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# Synthesis and electrochemical studies of ferrocene-dithiafulvalenes (Fc-DTF) and 1,1′-bis(dithiafulvalenyl)ferrocene (DTF-Fc-DTF). An approach towards new conducting organic materials

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**Abstract**—Novel π-conjugated donor compounds based on the strong electron-donating ferrocene moiety and dithiafulvalene donors exhibited increased electron donor ability. The ferrocenylketones **4a**,**b**, **5**, **8** and **9** were synthesized via described methods, and allowed to react with 2-dimethoxyphosphinyl-1,3-benzodithiole (**13**) in the presence of *n*-BuLi at −78°C in dry THF to afford the corresponding ferrocene-dithiafulvalenes **14a**,**b**, **18**, **19** and 1,1′-bis(benzo-1,3-dithiol-2-ylidene)ethyl]ferrocene (**15**). Electrochemical properties of these new donor compounds were studied using cyclic voltammetry (CV) and UV–Vis spectra. CV and absorption spectra of the new compounds were studied in comparison with ferrocene (**6**) and dibenzo-tetrathiafulvalene DB-TTF **3**. Two-electron and three-electron redox behaviors were observed as two waves. The absorption spectra showed a red-shift with a slight increase in the absorption intensities.

## 1. Introduction

The search for new electroactive materials is nowadays a very active research topic for chemists. Recently, the synthesis of new π-extended donors has become an area of great interest. The synthesis of ferrocene carbonyl compounds and their use in the Wittig–Horner reaction to afford new π-donors has been the subject of considerable research. Owing to the structural and electrochemical properties of ferrocene-containing tetrathiafulvalene derivatives, several ferrocene-tetrathiafulvalenes were constructed to be donors for conducting charge transfer (CT) complexes. Ueno et al. reported the first compound that belongs to this class of donor conducting materials[1] and recently a very similar type of donor molecule was reported by Bryce and co-workers.[2] The synthesis of two dithiole rings separated by a conjugated spacer has received great attention as a consequence of their potential interest in the preparation of compounds with non-linear optical properties or as semiconductors, Chart 1.

The synthesis of derivatives and analogues of dithiafulvalene and tetrathiafulvalene are of importance due to their conducting applications.[2–4] These types of ferrocene-tetrathiafulvalenes contain two electron donor sites, the ferrocene and tetrathiafulvalene units. CT complexes with

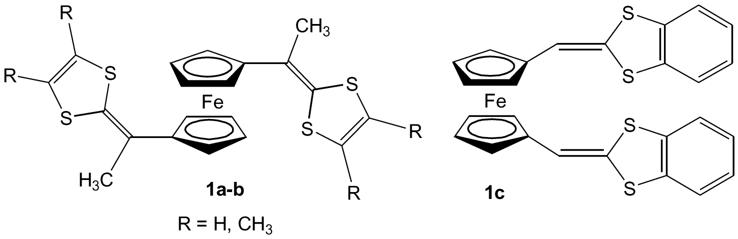

**Chart 1.**

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*Keywords*: electron-donors; synthesis; 1,4-benzo-1,3-dithiafulvalenes; ferrocene; cyclic voltammetry; UV–Vis spectroscopy; electrically conducting materials.

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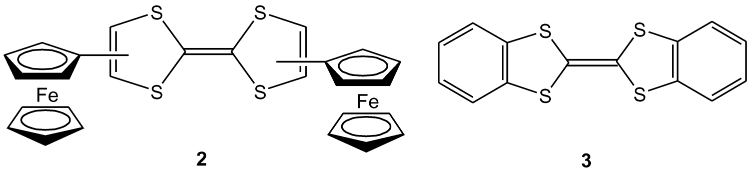


**2** **3**

**Chart 2.**

acceptor molecules like TCNQ or DDQ have been also isolated,[1] Chart 2.

Recently, several tetrathiafulvalenes-$C_{60}$[5] and tetrathiafulvalene-crown ethers[6] have been synthesized, their chemical structures, molecular structures, and electrochemical properties being studied by many researchers. From a biological point of view, the *N*-ferrocenylmethyl-benzimidazolium iodide salt showed excellent in vitro activity against the *P. falciparum* malarial parasite strain NF54.[7a] Several compounds bearing the ferrocenyl group have been developed also as interesting alternatives for the chemotherapy of drug-resistance in cancer and tropical diseases.[7b]

## 2. Results and discussions

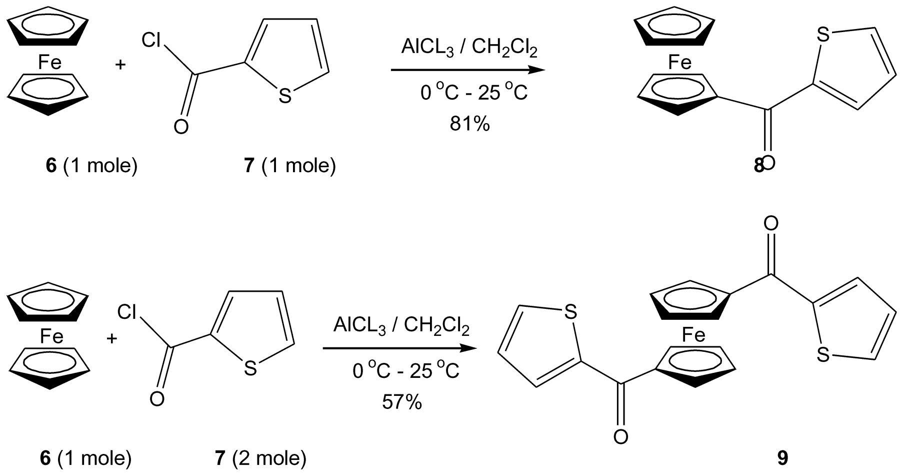
In continuation of our interest in the synthesis and electrochemical studies of new tetrathiafulvalenes incorporating ferrocene as electron donor molecules, we focus in the present work on the synthesis of compounds comprising covalently-linked 1,4-dithiafulvalene and ferrocene moieties[8] and study their electrochemical behavior using cyclic voltammetry (CV) and UV–Vis spectra.

The synthesis of ferrocenyl ketones has been carried out following the Friedel–Crafts method with purification by column chromatography before being subjected to Wittig–Horner cross-coupling reaction as described in this text. 1-Acetylferrocene (**4b**) and 1,1′-diacetylferrocene (**5**) were also prepared according to Friedel–Crafts reaction in good yields.[9] In the same manner, on reaction of 2-thiophenecarbonyl chloride (**7**) with ferrocene in a 1:1 molar ratio, 1-(2-thiophenecarbonyl)ferrocene (**8**) was obtained as dark red crystals in 81% yield, Scheme 1.

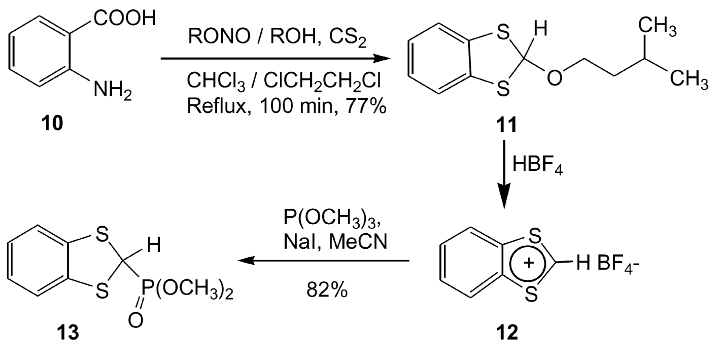
On reaction of 2-thiophenecarbonyl chloride (**7**) with ferrocene (**6**) in a 1:2 molar ratio under the same reaction conditions in dichloromethane at 0°C, in the presence of anhydrous $AlCl_3$ and following the Friedel–Crafts procedures, 1,1′-di(2-thiophenecarbonyl)ferrocene (**9**) was isolated as a major product (57%). In addition, **8** was also obtained as a minor product (35%), Scheme 1.

2-Dimethoxyphosphinyl-1,3-benzodithiole (**13**) was prepared in several steps by following well-established procedures starting from anthranilic acid **10**.[10] The 2-butoxy-1,3-benzodithiole (**11**) was obtained through four reaction steps, aprotic diazotization of anthranilic acid **10** by alkyl nitrite to give benzodiazonium-2-carboxylate, thermal decomposition of the carboxylate to benzyne, reaction of carbon disulfide with benzyne leading to 1,3-dithiole-2-carbene and addition of alcohol, either resulting from the diazotization of anthranilic acid by alkyl nitrite or added prior to the reaction.[10] This method was modified by us and the 2-butoxy-1,3-benzodithiole (**11**) was obtained in 77% yield.[11] The 2-butoxy-1,3-benzodithiole (**11**) was reacted with $HBF_4$ in acetic anhydride to give 1,3-benzodithiolium floroborate (**12**) in good yield. Refluxing of the floroborate **12** with $P(OMe)_3$ in acetonitrile in the presence of NaI gave the 2-dimethoxyphosphinyl-1,3-benzodithiole (**13**) in high yield,[10] Scheme 2.

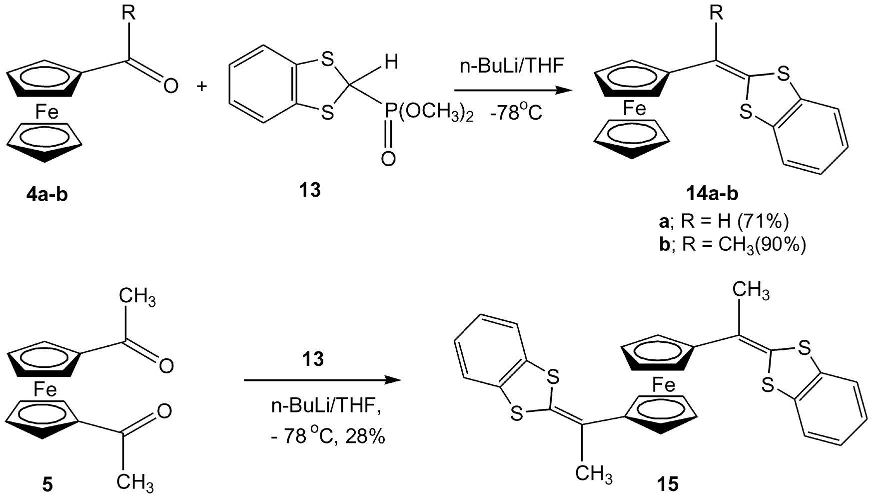
The reaction of 1-formylferrocene (**4a**) or 1-acetylferrocene (**4b**) with 2-dimethoxyphosphinyl-1,3-benzodithiole (**13**) using the Wittig–Horner reaction in dry THF in the presence of *n*-BuLi at −78°C afforded the corresponding



**Scheme 1.**



**Scheme 2.**



**Scheme 3.**

1-[(benzo-1,3-dithiol-2-ylidene)methyl/ethyl]ferrocene (**14a**,**b**) in 71 and 90% yield, respectively, Scheme 3.

On reaction of 1,1′-diacetylferrocene (**5**) with 1,3-benzodithiole derivative **13** the expected 1,1′-bis[(benzo-1,3-dithiol-2-ylidene)ethyl]ferrocene (**15**) was obtained as dark red crystals in 28% yield. In addition the unexpected ferrocene-dithiafulvalene (Fc-DTF) **16** was also isolated as dark orange–red oils in 25% yield, Scheme 3 and Chart 3.

Formation of **16** might be attributed to the addition of *n*-BuLi to the carbonyl group followed by hydrolysis to form the alcohol **17** which on dehydration afforded the corresponding **16** in 25% isolated yield. The alcohol derivative **17** was also obtained as dark yellow oils, but could not be

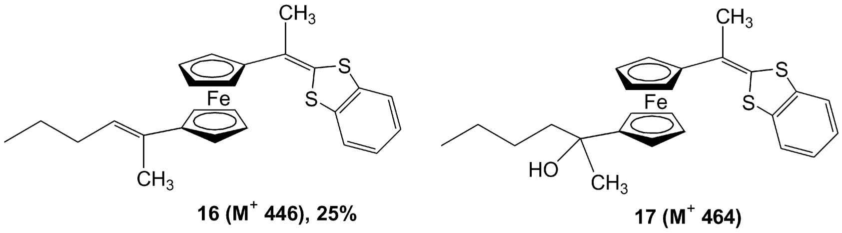
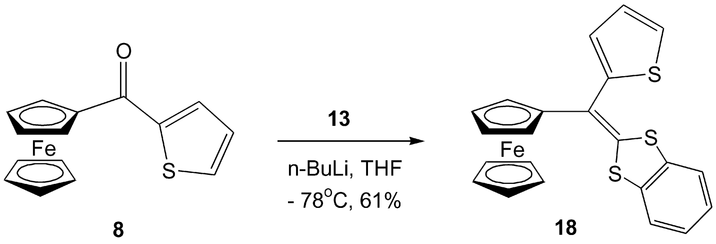
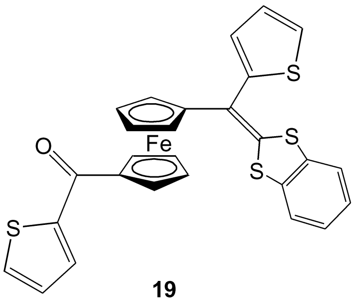


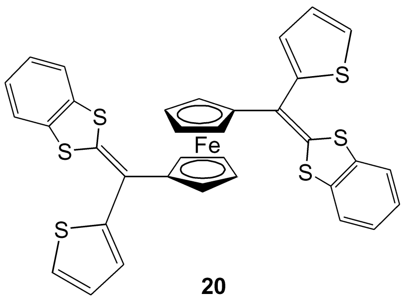
**Chart 3.**



**Scheme 4.**



**19**



**20**

**Chart 4.**

isolated as a single component. The structure of compound **16** was confirmed using $^{1}$H NMR, $^{13}$C NMR, IR and FAB-MS spectra, which gave the M$^{+}$ 446, Chart 3.

On the other hand, on application of the Wittig–Horner reaction to 1-(2-thiophenecarbonyl)-ferrocene (**8**), the Fc-DTF **18** was obtained in 61% yield, Scheme 4. While on reaction of the 1,1′-bis(2-thiophenecarbonyl)ferrocene (**9**) with 1,3-benzodithiole **13** the unexpected ferrocene-dithiafulvalene (Fc-DTF) **19** was obtained as orange–red oils in 33% yield. The expected **20** was obtained in very low yield, could not be isolated in pure form and could only be detected by FAB mass spectra (M$^{+}$ 678).

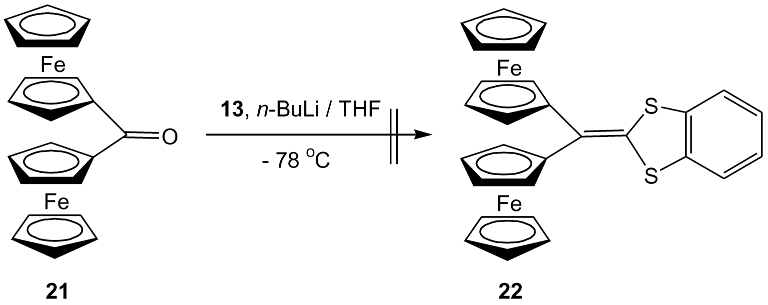
The reaction was changed in comparison to the 1,1′-diacetylferrocene (**5**) and one carbonyl group reacted with the 1,3-benzodithiole derivative **13** to give ferrocene-dithiafulvalene **19** as the major product. This yield of this reaction was lowered and the starting ketone **9** was recovered in 73.5%. The low yield of this reaction might be attributed to the retardation effect of the dithiafulvalene moiety on the other carbonyl group or to the steric hindrance of the two thiophene moieties. The structure of compound **19** was confirmed by $^{1}$H NMR, $^{13}$C NMR, FAB-MS and IR spectral analyses. The $^{1}$H NMR was of interest especially for the ferrocene protons. It revealed 8H as four sets at $\delta$ 4.28, 4.48, 4.62, 5.07 ppm in addition to four aromatic protons at $\delta$ 7.07–7.12 and six thiophene protons. The appearance of the ferrocene protons as four sets, is due to the different substituents on both rings of the 1,1′-ferrocene. The IR spectra exhibited, besides the absorption bands of ferrocene and thiophene moieties, the presence of a carbonyl group at $\nu$ 1724 cm$^{-1}$. The $^{13}$C NMR showed, besides the carbonyl group at $\delta$ 188.96 and the presence of 10 ferrocene carbons, another 16 aromatic-C for both thiophenes and benzo-1,3-dithiol-2-ylidene moieties. The FAB-MS showed the exact molecular ion peak at M$^{+}$ 542, Chart 4. An attempt to react the dicarbonyl compound **9** with **13** was carried out once more using three equivalents of compound **13**. The reaction after work up and chromatography on silica gel gave besides the ferrocene-dithiafulvalene **19** a very low yield of the impure **20**.

Compound **20** could be detected by FAB-MS but the purity of this compound was too low and it could not be purified either by using repeated flash column chromatography or paper chromatography. Furthermore, the reaction of **19** with **13** was carried out using the same Wittig–Horner reaction conditions. Compound **20** was not obtained and the starting **19** was recovered in 50% yield. In addition, an unknown yellow material was isolated in pure form. This unknown compound showed no ferrocene moiety in its NMR spectra.

Attempts were made to react 1,1′-diferrocenyl ketone **21**[12,13] with benzo-1,3-dithiole **13** using the Wittig–Horner reaction procedures ($n$-BuLi, −78°C, THF) but were unsuccessful. In all attempts **21** was recovered and the benzo-1,3-dithiol-2-ylidene derivative **22** was not formed, Scheme 5. This might be attributed to the steric hindrance of the two ferrocenes moieties around the carbonyl group. Ketone **21** was obtained using the Friedel–Crafts method via aroylation of the ferrocene in $CH_2Cl_2$ at 0°C in the presence of $AlCl_3$. The data for this compound are summarized in Section 4.

## 2.1. Electrochemistry

The electrochemical properties of the novel ferrocene-dithiafulvalenes (Fc-DTF) **14a**,**b**, **18** and **19** and dithiafulvalene-ferrocene-dithiafulvalene **15** were investigated by CV. The results were compared to ferrocene (**6**), and DBTTF **3** and ferrocenylketone compounds **4a**,**b**, **5**, **8** and **9** in $CH_2Cl_2$ as solvent in the presence of 0.1 M tetra-$n$-butylammonium perchlorate (TBAP) as the supporting



**Scheme 5.**

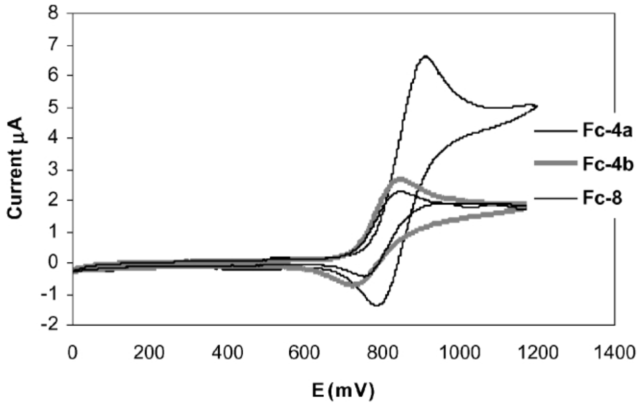


**Figure 1.** Cyclic voltammograms of ferrocenyl ketones **4a**,**b**, and **8**, recorded on a Pt working electrode, Pt gauze counter electrode and Ag/AgCl reference electrode in dry $CH_2Cl_2$ at ambient temperature using TBAP 0.1 mol/l concentration as the supporting electrolyte at scan rates 20 mV $s^{-1}$.

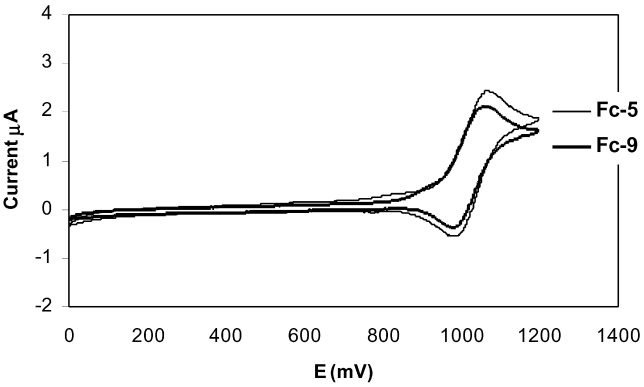


**Figure 2.** Cyclic voltammograms of 1,1′-ferrocenyl diketones **5** and **9**.

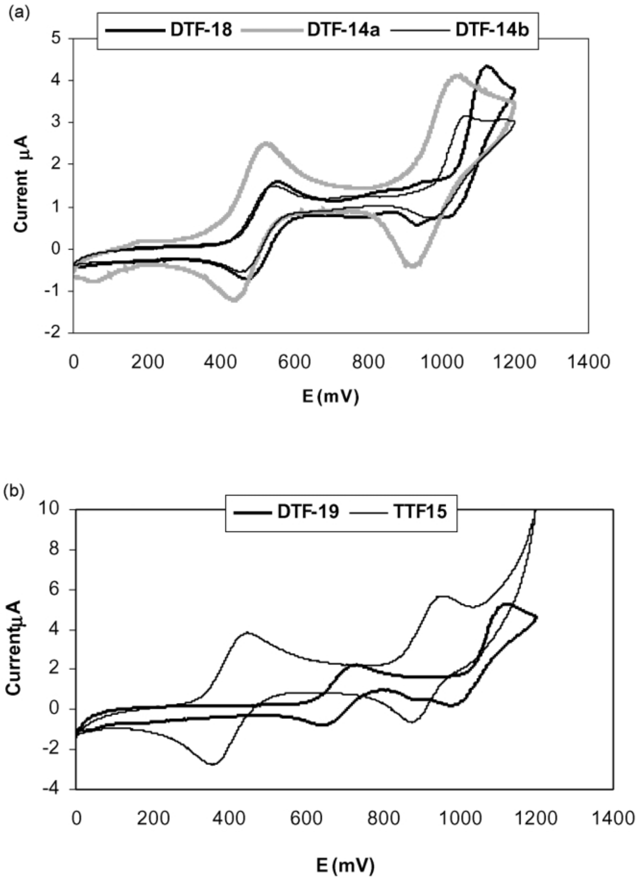


**Figure 3.** (a) Cyclic voltammograms of **14a**,**b** and **18** in $CH_2Cl_2$ at scan rate 20 mV $s^{-1}$. (b) Cyclic voltammograms of **19** and **15** in $CH_2Cl_2$ at scan rate 20 mV $s^{-1}$.

electrolyte using Pt working electrode, Pt gauze counter electrode and Ag/AgCl reference electrode at ambient temperature, $5\times10^{-4}$ mol concentration of all compounds.

## 2.2. Cyclic voltammetric behavior of ferrocenylketone compounds 4a,b, 5, 8 and 9

The electrochemical behaviors of ferrocenylketone compounds **4a**,**b**, **5**, **8** and **9** were investigated by CV (Figs. 1 and 2) which is a sensitive electrochemical method and permit the collection of excellent data at low concentration of electroactive substance.[14,15] The electrochemical results of the investigated compounds were compared to that of ferrocene. Summaries of cyclic voltammetric results are given in Table 1. The ferrocenyl ketones displayed one pair of redox waves corresponding to a one-electron transfer process.

**Table 1**. Cyclic voltammetric data in millivolts of ferrocenyl ketones **4a**,**b**, **8**, **9** and **5**, using a Pt working electrode, Pt gauze counter electrode and Ag/AgCl reference electrode in dry $CH_2Cl_2$ at ambient temperature using TBAP 0.1 mol/l concentration as the supporting electrolyte. Scan rate 20 mV

| Compound | $E^{1/2}_{\mathrm{Ox}}$ | $E^{1/2}_{\mathrm{Red}}$ | $E^{0\backslash}$ (mV) | $\Delta E$ (mV) |
|---|---|---|---|---|
| **6**[a] | 554 | 481 | 518 | 73 |
| **4a** | 908 | 790 | 849 | 118 |
| **4b** | 847 | 729 | 788 | 118 |
| **8** | 841 | 755 | 798 | 86 |
| **5** | 1067 | 985 | 1026 | 82 |
| **9** | 1057 | 982 | 1020 | 75 |

[a] Scan rate of the reference compound **6** was recorded at scan rate 50 mV $s^{-1}$.

The cyclic voltammetric behavior of ferrocenylketones showed one cathodic peak and the corresponding oxidation peak in the potential range of 650–1100 mV at the Pt electrode. The separation of the anodic and the cathodic peak potentials, $\Delta E_p$, were 73, 75, 82, 86, 118 and 118 mV at 20 mV $s^{-1}$ for compounds **6**, **9**, **5**, **8**, **4b** and **4a**, respectively. These values are larger than that expected for a reversible 2-electron transfer reaction, which is given by 57/$z$ mV, where $z$ is the number of electrons transferred in the process,[16] indicating that the irreversibility of the electron-transfer process was maintained under this condition. At higher scan rate, $\nu$ ($\nu\geq600$ mV $s^{-1}$, broadening of $\Delta E_p$ was observed ($\Delta E_p>150$ mV), possibly due to the onset of kinetic complications.

The formal potential, $E^{0\prime}$, taken as the average of $E_{pc}$ and $E_{pa}$, were 517, 849, 788, 798, 1026 and 1020 mV for **6**, **4a**,**b**, **8**, **5**, and **9**, respectively. $E^{0\prime}$ shifted to more positive potentials by ca. 200 mV for compounds **5** and **9** compared to compounds **4a**,**b** and **8**, which revealed that the reduction of compounds **5** and **9** become more easy at the Pt electrode. The significant differences between the $E^{0\prime}$ values of

**Table 2**. Cyclic voltammetric data of compounds **14a**,**b**, **18**, **19**, **15** and **3** at scan rates 20 mV s$^{-1}$

| Compound | $E_{\mathrm{pc}}$ (mV) | | $E_{\mathrm{pa}}$ (mV) | | $E^{0\backslash}$ (mV) | | $\Delta E_{\mathrm{p}}$ (mV) | |
|---|---|---|---|---|---|---|---|---|
| | $P_1$ | $P_2$ | $P_1$ | $P_2$ | $P_1$ | $P_2$ | $P_1$ | $P_2$ |
| DB-TTF **3** | 609 | 773 | 731 | 1117 | 670 | 945 | 122 | 344 |
| DTF **14a** | 435 | 928 | 522 | 1043 | 479 | 986 | 87 | 115 |
| DTF **14b** | 468 | 979 | 539 | 1067 | 504 | 1023 | 71 | 88 |
| DTF **18** | 473 | 1009 | 556 | 1138 | 515 | 1074 | 83 | 129 |
| TTF **15** | 361 | 876 | 447 | 955 | 404 | 916 | 86 | 79 |
| DTF **19** | 653 | 982 | 725 | 1119 | 689 | 1051 | 72 | 137 |

compounds **5** and **9** and other compounds are highly interesting considering the structural difference between these compounds, namely a single surplus carbonyl group of compounds **5** and **9** when compared with compounds **4a**,**b** and **8**.

### 2.3. Cyclic voltammetric behavior of Fc-DTF compounds

The nature of the electrochemical process of the Fc-DTF's **14a**,**b**, **18**, **19** and DTF-Fc-DTF **15** compounds were also studied by CV. Typical cyclic voltammetric behaviors of these compounds are shown in Figure 3(a) and (b), and two couples of redox waves are observed clearly in the cyclic voltammograms for all compounds in the potential range ca. 300–1200 mV. The first couple of redox waves in the potential range ca. 200–800 mV is due to the redox process of DTF/DTF$^{+}$ system. Whereas the second couple of redox waves in the potential range ca. 800–1300 mV is attributed to the ferrocene/ferrocenium$^{+}$ redox process. Furthermore, an additional redox process was observed for compound **15** in presence of $CH_2Cl_2$ as solvent, which may be due to the second DTF$^{+}$/DTF$^{2+}$ redox system. Summaries of cyclic voltammetric results are given in Table 2. The electrochemical behaviors of Fc-DTF compounds are markedly affected by the scan rate, in which at lower scan rate ($\nu \leq 20$ mV s$^{-1}$) all Fc-DTF compounds display two reversible couples of redox waves, however, at higher scan rate ($\nu \geq 50$ mV s$^{-1}$) the peak separation of the second couple of redox peaks begins to increase as predicted for the onset of kinetic irreversibility (Fig. 6). The oxidation potential values of the investigated compounds were markedly affected by the ring substitution and/or groups of the ferrocene moiety. When in a molecule of the type R$^1$-Fc-R$^2$ like compound **19** (where R$^1$=$COC_4H_3S$ and R$^2$=DTF) the oxidation potential shifted to more positive value ($E_{\mathrm{pa1}}$=725 mV) in compared to that of the type R$^1$-Fc-R$^1$ (R$^1$=DTF) like compound **15** ($E_{\mathrm{pa1}}$=447 mV). While, the oxidation potential of the compound **14b** (type Fc-R$^1$, R$^1$=DTF) is more positive ($E_{\mathrm{pa1}}$=539 mV) than that of the type R$^1$-Fc-R$^1$ (R$^1$=DTF) like compound **15** ($E_{\mathrm{pa1}}$=447 mV). On the other hand, the replacement of the hydrogen atom in compound **14a** by an electron-donating methyl group ($CH_3$) would be responsible for the positive shift of the oxidation potential in the case of compound **14b** ($E_{\mathrm{pa1}}$=539 mV) than **14a** ($E_{\mathrm{pa1}}$=522 mV) itself. The results show that, a slight change in chemical structure causes significant changes in the electrochemical behavior and consequently in conducting properties.

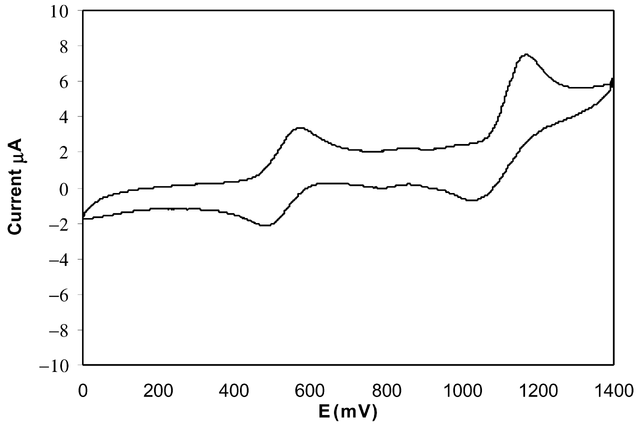


**Figure 4.** Cyclic voltammograms of the Fc-DTF **18** in $CH_2Cl_2$ at scan rate 10 mV s$^{-1}$.

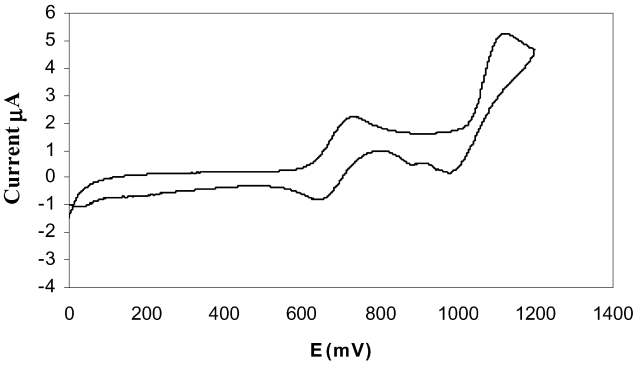


**Figure 5.** Cyclic voltammograms of the Fc-DTF **19** in $CH_2Cl_2$ at scan rate 20 mV s$^{-1}$.

Compounds **18** and **19** also show some common features depending on solvent and scan rate effects. In $CH_2Cl_2$ on a Pt electrode and at ambient temperature, **18** and **19** showed two oxidation waves with peak potentials of 575, 1187 for **18** at 10 mV s$^{-1}$ and 725, 1119 for **19** at scan rates 20 mV s$^{-1}$. For **18** and **19**, such a process is electrochemically reversible or quasi-reversible ($\Delta E_{\mathrm{p}}^{1}$ 91 mV and $\Delta E_{\mathrm{p}}^{2}$ 125 mV) for **18** and ($\Delta E_{\mathrm{p}}^{1}$ 72 mV and $\Delta E_{\mathrm{p}}^{2}$ 137 mV) for **19**. The $\Delta E_{\mathrm{p}}^{2}$ was not observed with an increase of scan rate and the second wave was distorted when increasing the scan rate to about 100–400 mV s$^{-1}$ (Figs. 4 and 5).

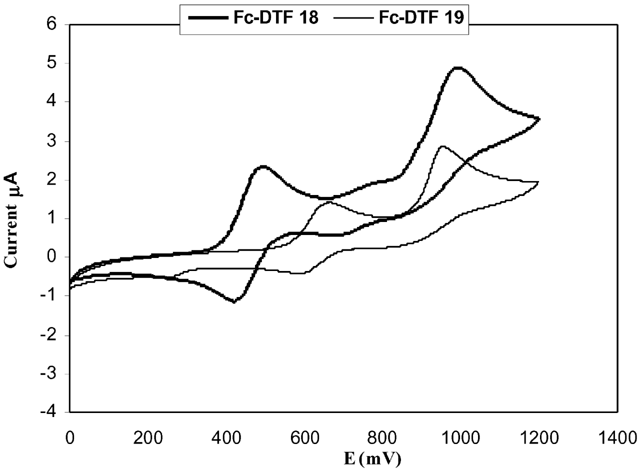


**Figure 6.** Cyclic voltammograms of the Fc-DTF **18** and **19** in $CH_3CN$ at scan rate 50 mV s$^{-1}$.

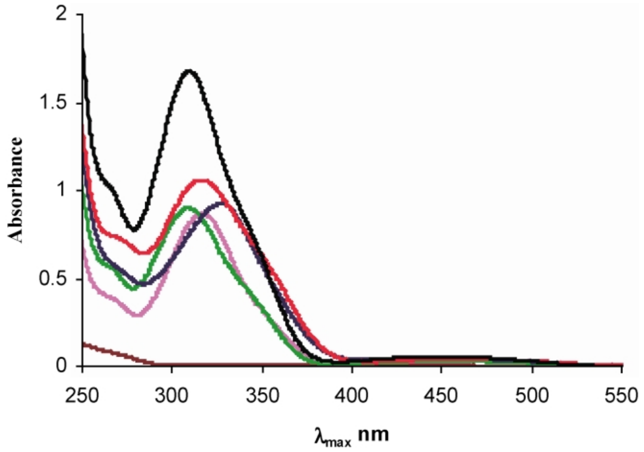


**Figure 7.** UV–Vis spectra of the Fc-DTF's **19** (black), **15** (red), **18** (blue), **14b** (green), **14a** (violet) and ferrocene **6** (brown) from up to down, respectively, in EtOH ($4.05\times10^{-5}$ M).

In $CH_3CN$ under the same conditions at different scan rates, **18** and **19** also showed two oxidation waves associated with one corresponding reduction peak in the reverse scan belonging to the first oxidation wave (Fig. 6).

## 2.4. Electronic spectroscopy

As shown in Figure 7, the UV–Vis spectra of the donors **14a**,**b**, **18**, **19** and **15** and ferrocene (**6**) in ethanol are mainly dominated by the absorption of donor moieties in the region of 275–375 nm. It is known that in the region 300–500 nm, no intense absorption is observed for ferrocene. The absorption of **14a**,**b**, **18**, **19**, **15** and **6** were observed as listed in Table 3.

On comparison of the $\lambda_{max}$ values of ferrocene (**6**) and the compounds **14a**,**b**, **18**, **19** and **15**, a red-shift and an increase in the absorption interactions are observed in the case of all donor compounds.

It should be mentioned that intramolecular interactions are observed in compounds **14a**,**b**, **18**, **19** and **15** by the appearance of a weak broad absorption band in the 400–500 nm region of their electronic spectra. This absorption is not observed in solution of ferrocene (**6**) or ferrocenyl ketones, and its intensity shows a linear dependence on concentration.

The absorption intensities of these compounds vary only slightly with the change of the substitution between the ferrocene and dithiole moiety. The lowest energy bands in ethanol related to the Fc-DTF's **14a**,**b**, **18**, **19** and DTF-Fc-DTF **15** were summarized in Table 3.

**Table 3.** Absorption maxima in the electronic spectra of both ferrocene **6** and the Fc-DTF's **14a**,**b**, **18**, **19** and DTF-Fc-DTF **15** in EtOH ($4.05\times10^{-5}$ M)

| Compound | $\lambda_{max}$ nm (log ε) in EtOH |
|---|---|
| Ferrocene **6** | 440 (2.01), 326 (1.77) |
| Fc-DTF **14a** | 454 (3.0), 317 (4.34) |
| Fc-DTF **14b** | 452 (2.88), 309 (4.35) |
| Fc-DTF **18** | 451 (3.04), 327 (4.36) |
| Fc-DTF **19** | 450 (3.16), 310 (4.62) |
| DTF-Fc-DTF **15** | 461 (3.06), 317 (4.42) |

## 3. Conclusion

Benzo-1,4-dithiafulvalenes **14a**,**b**, **18**, **19** and DTF-Fc-DTF **15** were synthesized by Wittig–Horner reaction and their structures were confirmed by spectral analyses. The electrochemical behavior of these compounds was studied using CV. The CV's exhibited good donor properties, showing a two electrons quasi-reversible oxidation wave to the dication. The oxidation potential values, and to a larger extent the reduction potential values processes, were strongly influenced by the scan rates. The oxidation potential values for the investigated compounds are markedly affected by the substitution on to the ferrocene ring. All Fc-DTF compounds displayed two reversible couples of redox waves in $CH_2Cl_2$ as solvent. The advantage of introducing ferrocene into the donor is that ferrocene has only a single one-electron redox process.

Considering the fact that these donors contain 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. In $CH_3CN$ under the same conditions at different scan rates, **18** and **19** also showed two oxidation waves associated with one reduction peak in the reverse scan belonging to the first oxidation wave. A comparison of the absorption bands in the UV–Vis spectra of **14a**,**b**, **18**, **19** and **15** with ferrocene showed a red-shift, and slight increase in the absorption intensities.

## 4. Experimental

### 4.1. General

Melting points were recorded on a Gallencamp melting point apparatus and are uncorrected. Infrared spectra (IR) were measured on a Hitachi 260-10 spectrometer. $^1$H NMR and $^{13}$C NMR spectra were recorded at room temperature on a Varian Nuclear Magnetic Resonance Spectrometer (500 MHz). Chemical shifts are denoted in $\delta$ units (ppm), relative to tetramethylsilane (TMS) as internal standard, $J$ values are given in Hz. $CDCl_3$ is used as a deuterated solvent unless otherwise stated. MS and FAB-MS spectra were obtained using a JEOL JMS-AX505HA. UV–Vis spectra were detected using a U-2010 spectrophotometer. CV was measured on a cyclic voltammeter (Model CS-1090/Model CS-1087). Column chromatography was performed on silica gel 60 (230–400 Mesh ASTM). Solvents were distilled before use. Ferrocenyl carbonyls were prepared according to the methods mentioned in this text and the ferrocene (**6**) was prepared according to the reported method.[17] 2-Thiophenecarbonyl chloride is commercially available and was used without further purification.

**4.1.1. 1-[2-Thiophenecarbonyl]ferrocene (8).** In a dried three-necked flask, a mixture of ferrocene (**6**; 3.72 g, 0.02 mol) and 2-thiophenecarbonyl chloride (2.93 g, 0.02 mol) was stirred in dry $CH_2Cl_2$ (100 ml) at 0°C for

10 min. Anhydrous aluminium chloride (2.8 g, 0.021 mol) was added at such a rate that the reaction mixture remained below 5°C. The appearance of a blue color indicates that the reaction is occurring. This addition required ca. 20 min, and after its completion stirring was continued for 30 min with ice cooling and for further 2 h at room temperature. The reaction mixture was cooled again in ice, 50 ml of water was added cautiously, and the resulting two phases were stirred vigorously for 30 min. After transferring the mixture to a separatory funnel, the layers were separated, and the aqueous layer was extracted with two 50 ml portions of dichloromethane. The combined dichloromethane extracts were washed once with 50 ml of water, twice with 50 ml portions of 10% aqueous sodium hydroxide and dried over sodium sulfate. The dichloromethane was removed under vacuum and the residue was collected and chromatographed on silica gel using chloroform to give 0.4 g of yellow crystals of ferrocene in the early fractions followed by dark red crystals of 1-[2-thiophenecarbonyl]ferrocene (**8**), 4.8 g, 81% yield, mp 121–123°C, in the second fractions. IR (KBr) $\nu$ 3097s, 2360w, 1635m, 1604s, 1590s, 1511s, 1448s, 1411s, 1351s, 1294s, 1157s, 1043s, 865s, 821s, 798s, 725s cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta$ 7.93 (s, 1H, thiophene), 7.6 (d, $J$=4.5 Hz, 1H, thiophen-H), 7.16 (d, $J$=4 Hz, 1H, thiophene-H). 5.03 (s, 2H, ferrocene-H), 4.59 (s, 2H, ferrocene-H), 4.22 (s, 5H, ferrocene-H). $^{13}$C NMR ($CDCl_3$) $\delta$ 189.37 (CO), 144.17 (thiophene, C-2), 131.72, 131.53, 127.63 (thiophene-CH), 78.87 (ferrocene-C), 72.33, 70.97, 70.40 (ferrocene-CH). FAB MS $m/z$ (%) [M$^+$, 296 (13)]. Elemental analysis for $C_{15}H_{12}FeOS$ (296.1618), calcd: C; 60.83, H; 4.08, S; 10.83. Found: C; 60.68, H; 4.20, S; 10.70.

**4.1.2. 1,1′-Bis[2-thiophencarbonyl]ferrocene (9).** Using the same method as for the synthesis of compound **8** only adding two equivalents of 2-thiophenecarbonyl chloride (7.325 g, 0.05 mol) to the ferrocene (3.72 g, 0.02 mol) and stirring in dry $CH_2Cl_2$ (150 ml) at 0°C for 10 min. Anhydrous aluminum chloride (7 g, 0.0525 mol) was added. The reaction after work up and chromatography gave 0.24 g of yellow crystals of ferrocene in the early fractions followed by dark red crystals of the dicarbonyl compound **9**, 4.63 g, 57% yield in the second fractions. The last fractions were collected as the mono carbonyl compound **8**, 2.1 g 35.5% yield.

**4.1.3. Analytical data of 9.** Yield 57%, mp 154–155°C. IR (KBr) $\nu$ 3112s, 3110s, 2960m, 1660m, 1606s, 1517s, 1446s, 1413s, 1375s, 1292s, 1240s, 1159s, 1047s, 865s, 836s, 794s, 754s, 725s cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta$ 7.84 (m, 2H, thiophene), 7.63 (m, 2H, thiophen-H), 7.13 (m, 2H, thiophene-H). 5.06 (s, 4H, ferrocene-H), 4.60 (s, 4H, ferrocene-H). $^{13}$C NMR ($CDCl_3$) $\delta$ 188.20 (2 CO), 143.77 (thiophene, 2 C-2), 132.51, 131.99, 127.86, 126.01, 122.17 (thiophene-CH), 80.34 (ferrocene-C), 74.61, 72.60 (ferrocene-CH). FAB MS $m/z$ (%) [M$^+$, 406 (8)]. Elemental analysis for $C_{20}H_{14}FeO_2S_2$ (406.2876), calcd: C; 59.13, H; 3.47, S; 15.78. Found: C; 58.80, H; 3.71, S; 16.03.

**4.1.4. 1-[(Benzo-1,3-dithiol-2-ylidene)thien-2-ylmethyl]-ferrocene (18).** A sample of 2-dimethoxy-phosphinyl-1,3-benzdithiole (**13**) (0.786 g, 3 mmol) is stirred in dry THF (50 ml) under a stream of nitrogen at −78°C. A solution of $n$-BuLi (2.3 ml, 2.6 M) was added and the mixture was stirred for 15 min. A solution of 1-(2-thiophenecarbonyl)-ferrocene (**8**; 0.888 g, 3 mmol) in dry THF (75 ml) was added portion wise. The temperature of the reaction was raised to room temperature and the reaction mixture was kept over night with stirring. The tetrahydrofuran was removed under vacuum and the residue was washed with water and extracted with chloroform and dried over sodium sulfate. The crude oil product was chromatographed on silica gel using chloroform/hexane mixture (1:1) to give the ferrocene-dithifulvalene **18** as a dark red oil which solidified after standing in the refrigerator to be red crystals, 0.7 g, 61% yield, mp 122–124°C. IR (KBr) $\nu$ 3095w, 3058w, 1654m, 1612m, 1569s, 1448s, 1272m, 1220m, 1105s, 1049m, 1000s, 819s, 742s, 698s cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta$ 7.43 (dd, $J$=1, 5 Hz, 1H, thiophene-H), 7.28–7.27 (dd, $J$= 1.5, 8 Hz, 1H, thiophen-H), 7.12 (m, 1H, thiophene-H). 7.11–7.02 (m, 4H, aromatic-H), 4.44 (t, $J$=2 Hz, 2H, ferrocene-H), 4.24 (t, $J$=2 Hz, 2H, ferrocene-H), 4.19 (s, 5H, ferrocene-H). $^{13}$C NMR ($CDCl_3$) $\delta$ 143.15 (thiophene, C-2), 136.87, 135.70 (thiafulvalene C=C), 131.91, 127.43, 126.88 (thiophene-CH), 125.95, 125.68, 125.40, 121.54, 120.85, 116.05 (aromatic-C and CH), 86.52 (ferrocene-C), 70.40, 69.30, 68.29, 67.71 (ferrocene-CH). FAB MS $m/z$ (%) [M$^+$, 432 (94)]. Elemental analysis for $C_{22}H_{16}FeS_3$ (432.3954), calcd: C; 61.11, H; 3.73, S; 22.24. Found: C; 60.69, H; 3.80, S; 22.68.

**4.1.5. 1-(2-Thenoyl)-1′-[(benzo-1,3-dithiol-2-ylidene)-thien-2-methyl]ferrocene (19).** As described for the synthesis of compound **18**, a sample of **13** (0.843 g, 3.2 mmol) is stirred in dry THF (50 ml) under a stream of nitrogen at −78°C. A solution of $n$-BuLi (2.4 ml, 2.6 M) was added and the mixture was stirred for 15 min. A solution of **9** (0.653 g, 1.6 mmol) in dry THF (50 ml) was used. The crude oil product was chromatographed on silica gel using chloroform/hexane 1:1 to give 0.285 g, 33% yield of ferrocene-dithifulvalene **19** as dark red oil in the second fractions. The polarity was increased and chloroform was used to elute 0.48 g of dark red needles of the starting diketone **9**, 73.5% recovered yield. IR (neat) $\nu$ 3100m, 3006w, 2958m, 2360s, 1724s, 1654s, 1614s, 1515s, 1448s, 1413s, 1288s, 1220m, 1143s, 1041s, 831m, 796s, 748s, 703s cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta$ 7.89 (d, $J$=2.5 Hz, thiophene-H), 7.54 (d, $J$=4 Hz, thiophene-H), 7.43 (d, $J$= 4.5 Hz, thiophene-H), 7.25 (d, thiophene-H), 7.12–7.04 (m, 5H, thiophene-H and 4 aromatic-H), 7.00 (d, $J$=2.5 Hz, thiophene-H), 5.07 (t, $J$=1.5 Hz, 2H, ferrocene-H), 4.62 (t, $J$=1.5 Hz, 2H, ferrocene-H), 4.47 (t, $J$=1.5 Hz, 2H, ferrocene-H), 4.28 (t, $J$=1.5 Hz, 2H, ferrocene-H). $^{13}$C NMR ($CDCl_3$) $\delta$ 188.96 (CO), 144.33, 142.64, 136.69, 135.57, 134.53, 131.78, 131.67 (thiophene-C), 127.76, 127.62, 127.10, 126.24, 125.84, 125.52, 121.66, 120.91 aromatic-C, CH, thiophene-CH and C=C), 113.89 (dithiole-C), 88.59 (ferrocene-C), 79.08 (ferrocene-C), 74.17, 71.75, 71.06, 69.34 (8 ferrocene-CH). FAB MS $m/z$ (%) [M$^+$, 542 (10)]. Elemental analysis for $C_{27}H_{18}FeOS_4$ (542.5212), calcd: C; 59.78, H; 3.34, S; 23.64. Found: C; 59.34, H; 3.74, S; 23.58.

**4.1.6. Reaction of dithiafulvalene-ferrocene derivative (19) with 2-dimethoxyphosphinyl-1,3-benzodithiole (13).** As described above a sample of **13** (122 mg, 0.46 mmol) is stirred in dry THF (20 ml) under a stream of nitrogen at −78°C. A solution of *n*-BuLi (0.35 ml, 2.6 M) was added and the mixture was stirred for 15 min. A solution of compound **19** (0.228 g, 0.42 mmol) in dry THF (20 ml) was added under a stream of dry $N_2$ at −78°C. The crude oil product was chromatographed on silica gel using chloroform/hexane (1:1) to elute 100 mg of yellow oil which has no ferrocene in $^1$H NMR spectra followed by 115 mg of the starting **19** in 50% recovered yield in the next fractions. The data of **19** separated from this reaction were in agreement with the prepared compound.

**4.1.7. Synthesis of 1-[(benzo-1,3-dithiol-2-ylidene)methyl]ferrocene (14a) and 1-[(benzo-1,3-dithiol-2-ylidene)ethyl]ferrocene (14b).** A mixture of formylferrocene (**4a**) or 1-acetylferrocene (**4b**) and compound **13** was used according to the Wittig–Horner reaction described above. The benzo-1,4-dithiafulvalenes **14a**,**b** were prepared and chromatographed on silica gel using chloroform/hexane (1:4).

**4.1.8. 1-[(Benzo-1,3-dithiol-2-ylidene)methyl]ferrocene (14a).** This compound was obtained as orange red crystals, mp 154–155°C, 71% yield. IR (KBr): $\nu$ 3091m, 2994w, 1589s, 1448s, 1430s, 1407s, 1292m, 1259m, 1124m, 1101m, 1049m, 1029m, 998s, 809s, 744s cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta$ 7.24 (m, 1H, aromatic-H), 7.17 (m, 1H, aromatic-H), 7.08 (m, 2H, aromatic-H), 6.16 (s, CH=C), 4.42 (t, $J$=2 Hz, 2H, ferrocene-H), 4.23 (t, $J$=2 Hz, 2H, ferrocene-H), 4.17 (s, 5H, ferrocene-H). $^{13}$C NMR ($CDCl_3$) $\delta$ 137.64, 136.20, 128.26, 126.41, 126.09, 122.26, 121.64 (aromatic-C, CH and thiafulvalene-*C*=CH), 112.71 (thiafulvalene-C=*CH*), 83.42 (ferrocene-C), 69.78, 69.04, 68.06 (ferrocene-CH). FAB MS *m*/*z* (%) [M$^+$, 350 (90)]. Elemental analysis for $C_{18}H_{14}FeS_2$ (350.2756), calcd: C; 61.72, H; 4.03, S; 18.31. Found: C; 61.51, H; 4.22, S; 18.61.

**4.1.9. 1-[(Benzo-1,3-dithiol-2-ylidene)ethyl]ferrocene (14b).** This compound was obtained as orange red crystals, mp 64–66°C, 90% yield. IR (KBr) $\nu$ 3056s, 2952m, 2923m, 2848w, 1581s, 1448s, 1371m, 1278m, 1105s, 1000s, 902m, 817s, 740s cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta$ 7.18–7.16 (m, 2H, aromatic-H), 7.03–7.04 (m, 2H, aromatic-H), 4.57 (s, 2H, ferrocene-H), 4.32 (s, 2H, ferrocene-H), 4.20 (s, 5H, ferrocene-H), 2.2 (s, 3H, $CH_3$). $^{13}$C NMR ($CDCl_3$) $\delta$ 137.19, 135.58 (thiafulvalene C=C), 125.42, 125.30, 123.63, 121.28, 120.96, 118.21 (aromatic-C and CH), 88.63 (ferrocene-C), 69.30, 68.46, 66.91 (ferrocene-CH). FAB MS *m*/*z* (%) [M$^+$, 364 (100)]. Elemental analysis for $C_{19}H_{16}FeS_2$ (364.3024), calcd: C; 62.64, H; 4.42, S; 17.60. Found: C; 62.63, H; 4.37, S; 17.72.

**4.1.10. 1,1′-Bis[(benzo-1,3-dithiol-2-ylidene)ethyl]ferrocene (15).** In the same manner, application of the Wittig–Horner reaction on 1,1′-diacetylferrocene (**5**), dithiafulvalene-ferrocene-dithiafulvalene (**15**) was obtained after chromatography (chloroform/hexane 1:4) as red crystals in 28% yield, in the early fractions. Increasing the polarity of the eluent to 1:2 gave compound **16** in 25% yield as a dark orange–red oil.

**4.1.11. DTF-Fc-DTF 15.** Red crystals, mp 158–159°C, 28% yield. IR (KBr) $\nu$ 3097w, 3045m, 2952w, 1575s, 1432s, 1272s, 1124s, 1020s, 908s, 808s, 727s cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta$ 7.11–7.10 (d, 4H, aromatic-H), 6.97–6.90 (m, 4H, aromatic-H), 4.92 (s, 4H, ferrocene-H), 4.45 (s, 4H, ferrocene-H), 2.27 (s, 6H, 2 $CH_3$). $^{13}$C NMR ($CDCl_3$) $\delta$ 137.14, 135.38 (thiafulvalene C=C), 125.43, 125.20, 121.33, 121.28, 120.86, 117.15 (aromatic-C and aromatic-CH), 70.45, 66.08 (ferrocene-C), 22.16 (2 $CH_3$). FAB MS *m*/*z* (%) [M$^+$, 542 (100)]. Elemental analysis for $C_{28}H_{22}FeS_4$ (542.5688), calcd: C; 61.98, H; 4.08, S; 23.63. Found: C; 61.59, H; 4.10, S; 23.40.

**4.1.12. Ferrocene-dithiafulvalene (Fc-DTF) 16.** This compound was obtained as dark orange–red oil, 25% yield. IR (KBr) $\nu$ 3091m, 2954s, 2927s, 2859s, 1579s, 1448s, 1375m, 1276m, 1124s, 1029s, 821s, 740s cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta$ 7.20–7.17 (m, 2H, aromatic-H), 7.04–7.01 (m, 2H, aromatic-H), 5.49 (bt, 1H, CH=C), 4.56 (s, 2H, ferrocene-H), 4.44 (s, 2H, ferrocene-H), 4.29 (s, 2H, ferrocene-H), 4.24 (s, 2H, ferrocene-H), 2.19–2.13 (m, 5H, $CH_2$ and $CH_3$), 1.86 (s, 3H, $CH_3$), 1.41–1.36 (m, 2H, $CH_2$), 0.92–0.89 (t, 3H, $CH_3$). $^{13}$C NMR ($CDCl_3$) $\delta$ 137.23, 135.55, 130.00, 125.41, 125.30, 121.29, 120.91, 118.07 (C=C aromatic-C and CH), 69.98, 69.70, 68.73, 67.40, 65.85 (ferrocene-CH and ferrocene-C), 30.29 ($CH_2$), 23.40, ($CH_3$), 22.30 ($CH_3$), 15.46 ($CH_2$), 13.93 ($CH_3$). FAB MS *m*/*z* (%) [M$^+$, 446 (100)]. Elemental analysis for $C_{25}H_{26}FeS_2$ (446.4474), calcd: C; 67.26, H; 5.87, S; 14.36. Found: C; 67.38, H; 5.49, S; 14.67.

**4.1.13. 1,1-Diferrocenylketone (21).** This compound was obtained from ferrocenylcarbonyl chloride[18] by adapting the Friedel–Crafts method as for the synthesis of compound **8**. Yield 75%, red crystals, mp 202–205°C (decomp.). IR (KBr) $\nu$ 3089w, 2358m, 2329w, 1662w, 1608s, 1453s, 1376s, 1292s, 1201m, 1105s, 1052s, 998s, 902m, 835s, 806s, 771s cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta$ 4.99 (t, $J$=2 Hz, 4H, ferrocene-H), 4.52 (t, $J$=2 Hz, 4H, ferrocene-H), 4.20 (s, 10H, ferrocene-H). $^{13}$C NMR ($CDCl_3$) $\delta$ 199.35 (CO), 80.42, (ferrocene-C), 71.44, 70.61, 69.98 (ferrocene-CH). FAB MS *m*/*z* (%) [M$^+$, 398 (27)].

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