

### 2.1. Synthesis of charge-transfer complexes

Compounds **7a–b**, **12** and **13** were found to readily form CT complexes with the well-known organic acceptor TCNQ (Chart 2). While the CT complex of the donor **12** was obtained under reflux temperature for long time and long standing (3 months) at room temperature in 21% yield (Chart 3). The donor compounds and TCNQ were separately dissolved in equal volumes of hot dichloromethane and the solution mixed and briefly stirred.

The dark brown solution was allowed to slowly cool to room temperature, whereby fine dark green–black crystals of the corresponding CT complexes **14a–b**, **15** and **16** were deposited. These were isolated in variant yields. The CT complexes thus obtained were characterized using IR spectra and microanalysis and the results are summarized in Table 3 and Section 4.6. Complexes **14a–b**, **15** and **16** showed strong  $\nu_{\text{CN}}$  bands at 2190, 2123 (**14a**) [12], 2154 (**14b**), 2221, 2186 (**15**)  $\text{cm}^{-1}$  respectively, indicative of partially reduced TCNQ ( $[(\text{TCNQ})_2]^-$ ) [16]. The  $\nu_{\text{CN}}$  band for complexes **15** is shifted to 2154  $\text{cm}^{-1}$  compared to 2223  $\text{cm}^{-1}$  for TCNQ, indicating that in this complex only weak charge-transfer interactions are existed.

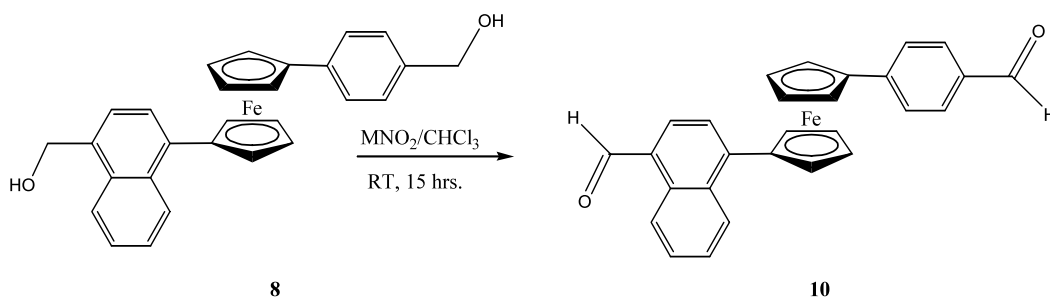
The CT complexes **14a–b**, **15** and **16** were subjected in the form of polycrystalline pressed pellets to measurements of the electrical conductivity at room temperature by the four-probe method. The results obtained are summarized along with the physical properties in Table 1.

The CT complex **14a** was found in agreement with the previously prepared by Togni et al. [12]. The electrical conductivity measurements thus obtained are summarized in Table 1, whereas CT complex **14a** showed a substantial conductivity ( $\sigma = 0.2 \text{ S cm}^{-1}$ ), complex **14b** exhibited less conductivity ( $\sigma = 4.8 \times 10^{-4} \text{ S cm}^{-1}$ ), and compounds **15** and **16** are essentially as insulator ( $\sigma < 10^{-10} \text{ S cm}^{-1}$ ).

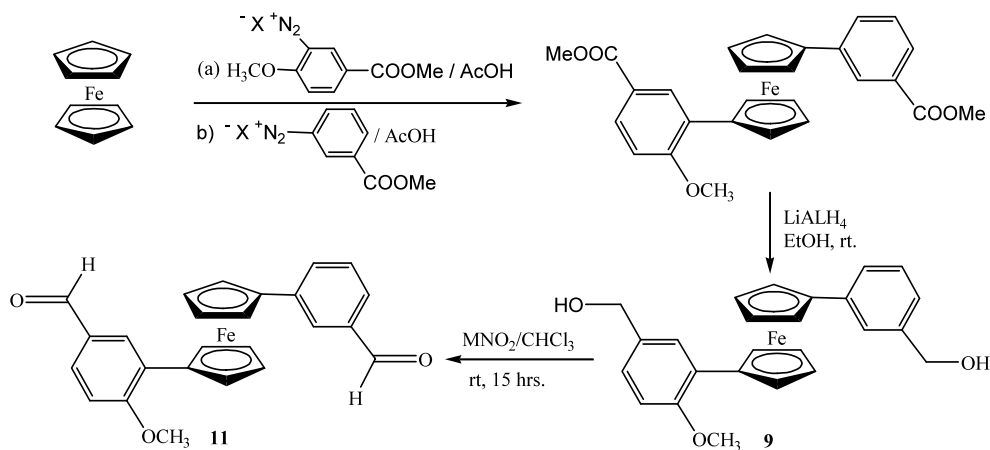
### 2.2. Electrochemistry

The electrochemical properties of the synthesized 1,1'-di-substituted ferrocenes **7a–b**, **12** and **13** compared to the ferrocene, and DB-TTF **4** and the ferrocene-dialdehyde derivatives **5a–b**, **10** and **11** were investigated by cyclic voltammetry (CV) in  $\text{CH}_2\text{Cl}_2$ ,  $5 \times 10^{-3}$  concentration. The ferrocene-dialdehydes **5a–b**, **10** and **11** showed one pair of redox waves corresponding to one-electron transfer process. The redox potentials are summarized in Table 2.

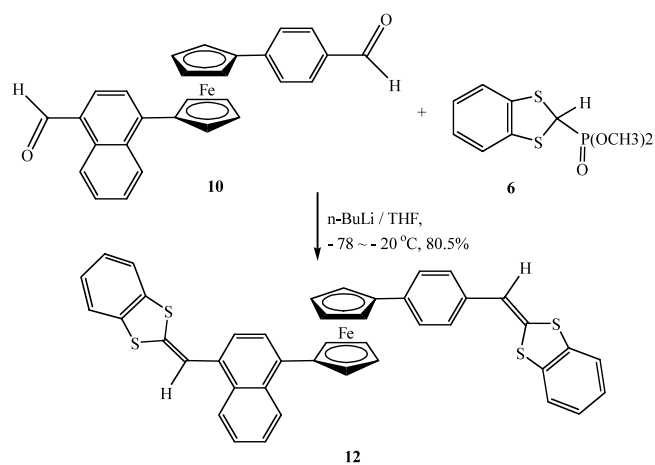
The electrochemical properties of the new synthesized ferrocene-dialdehyde derivatives **5a–b**, **10** and **11** were investigated by CV (Fig. 1). The electrochemical results of the investigated compounds were compared to that of ferrocene and summarized in Table 2. These results indicate that there is a significant difference between the electrochemical behaviors of ferrocene aliphatic-alde-



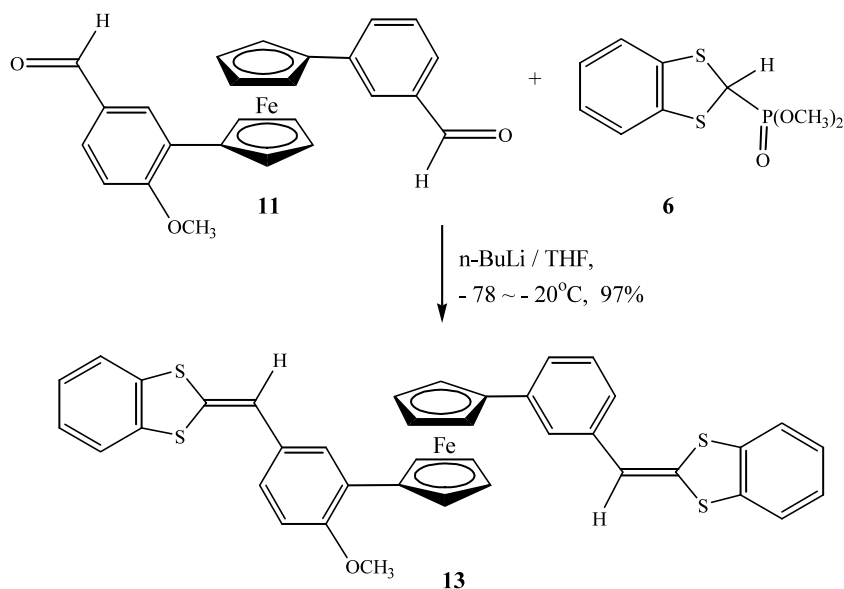
Scheme 2.



Scheme 3.



Scheme 4.



Scheme 5.

hyde derivatives like **5a** and **5b** and ferrocene aromatic-aldehyde derivatives **10** and **11**.

These results indicate also that the separation of the anodic and the cathodic peak potentials,  $\Delta E_p$  values are the same for compounds **5a** and **5b**, while, a small positive shift in the formal potential,  $E^{0'}$ , (58 mV) for compound **5a** was observed in compared to compound **5b**. This shift can be attributed to the replacement of hydrogen atom in **5a** by the electron donating methyl group in **5b**, which facilitate the redox process of compound **5b**. On the other hand, the cyclic voltammetric behavior of compounds **10** and **11** are more or less the same, in which  $\Delta E_p$  values are 93 and 91 mV for **10** and **11**, respectively, whereas, a positive shift of 65 mV in the  $E^{0'}$  was observed for compounds **10** in compared to compound **11**. This confirm that the introducing of methoxy group in compound **11** enhance

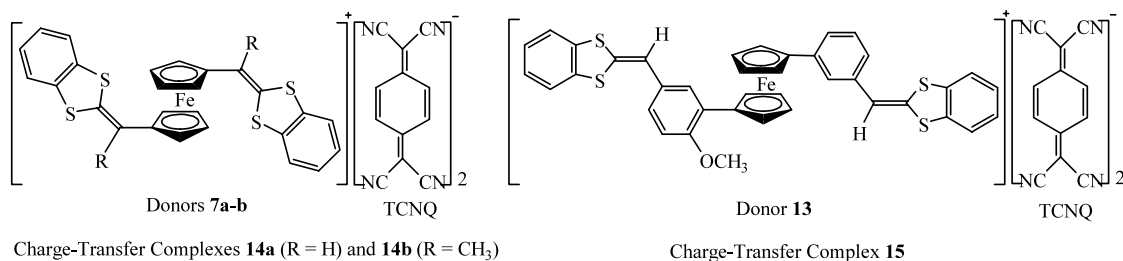


Chart 2.

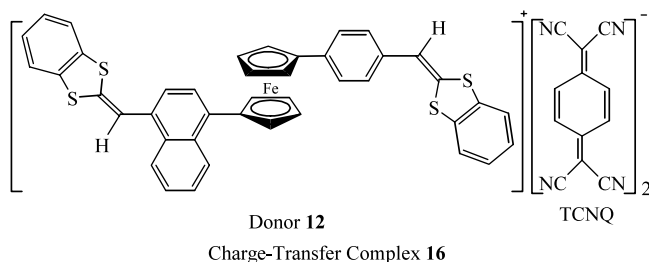


Chart 3.

Table 2

Cyclic voltammetric data in millivolts of ferrocenyl ketones, recorded on a Pt working electrode, Pt gauze counter electrode and Ag/AgCl reference electrode in CH<sub>2</sub>Cl<sub>2</sub> at ambient temperature, scan rate 200 mV using TBAP 0.1 mol l<sup>-1</sup> concentration as supporting electrolyte

Compound	$E_{pc}/mV$	$E_{pa}/mV$	$E^0/mV$	$\Delta E_p/mV$
Ferrocene	485	564	525	79
<b>5a</b>	1041	1141	1091	100
<b>5b</b>	983	1083	1033	100
<b>10</b>	632	725	679	93
<b>11</b>	568	659	614	91

the electron transfer process and consequently its redox behavior.

The electrochemical behaviors of ferrocene-dialdehyde derivatives **5a–b**, **10** and **11** are markedly affected by the scan rate, in which at higher scan rate,  $\nu$  ( $\nu \geq 600$  mV s<sup>-1</sup>), broadening of  $\Delta E_p$  was observed ( $\Delta E_p > 150$  mV), indicating that the irreversibility of the electron-transfer process was maintained under this condition, possibly due to the onset of kinetic complications.

The electrochemical redox properties of compounds **7a–b**, **12** and **13** were studied by CV and the data are listed in Table 2. The CV behavior of these compounds were shown in Fig. 2, and two couples of redox waves were observed clearly in the cyclic voltammograms for all compounds in the potential range ca 0.20–1.2 V at lower scan rate (50–100 mV s<sup>-1</sup>). The first couple of redox waves in the potential range ca 200–800 mV is due to the redox process of DTF/DTF<sup>+</sup> system. Whereas the second couple of redox waves in the potential range ca 600–1000 mV is attributed to the Fc/Fc<sup>+</sup> redox process. However, at higher scan rate (200–800 mV s<sup>-1</sup>), an additional oxidation process was observed for the investigated compounds in the presence of CH<sub>2</sub>Cl<sub>2</sub> as solvent, which attributed to the second DTF<sup>+</sup>/DTF<sup>2+</sup> redox system. Further increasing of the

scan rate ( $> 800$  mV s<sup>-1</sup>) leads to a decrease and finally almost a disappearance of the splitting in the reduction direction and a well developed, one reduction process was observed. The aforementioned results confirm that the electrochemical behaviors of compounds **7a–b**, where ferrocene is a spacer of the two 1,3-dithiole units, and **12** and **13**, where conjugated spacers like phenyl or naphthyl rings are connected in between both ferrocene and 1,3-dithiole units, are different (Table 3). This indicates that the interaction of ferrocene with the DTF rings directly as **7a–b** or through conjugated spacers as for **12** and **13** causes significant changes in the electron donating properties and consequently the electrochemical behaviors of these compounds. Comparing the data of compound **7a** with that previously prepared by Togni et al. we found that the CV data obtained here was in agreement with that reported [12]. Controlled potential coulometry in corresponding to the first anodic step ( $E = 445$  mV) consumed one electron/molecule. We also found that the third anodic process in all cases is irreversible in character. Analysis of the cyclic voltammograms relevant to the first oxidation process with scan rates varying from 100 to 1200 mV s<sup>-1</sup> shows

Table 1  
Physical properties of the CT-complexes **14a–b**, **15** and **16**

No.	Color	Yield (%)	Mol. formula (M.Wt)	D/A ratio	$\sigma_{rt}$ (S cm <sup>-1</sup> )
<b>14a</b>	Black	47 mg (81)	C <sub>50</sub> H <sub>26</sub> FeN <sub>8</sub> S <sub>4</sub> (922.896)	1:2	0.2
<b>14b</b>	Black	84 mg (91)	C <sub>52</sub> H <sub>30</sub> FeN <sub>8</sub> S <sub>4</sub> (950.949)	1:2	$4.8 \times 10^{-4}$
<b>15</b>	Green	62 mg (45)	C <sub>63</sub> H <sub>36</sub> FeN <sub>8</sub> OS <sub>4</sub> (1105.113)	1:2	$< 4.8 \times 10^{-10}$
<b>16</b>	Black	30 mg (21)	C <sub>66</sub> H <sub>36</sub> FeN <sub>8</sub> S <sub>4</sub> (1125.151)	1:2	$< 4.8 \times 10^{-10}$

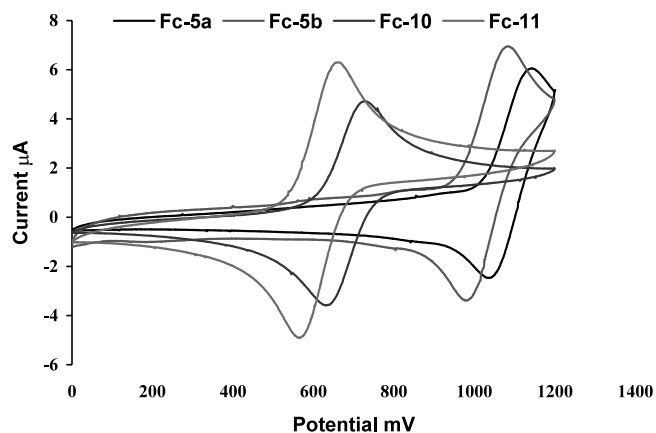


Fig. 1. Cyclic voltammograms of Fc-dialdehydes **5a–b**, **10** and **11** in  $\text{CH}_2\text{Cl}_2$  as the same conditions described in Table 2.

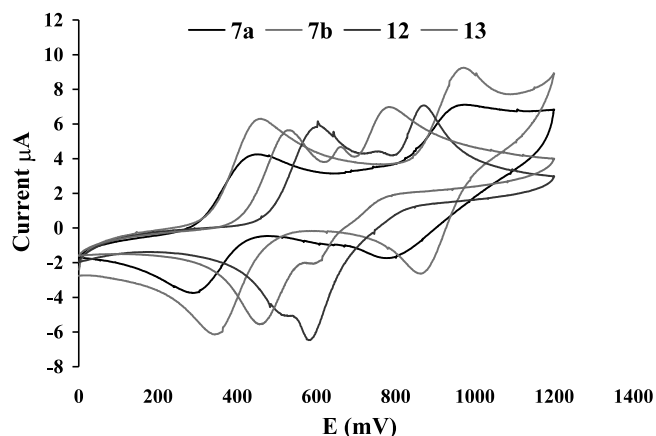


Fig. 2. Cyclic voltammograms of Fc-TTF **7a–b**, **12** and **13**, in  $\text{CH}_2\text{Cl}_2$  at scan rate 200 mV.

Table 3

Cyclic voltammetric data of TTF **4** and  $\pi$ -donors **7a–b**, **12** and **13** in  $\text{CH}_2\text{Cl}_2$  at 200 mV

Compound	$E_{pc}/\text{mV}$		$E_{pa}/\text{mV}$		$E^0/\text{mV}$		$\Delta E_p/\text{mV}$	
	$P_1$	$P_2$	$P_1$	$P_2$	$P_1$	$P_2$	$P_1$	$P_2$
TTF <b>4</b>	696	1061	751	1165	724	113	55	104
<b>7a</b>	314	817	419	941	367	879	105	124
<b>7b</b>	361	876	446	955	404	916	85	79
<b>12</b> *	512	585	602	755	557	670	90	170
<b>13</b> **	457	593	526	659	492	626	69	66

\*  $E_{pa3} = 868$ .

\*\*  $E_{pa3} = 783$ .

that the peak-to-peak separation progressively increases from 69 to 283 mV.

Increasing the scan rate (200–1200 mV) leads to complete separation of the oxidation potential waves, while the second and third associated reduction peaks totally disappeared. Interaction of ferrocene with the benzo-1,3-dithiol-2-ylidene moiety directly or through

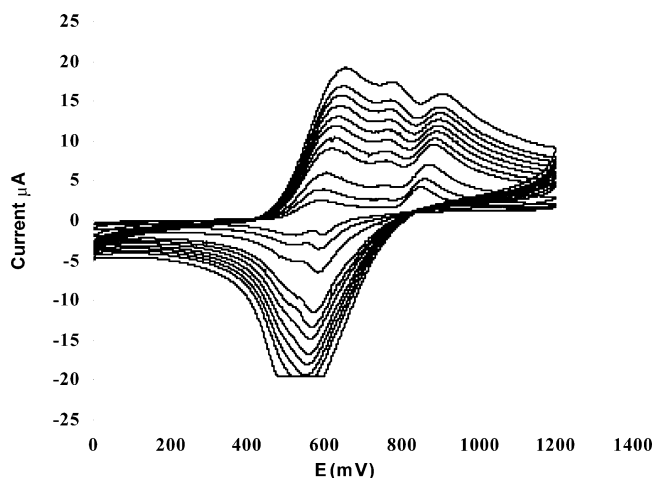


Fig. 3. Cyclic voltammograms of compound **12** in  $\text{CH}_2\text{Cl}_2$  at scan rates from 50 to 1200 mV.

conjugated spacers changed the electron-donating ability of compounds **7a–b**, **12** and **13** (Fig. 3).

A striking feature of the data for **12** and **13** is that the third oxidation process from the second 1,3-dithiol-2-ylidene to 1,3-dithiol-2-ylidene<sup>+</sup> cation radical can be clearly observed at scan rate  $\sim 100$  mV (Fig. 4), while becoming irreversible at higher scan rates (200–1200 mV). We therefore assign this feature to the oxidation of the entire delocalized system involving significant interaction between the two 1,3-dithiole rings and ferrocene from one side, and aromatic rings and ferrocene from the other side.

The minimum energy conformation of compound **12** is shown in Fig. 5. The donor molecule adopts a *trans*-conformer with the central ring in a non-planar conformation, which is in agreement with the suggested structures. The conjugation between the donor and the ferrocene moiety is rather pronounced, corresponding to the experimental data. Semi-empirical calculations AM1 of compound **12** using WinMopac showed that the ferrocenyl and benzo-1,3-dithiol-2-ylidene moieties both

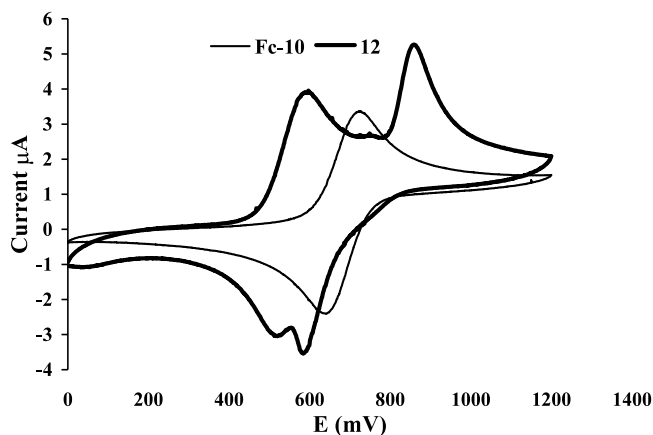


Fig. 4. Cyclic voltammograms of Fc-**10** and donor **12** recorded in  $\text{CH}_2\text{Cl}_2$  at scan rate 100 mV.



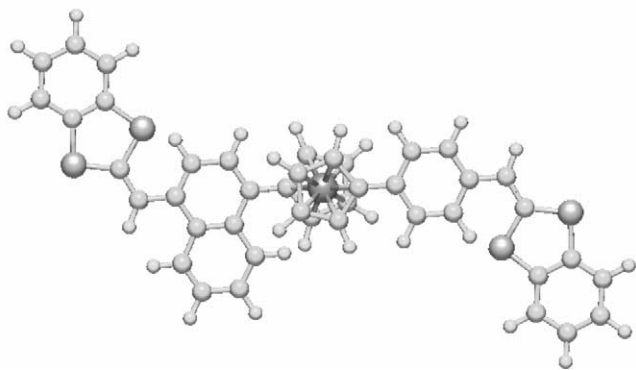


Fig. 5. AM1-optimized geometry of **12** for minimum energy conformation calculated by WinMopac (heat of formation = 324.40441 kcal mol<sup>-1</sup>).

have large atomic orbital coefficients in the HOMO level indicative of a highly delocalized system involving significant interaction between the ferrocene and 1,3-dithiol ring systems [12].

### 3. Conclusions

In conclusion, we have described a short and efficient synthetic route for the useful 1,1'-ferrocene-dialdehydes **5a–b**, **10** and **11**. The potentially useful symmetric 1,1'-bis(benzo-1,3-dithiol-2-ylidene)ferrocenes **7a–b** and asymmetric **12** and **13** were synthesized successfully and the electrochemical properties in comparison with ferrocene and DB-TTF **4** were investigated. The  $\pi$ -donor ability of the synthesized compounds makes them good candidates for the preparation of organic metals. In our present work we have found that the addition of the aldehydes to the dithiolium salts at about  $-20$  to  $-5$  °C with continuous stirring is an efficient use for the Wittig–Horner reaction. The electrochemical study reveals that these compounds **7a–b** and **12–13** exhibit good donor properties, shown in the three subsequent oxidation processes. The results confirm that the electrochemical behaviors of compounds **7a–b**, where ferrocene is a spacer of the two 1,3-dithiole units, and **12** and **13**, where conjugated spacers like phenyl or naphthyl rings are connected in between both ferrocene and 1,3-dithiole units, are different. Polycrystalline samples of **14a–b** are conducting  $\sigma_{rt}$  **14a** = 0.2 S cm<sup>-1</sup> and  $\sigma_{rt}$  **14b** =  $4.8 \times 10^{-4}$  S cm<sup>-1</sup> respectively, while compound **15** and **16** are essentially as insulators ( $\sigma_{rt} < 10^{-10}$  S cm<sup>-1</sup>). The molecular structure of compounds **12** and **13** was optimized geometrically using WinMopac calculation program and the AM1-optimized geometries. The combination of different donor fragments within the same molecule affords systems from which one or two electrons can be reversibly removed.

### 4. Experimental

Melting points were recorded on a Gallencamp melting point apparatus and are uncorrected. Infrared spectra (IR) were measured on a Hitachi 260-10 spectrometer (Hitachi Ltd, 1-5-1, Marunouchi, Chiyod-ku, Tokyo, Japan). <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded at room temperature on INOVA-Varian Nuclear Magnetic Resonance Spectrometer (500 MHz). Chemical shifts are denoted in  $\delta$  units (ppm), relative to Me<sub>4</sub>Si as internal standard,  $J$  values are given in Hz. CDCl<sub>3</sub> is used as a deuterated solvent unless otherwise stated. MS and FABMS spectra were obtained using a JEOL JMS-AX505HA. CV was measured on a potentiostat (Model CS-1090/Model CS-1087). Column chromatography was performed on silica gel 60 (230–400 Mesh ASTM). Solvents were distilled before use. Compounds **7a–b** were prepared following the previously reported methods [12,15].

#### 4.1. Synthesis of ferrocene-di-aromatic aldehydes **10** and **11**

A mixture of ferrocene-dialcohol **8** (3 g, 6.7 mmole) and MnO<sub>2</sub> (30 g) was stirred at room temperature (r.t.) in CHCl<sub>3</sub> (300 ml) for 15 h. The reaction mixture was filtered off through glass wool and the filtrate was distilled under reduced pressure at 30 °C. The residue was chromatographed on silica gel using chloroform/hexane (3:1) to give the corresponding ferrocene-di-aldehydes **10** and **11**.

#### 4.2. 1-(*p*-Formylphenyl)-1'-(4-formyl-1-naphthyl)ferrocene (**10**)

Dark red crystals, m.p. 106–107 °C, yield 2.2 g, 73%, IR (KBr)  $\nu$  3089m, 2973m, 1691s, 1602s, 1567s, 1513s, 1216s, 1168s, 1058s, 829s, 765s cm<sup>-1</sup>. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  10.35 (s, 1H, CHO), 9.92 (s, 1H, CHO), 9.30 [dd,  $J$  = 8.5 Hz,  $J$  = 0.5 Hz, 1H, CH=CH (naphthalene-H)], 8.54 [dd,  $J$  = 8.5 Hz,  $J$  = 0.5 Hz, 1H, CH=CH (naphthalene-H)], 7.82 (d,  $J$  = 1 Hz, 2H, naphthalene-H), 7.66 (m, 3H, aromatic-H), 7.63 (m, 1H, aromatic-H), 7.45 (d,  $J$  = 8 Hz, 2H, aromatic-H), 4.72 (t,  $J$  = 1.5 Hz, 2H, ferrocene-H), 4.64 (t,  $J$  = 1.5 Hz, 2H, ferrocene-H), 4.45 (t,  $J$  = 1.5 Hz, 2H, ferrocene-H), 4.37 (t,  $J$  = 1.5 Hz, 2H, ferrocene-H). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  192.92, 191.57 (2 CHO), 145.56, 143.53 (aromatic-C), 135.55, 134.23 (aromatic-C), 131.85, 131.13 (aromatic-C), 129.81, 129.57, 128.64, 126.85, 126.44, 126.36, 126.32, 125.14 (aromatic-CH), 86.47, 84.30 (ferrocene-C), 72.49, 72.27, 71.40, 68.85 (ferrocene-CH). FABMS  $m/z$  [ $M^+$ , 444 (92)].

#### 4.3. 1-(3-Formylphenyl)-1'-(3-formyl-5-methoxyphenyl)ferrocene (**11**)

Orange red crystals, m.p. 87–88 °C, yield 71%, IR (KBr)  $\nu$  3095s, 2975w, 2840m, 2800s, 2721s, 1702s, 1677s, 1590s, 1504s, 1461s, 1438s, 1388s, 1272s, 1249s, 1186s, 1147s, 1079s, 1018s, 935s, 815s, 790s, 688s  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.8 (s, 1H, CHO), 9.7 (s, 1H, CHO), 7.62–7.18 (m, 6H, aromatic-CH), 6.67 (m, 1H, aromatic-CH), 4.82 (s, 2H, ferrocene-CH), 4.61 (s, 2H, ferrocene-H), 4.36 (s, 2H, ferrocene-H), 4.32 (s, 2H, ferrocene-H), 3.81 (s, 3H,  $\text{OCH}_3$ ).  $^{13}\text{C-NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  193.24, 191.76 (2 CHO), 162.10 (aromatic-C), 139.18, 137.19, 132.63, 130.56 (aromatic-C), 130.45, 129.55, 128.15, 127.09, 126.81, 111.72 (aromatic-CH), 86.00, 83.79 (ferrocene-C), 71.57, 71.24, 70.89, 68.68 (ferrocene-CH), 56.43 ( $\text{OCH}_3$ ). FABMS  $m/z$  (%) [ $\text{M}^+$ , 424 (45)]. Anal. Calc. for  $\text{C}_{25}\text{H}_{20}\text{FeO}_3$ : C, 70.77; H, 4.75. Found: C, 71.01; H, 4.51%.

#### 4.4. 1-[4-(Benzo-1,3-dithiol-2-ylidenemethyl)phenyl]-1'-[4-(benzo-1,3-dithiol-2-ylidene-methyl)naphthyl]-ferrocene (**12**)

A sample of 1,3-benzodithiole **6** (0.56 g, 2.1 mmole) is stirred in dry THF (50 ml) under a stream of  $\text{N}_2$  at –78 °C. A solution of *n*-BuLi (1.5 ml, 2.6 mol  $\text{l}^{-1}$  in hexane) was added portion wise and the mixture was stirred for 15 min. The reaction mixture was allowed to warm to –20 °C with continuous stirring and a solution of dialdehyde **10** (0.444 g, 1.0 mmol) in dry THF (50 ml) was added portionwise. The temperature of the reaction was raised to r.t. and the reaction mixture was stirred for a further 4 h. The THF was removed under vacuum and the residue was washed with  $\text{H}_2\text{O}$  and extracted with  $\text{CHCl}_3$  and dried over  $\text{Na}_2\text{SO}_4$ . The crude oily product was chromatographed on silica gel using  $\text{CHCl}_3$ /hexane (1:2) to give in the early fractions 0.58 g orange crystals of **12** (80.5%) m.p. 111–113 °C. IR (KBr)  $\nu$  3087w, 3054m, 2952w, 2917w, 2848w, 2358m, 1654s, 1577s, 1548s, 1446s, 1386m, 1285m, 1159m, 1122s, 1083s, 1029s, 842s, 761s, 738s, 678s  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.5 [(d,  $J=8$  Hz, 1H,  $\text{CH}=\text{CH}$  (naphthalene-H)], 8.02 [d,  $J=8.5$  Hz, 1H,  $\text{CH}=\text{CH}$  (naphthalene-H)], 7.73 (d,  $J=7.5$  Hz, 1H, naphthalene-H), 7.53 (d,  $J=7$  Hz, 1H, naphthalene-H), 7.45 (m, 2H, naphthalene-H), 7.36 (d,  $J=8.5$  Hz, 2H, aromatic-H), 7.25–7.05 (m, 11H, aromatic-H and  $\text{CH}=\text{C}$ ), 6.5 (s, 1H,  $\text{CH}=\text{C}$ ), 4.65 (t,  $J=1.5$  Hz, 2H, ferrocene-H), 4.56 (t,  $J=1.5$  Hz, 2H, ferrocene-H), 4.35 (t,  $J=1.5$  Hz, 2H, ferrocene-H), 4.28 (t,  $J=1.5$  Hz, 2H, ferrocene-H).  $^{13}\text{C-NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  136.56, 135.98, 135.94, 135.14, 134.78, 134.68, 134.28, 132.77, 131.93, 131.36, 131.08 (aromatic-C, 2  $\text{CH}=\text{C}$ ), 127.49, 126.87, 126.52, 126.29, 125.90, 125.75, 125.62, 125.51, 124.38, 123.89, 121.70, 121.67, 121.04, 120.89 (aromatic-CH), 114.66

( $\text{CH}=\text{C}$ ), 112.52 ( $\text{CH}=\text{C}$ ), 87.65, 86.02 (ferrocene-C), 71.77, 70.96, 70.39, 67.89 (ferrocene-CH). FABMS  $m/z$  (%) [ $\text{M}^+$ , 716 (18)]. Anal. Calc. for  $\text{C}_{42}\text{H}_{28}\text{FeS}_4$ : C, 70.38; H, 3.94; S, 17.89. Found: C, 70.04; H, 4.20; S, 18.08%.

#### 4.5. 1-[3-(Benzo-1,3-dithiol-2-ylidenemethyl)phenyl]-1'-[3-(benzo-1,3-dithiol-2-ylidene-methyl)-2-methoxyphenyl]-ferrocene (**13**)

Compound **13** was obtained as orange crystals in 97% yield, m.p. 93–94 °C. IR (KBr)  $\nu$  3083m, 3052m, 2992m, 2950m, 2830m, 2360m, 1598s, 1581s, 1558s, 1504s, 1448s, 1386m, 1268s, 1241s, 1153s, 1122s, 1081s, 1029s, 813s, 740s, 692s  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29–7.05 (m, 15H, aromatic-H), 6.71–6.69 (dd,  $J=2$  Hz,  $J=8.5$  Hz, 1H,  $\text{CH}=\text{C}$ ), 6.41–6.39 (dd,  $J=2$  Hz,  $J=7$  Hz, 1H,  $\text{CH}=\text{C}$ ), 4.73 (dd,  $J=2$  Hz,  $J=1.5$  Hz, 2H, ferrocene-H), 4.53 (dd,  $J=2.5$  Hz,  $J=1.5$  Hz, 2H, ferrocene-H), 4.30 (dd,  $J=2$  Hz,  $J=1.5$  Hz, 2H, ferrocene-H), 4.27 (dd, 2.5 Hz,  $J=1.5$  Hz, 2H, ferrocene-H), 3.77 (d,  $J=2$  Hz, 3H,  $\text{OCH}_3$ ).  $^{13}\text{C-NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  154.83 (aromatic-C), 137.90, 136.55, 136.19, 135.00, 134.83, 131.65, 129.10, 129.03 (aromatic-C), 128.15, 127.73, 125.82, 125.74, 125.70, 125.50, 125.42, 125.35, 124.90, 124.27, 123.77, 121.65, 120.83, 120.79 (aromatic-CH), 114.87 ( $\text{CH}=\text{C}$ ), 110.96 ( $\text{CH}=\text{C}$ ), 86.22, 83.57 (ferrocene-C), 70.31, 70.29, 69.97, 69.73, 67.99 (ferrocene-CH), 55.22 ( $\text{OCH}_3$ ). FABMS  $m/z$  (%) [ $\text{M}^+$ , 696 (23)]. Anal. Calc. for  $\text{C}_{39}\text{H}_{28}\text{FeOS}_4$ : C, 67.23; H, 4.05; S, 18.40. Found: C, 67.19; H, 4.26; S, 18.77%.

#### 4.6. Preparation of charge-transfer complexes **14a**, **14b**, **15** and **16**

##### 4.6.1. Charge-transfer complexes **14a–b**

Donor **7a** or **7b** (67 mg, 0.125 mmol) and TCNQ (51 mg, 0.25 mmol) were dissolved in equal amounts of 1,2-dichloromethane (15 ml), the solutions were heated to reflux temperature. The solution of **7a** or **7b** was then added to that of TCNQ and the resulting dark green solution briefly stirred. Slow cooling to r.t. led to the formation of dark crystals. These were filtered off, washed with small portion of 1,2-dichloromethane, and dried under vacuum to give the corresponding CT-complexes **14a** and **14b** respectively in high yields.

##### 4.6.2. CT-complex **14a**

Yield 47 mg, 81%. Data were in agreement with that reported in literature [12]. Anal. Calc. for  $\text{C}_{50}\text{H}_{26}\text{FeN}_8\text{S}_4$  (922.896): C, 65.07; H, 2.84; N, 12.14; S, 13.89. Found: C, 65.28; H, 3.10; N, 12.04; S, 13.92. Found: C, 65.28; H, 3.10; N, 12.04; S, 13.92.



#### 4.6.3. CT-complex 14b

Yield 84 mg, 91%. IR (KBr)  $\nu$  2202s, 2154s, 1598m, 1558s, 1508s, 1430s, 1388s, 1288s, 1191s, 1120s, 1066s, 1024s, 950s, 835s, 736s, 688s  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{52}\text{H}_{30}\text{FeN}_8\text{S}_4$  (950.9488): C, 65.68; H, 3.18; N, 11.78; S, 13.48. Found: C, 65.48; H, 3.21; N, 11.93; S, 13.49%.

#### 4.6.4. CT-complex 15

DTF-Fc-DTF **13** (87 mg, 0.125 mmol) and TCNQ (51 mg, 0.25 mmol) were dissolved in equal amounts of 1,2-dichloroethane (15 ml), the solutions were heated to reflux temperature. The solution of Fc-TTF **13** was then added to that of TCNQ and the resulting brown red mixture briefly stirred. Slow cooling to room temperature led to the formation of green crystals. These were filtered off, washed with small portion of 1,2-dichloroethane, and dried under vacuum to give **15** as dark green crystals, yield 62 mg, 45%. IR (KBr)  $\nu$  3050s, 2921m, 2890m, 2850m, 2362m, 2225s, 1654m, 1602m, 1573s, 1544s, 1511s, 1448s, 1282m, 1261m, 1159m, 1122s, 1014m, 862s, 840s, 761s, 740s  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{63}\text{H}_{36}\text{FeN}_8\text{OS}_4$  (1105.113): C, 68.47; H, 3.28; N, 10.14; S, 11.77. Found: C, 68.14; H, 3.15; N, 9.86; S, 11.97%.

#### 4.6.5. CT-complex 16

This was obtained from DTF-Fc-DTF **12** (90 mg, 0.125 mmol) and TCNQ (51 mg, 0.25 mmol). The same method described above followed by refluxing the mixture in dry  $\text{CH}_3\text{CN}$  for about 72 h. The resulting brown solution was cooled and kept at r.t. for ~3 months. The precipitate thus formed was collected by filtration and washed with chloroform (3  $\times$ ) and twice with acetone to give 30 mg (21%) of dark brown crystals of the CT-complex **16**. IR (KBr)  $\nu$  3050s, 2225s, 1602m, 1575s, 1546s, 1513s, 1448s, 1284m, 1187m, 1159m, 1122s, 1029s, 929m, 889m, 862s, 840s, 761s, 740s/678s/640s  $\text{cm}^{-1}$ .  $\text{C}_{66}\text{H}_{36}\text{FeN}_8\text{S}_4$  (1125.151), FAB-MS  $m/z$  (%) [ $\text{M}^+$ , 1125 (0.2), 919 (1)].

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