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ORIGINAL PAPER

Synthesis, cyclic voltammetry, and UV–Vis studies of ferrocene-dithiafulvalenes as anticipated electron-donor materials

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Abstract New ferrocenyl ketones were obtained as precursors of novel π-conjugated ferrocene-dithiafulvalene (Fc-DTF) and π-extended-ferrocenedithia-fulvalenes (π-exFc-DTF) as electron-donor conducting materials from ferrocene by a direct aroylation process using the Friedel–Crafts reaction. Novel Fc-DTF conjugates were synthesized using the Wittig–Horner reaction and their structures were determined. The redox behavior of the ferrocenyl carbonyl compounds Fc-DTF and Fc-π-exDTF was investigated in comparison to the parent ferrocene by means of cyclic voltammetry. A one-electron redox behavior was observed for carbonylferrocenes as one wave potential, while a two-electron process was observed as two oxidation waves for the conjugates. Introduction of electron-withdrawing groups led to increasing E_{pa} values and decreasing ΔE_p values. The UV–Vis spectra of some compounds were studied in comparison with ferrocene. The absorption spectra showed a red-shift with a slight increase in the absorption intensities.

Keywords Wittig–Horner reaction · Electron donors · Ferrocene derivatives · Dithiafulvalene derivatives · π-Conjugates

Introduction

Ferrocene chemistry has revived in recent years because ferrocenyl derivatives have found numerous uses in various fields of science from biology to materials chemistry [1]. Ferrocene has attracted the interest of many scientists and research groups worldwide because of its applications in materials science and asymmetric synthesis [2, 3]. Spectrochemical and electrochemical behaviors of ferrocene-heteroaromatic analogues have also been observed [4, 5]. It has been reported that a wide variety of macrocycles, cryptands, and cavitands containing the ferrocene unit have been synthesized and characterized [1]; some ferrocenes have also been incorporated into a number of anion sensors [6, 7]. Due to the structural and electrochemical properties of ferrocene-containing tetrathiafulvalene derivatives, several ferrocene-tetrathiafulvalenes have been constructed as donors for conducting CT complexes. Recently, 1,1′-disubstituted ferrocenes were synthesized as novel donors for the preparation of CT complexes, which are structurally and electronically conjugated to the tetrathiafulvalenes (TTFs) heterocycle with a ferrocene moiety [8]. These findings prompted us to synthesize a number of new heterocyclic systems incorporating ferrocene moieties separated by aryl rings as conjugated spacers and to study the electrochemical redox behavior of these new types of heterocyclic donors comparing them with the parent ferrocene and acetylferrocene.

Results and discussion

In this work, we describe the synthesis of some 1-ferrocenyl ketones and 1.1′-ferrocenyl-dicarbonyl compounds conjugated to a heterocyclic ring. In connection with our

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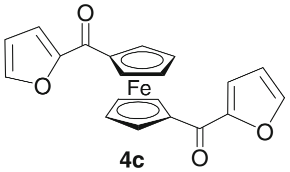
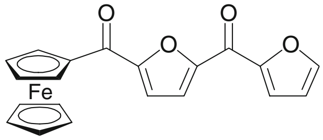
interest in ferrocene and ferrocene-substituted aldehydes and ketones, we envisioned the electrophilic substitution by a Friedel–Crafts reaction as an efficient route to these classes of electron-donor compounds. We investigated the viability of ferrocene as a substituted electron-donor moiety to several dithiafulvalenes (DTF) [9, 10] and ferrocene-dithiafulvalenes (Fc-DTF) [8, 11, 12] connected directly or through a conjugated spacer. We found that the ferrocene moiety increases the electron-donor ability of both Fc-DTF and Fc-exDTF compounds. Formylferrocene (**3i**) was prepared according to the method previously reported in literature [13–15]. Compounds **3a**–**3h** were prepared according to the Friedel–Crafts reaction in good yields (Scheme 1) [16–23]. We report herein the facile synthesis of ferrocenyl carbonyl compounds bearing one or two substituents in the 1 and 1,1′-positions. The underlying idea is to synthesize precursors of novel π-extended electron-donor systems such as Fc-DTF and Fc-π-exDTF, which are capable of intramolecular stacking by virtue of the eclipsed conformation of the ferrocene moiety. This modification involves the replacement of the ethylenic bond of TTF by a conjugated spacer ferrocene or a furan that might favor intra- and interchain interactions between the new donors, which should decrease the Coulombic repulsions in the dicationic state of the donors.

The *N*-methylpyrrol-2-ylcarbonylferrocene (**3e**) was prepared in 22% yield by methylation of **3d** in THF in the presence of methyl iodide and NaH as basic catalyst. The yield of the ferrocene-1-carbonyl derivatives **3a**–**3i** obviously depends on the electrophilicity of RCO^+, as shown by the following order according to yields: $CH_3CO^+ > PhCO^+ >$ thienyl-$CO^+ >$ pyrryl-$CO^+ >$ furyl-$CO^+ > ClCH_2CO^+ >$ *N*-methylpyrryl-$CO^+ >$ indolyl-CO^+. On the other hand, ferrocene-1,1′-dicarboxaldehyde (**4f**) was synthesized in 70% yield following the routes previously reported in Refs. [24, 25]. Following aroylation of ferrocene using the same procedure but with two moles of the carbonyl chloride, the ferrocene-1,1′-dicarbonyl derivatives **4a**–**4e** were obtained as a major products, while the mono-substituted derivatives **3a**–**3e** were obtained as byproducts (Scheme 2) [26].

Upon reaction of ferrocene (**1**) with furan-2-carbonyl chloride (**2c**), in addition to the expected products **3c** and **4c,** a considerable amount of the dicarbonyl derivative **5** was obtained as dark red-brown oil. The structure of **5** was confirmed by IR, ^{1}H-NMR, ^{13}C-NMR, and FAB-MS spectral analysis, and the data obtained were in satisfactory agreement with the suggested structure. The ^{1}H-NMR spectra of **4c** revealed eight ferrocene-H in a ratio of 1:1 at δ 5.16 ppm (d, $J = 2$ Hz, 4H, ferrocene-H), 4.55 ppm (d, $J = 2$ Hz, 4H, ferrocene-H) and six furan-H in a ratio of 2:2:2 at δ 7.5 ppm (s, 2H, furan-H), 6.54 ppm (d, $J = 1$ Hz, $J = 1$ Hz, $J = 2$H, furan-H). In addition to nine ferrocene-H protons in a ratio of 5:2:2, the NMR spectra of the di-carbonyl compound **5** showed another five furan-H in a ratio of 1:2:1:1


4c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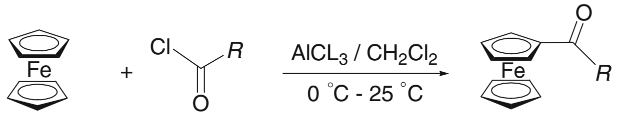
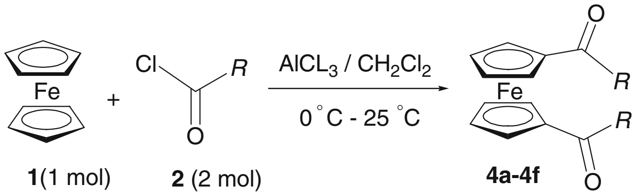
The ^{13}C-NMR spectra of compound **5** showed, in addition to the furan-C, ferrocene-C and CH, the presence of two different carbonyl (2 CO) groups, one at δ 185.18 ppm belonging to CO-ferrocene and one at δ 168.66 ppm incorporated to furan-CO-furan. In the case of compound **4c**, the two similar carbonyls related to furan–CO–Fc–CO–furan appeared at δ 183.60 ppm. The FAB-MS spectrum exhibited an exact M^+ at 374 as in **4c**. Full details of ^{1}H-NMR and ^{13}C-NMR are summarized in the "Experimental" section.



1(1 mol) **2a-2h** (1 mol) **3a-3h**

Comps	R	Yields/%	Comps	R	Yields/%
2a-3a	Phenyl	94	**2e-3e**	2-(N-CH_3Pyryl)	22
2b-3b	2-Theiny	81	**2f-3f**	2-Indolyl	10
2c-3c	2-Furyl	36	**2g-3g**	CH_2Cl	23
2d-3d	2-Puryl	46	**2h-3h**	CH_3	98
			3i	H	61

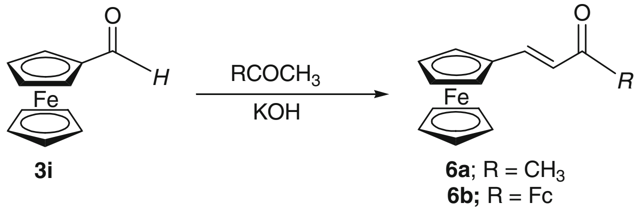
Scheme 1



1(1 mol) **2** (2 mol) **4a-4f**

Compounds	R	Yield/%
2a-4a	Phenyl	99
2b-4b	2-Theinyl	57
2c-4c	2-Furyl	21
2d-4d	2-Methyl	98
2e-4e	3-Tolyl	67
4f	H	70

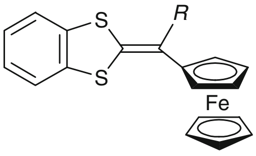
Scheme 2



Scheme 3

Following the same methods reported in the literature [27], the derivatives **6a** and **6b** were synthesized directly in yields of 88 and 76% from the condensation of formylferrocene (**3i**) with acetone or 1-acetylferrocene (**2h**) in the presence of KOH as basic catalyst (Scheme 3).

In previous work we examined and studied several examples of new ferrocene-dithiafulvalenes (Fc-DTF) **7** and Fc-π-exTTF **8**. The electrochemical properties of these new donor compounds have been studied using UV–Vis spectra and cyclic voltammetry (CV). It has been found that these types of electron-donor compounds have good donor ability and form CT-complexes [28–32]



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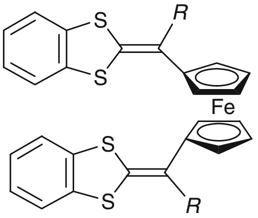

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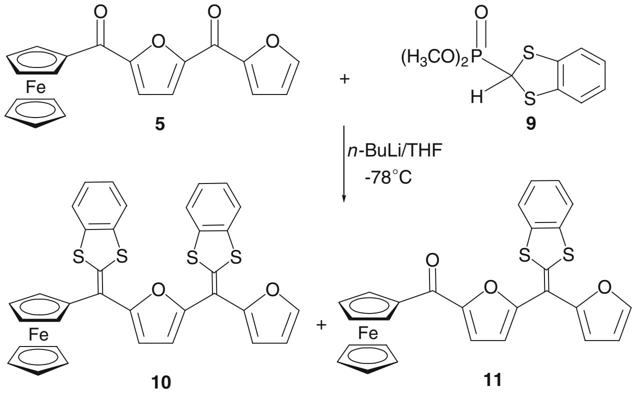
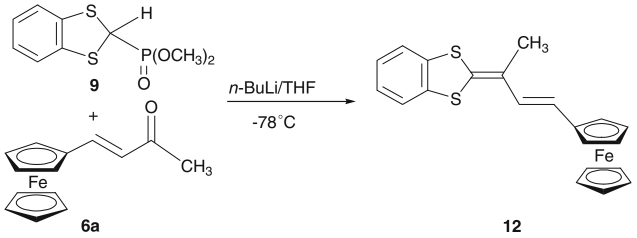
Cross-coupling reaction of **5** with benzo-1,3-dithiole-2-phosphonate (**9**) [33–36] in the presence of *n*-BuLi/THF at −78 °C afforded ferrocene-π-extended dithiafulvalene derivatives Fc-π-exDTF **10** and Fc-DTF **11** in good yields. The structure of these dithiafulvalenes was confirmed and characterized by spectral analysis, and the electrochemical behaviors were studied using CV studies. It was found that the donor ability of Fc-DTF increased by increasing the extension of conjugation; see Scheme 4.



Scheme 4



Scheme 5

In the same manner, the reaction of **6a** with benzo-1,3-dithiole-2-phosphonate (**9**) [33–36] in the presence of n-BuLi/THF at −78 °C afforded ferrocene-dithiafulvalene (Fc-DTF) **12** in 82% yield. The electrochemical behavior of **12** was studied using CV. It was found also that the donor ability of Fc-DTF increased with increased extension of conjugation (Scheme 5). Reaction of **6b** with the dithiole **9** under the same conditions gave no product. This might be explained by the fact that the Wittig–Horner reaction relies in part on the carbonyl reactivity of the carbonyl component. In the case of **6b**, the ketone is substituted with the strongly electron-donating substituent Fc. This outcome also might be attributed to the steric hindrance around the carbonyl group.

Following the same procedure, treatment of ferrocenyl ketones **3d–3f** with **9** gave no products even after increasing the reaction temperature to reflux—thus, the compounds **13d–13f** could not be obtained. This might be explained by the fact that the heterocycles are electron-rich and thus reduce the carbonyl reactivity of **3** to an extent that does not allow the reaction with the ylide. In addition, the negative charge in the ylide is highly stabilized by the sulfur atoms making the ylide less nucleophilic. Also the nature of the amidic character of the carbonyl group or the hydrogen bonding arising between the NH and the CO groups might play a negative role in this reaction.

Electrochemical properties

The electrochemical properties of compounds **3a–3e** and **4a–4e** in comparison to ferrocene (**1**) were investigated by CV with CH_2Cl_2 as the solvent in the presence of tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte using Pt working and counter electrodes and Ag/AgCl as reference electrode at ambient temperature. The ferrocene carbonyls displayed one redox wave corresponding to a one-electron transfer process. The redox potentials are summarized in Table 1. Comparing **1** with the conjugated carbonyl **6a** showed that increasing the

Table 1 Cyclic voltammetric data (CV) of ferrocenyl ketones **1** and **3b**–**3j**, scan rate 100 mV

No.	Compound	E^{ox}/mV	E^{red}/mV	$E^{o\prime}$/mV	ΔE_p/mV
1	Ferrocene	556	473	515	83
3b	$Fc\text{-}COC_4H_3S$	846	753	798	93
3c	$Fc\text{-}COC_4H_3O$	868	774	821	94
3d	$Fc\text{-}COC_4H_4N$	740	662	701	78
3f	Fc-CO-2-indolyl	766	682	724	84
3h	$Fc\text{-}COCH_3$	847	729	788	118
3i	Fc-CHO	908	790	849	112
3j	$Fc\text{-}COCH_2O\text{-}^nBu$	943	738	841	105

conjugation leads to an increase in the $E^{1/2}$ values. This suggests that the replacement of an H atom by an electron-acceptor group leads to a decrease in the electron-donating ability of ferrocene derivatives (Fig. 1).

At a scan rate of 100 mV/s, the peak-to-peak separation (ΔE_p) of mono carbonyl ferrocene increases in the following order: **3d** (78 mV) < **1** (83 mV) < **3f** (84 mV) < **3b** (93 mV) < **3j** (105 mV) < **3i** (112 mV) < **3h** (118 mV) indicating that the electron transfer between ferrocene and the electrode slowed with the increase of generation. Moreover, when the scan rates increased from 10 to 600 mV, the ΔE_p increased, indicating a quasi-reversible electrochemical process for all ferrocenyl ketones. This relationship between the molecular structure and electron-transfer rate could be rationalized by the environmental change of redox in the ferrocene component. As already mentioned in literature, substitution of an H-atom of ferrocene by electron-withdrawing carbonyl groups increases the $E_{1/2}$ values, but decreases the ΔE value. Introduction of the carbonyl group with an electron-donating group such as CH_3 decreases the $E_{1/2}$ values as well (Table 1 and Fig. 1).

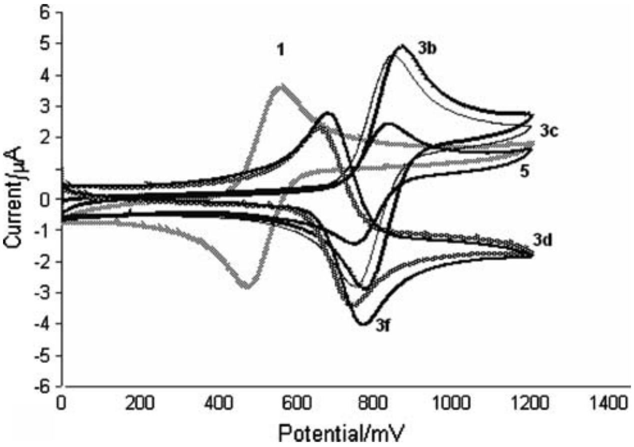


Fig. 1 Cyclic voltammetry (CV) of **1**, **3b**, **3c**, **3d**, **3f**, and **5** in CH_2Cl_2 as the solvent and at a scan rate of 100 mV using TBAP as the supporting electrolyte in 0.1 mol concentration

Table 2 Cyclic voltammetric data (CV) of ferrocenyl ketones **4b**–**4f**, and **5**, scan rate 100 mV

No.	Compound	E^{ox}/mV	E^{red}/mV	$E^{o\prime}$/mV	ΔE_p/mV
4b	$Fc\text{-}(COC_4H_3S)_2$	1,076	969	1,023	107
4c	$Fc\text{-}(COC_4H_3O)_2$	1,015	901	958	114
4d	$Fc\text{-}(COCH_3)_2$	1,075	985	1,030	90
4e	$Fc\text{-}(COC_6H_4CH_3\text{-}m)_2$	1,028	913	971	115
4f	$Fc\text{-}(CHO)_2$	1,133	1,047	1,090	86
5	Fc-CO-furyl-CO-furyl	835	748	791	87

As seen in Table 1, introduction of two carbonyl groups (electron-withdrawing) also leads to an increase in the E_{pa} values above those for Fc-CHO (**3i**), which leads to the preparation of unstable conducting salts [24, 25].

In comparing **1** and 1-carbonyl ferrocenes **3b**–**3j** with 1,1′-dicarbonyl ferrocenes **4b**–**4f**, we found that the oxidation potential $E_{1/2}$ values of the dicarbonyl ferrocene are higher than for 1-carbonyl ferrocenes by virtue of the E^{ox} (di) $-$ E^{ox} (mono) = 200–220 mV; this also indicates that the electron-withdrawing groups increase the oxidation potential values (Table 2).

The π-extended-DTF **10** and Fc-DTF **11** derivatives displayed two pairs of redox waves corresponding to one-electron transfer process. The redox potentials are summarized in Figs. 2, 3, and Table 3. Compound **10** should undergo three oxidation processes for three electrons, but only a single three-electron chemically reversible but electrochemically irreversible oxidation process to form the tricationic state in CH_2Cl_2 was observed (Fig. 2).

Increasing the scan rate results in a significant increase in the E_{pa} (SR = 10–600 mV) and decreases the E_{pc} values. At low scan rate of 10–20 mV compound **10** showed two oxidation waves associated with one reduction peak in the reverse scan on the Pt electrode. Increasing the scan rate of the extended-DTF **10** showed that the CV becomes

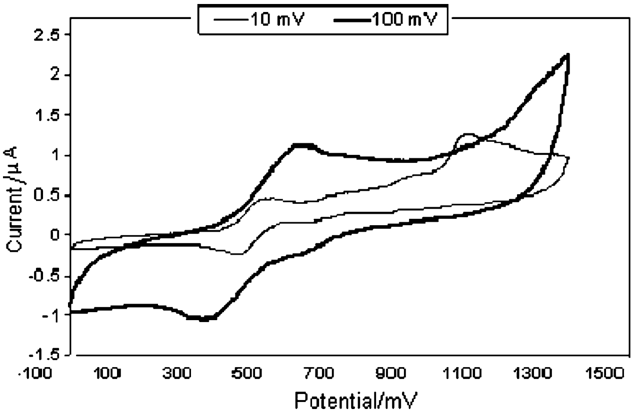


Fig. 2 Cyclic voltammetry (CV) of **10** in CH_2Cl_2 at scan rates 10 and 100 mV using TBAP as the supporting electrolyte at 0.1 mol concentration

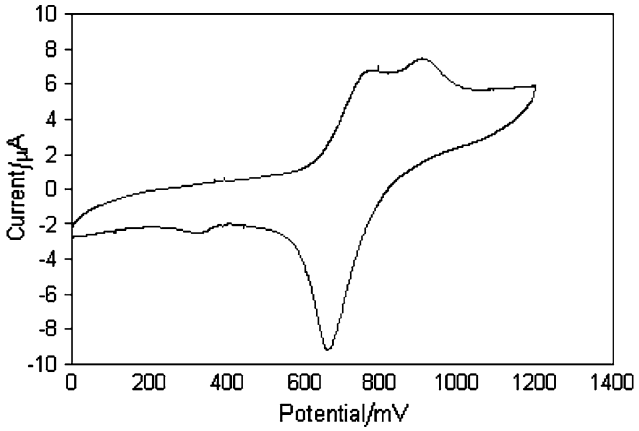


Fig. 3 Cyclic voltammetry (CV) of **11** in CH_2Cl_2 at scan rate 600 mV

irreversible and only one oxidation process is clearly seen. At a scan rate 100–600 mV or higher only one oxidation wave was observed and the reduction peak was observed at around 220–280 mV in the reverse scan for compound **10**. It should be mentioned that attempts to separate this three-electron oxidation wave into two or three peaks by changing the scan rate at ambient temperature were not successful. This indicated, however, that when the exDTF moiety was oxidized to the dicationic state, oxidation of the Fc moiety in **10** became more difficult, showing the inductive effect of the positively charged dicationic state of the exDTF. This also indicated that the intramolecular electron-withdrawing effect of the exDTF moiety on the oxidation of the Fc moiety in **10** is larger relative to the parent ferrocene. It is possible that coupling could take place between the two radical cations of **10**. Only at 10 mV scan rate were two oxidation waves observed associated with only one reduction wave. Compound **11** showed two oxidation waves at peak potentials 773 and 907 mV (v = 600 mV s^{-1}) with only one associated reduction peak in the reverse scan (Fig. 3).

In addition, as can be seen in Fig. 3, the ferrocene-based oxidation wave for **11** is more positive than that of the parent ferrocene (556 mV) by 223 mV. This indicates that in addition to the intramolecular electronic interactions between the Fc and DTF moieties, the electron-withdrawing effect of the CO-Fc moiety plays a role. Considering the fact that **12** contains two different types of donor moieties, namely ferrocene and dithiol, it was important to determine which was easier to oxidize. Thus, careful comparison was made between the electrochemical data of ferrocene **1**, **6a**, and π-extended dithiafulvalene **12**. In CH_2Cl_2, **1** is easier to oxidize than both **6a** and **12** (see Fig. 4 and Table 4). Therefore, the first oxidation corresponds to the ferrocene moiety and the second oxidation process corresponds to 1.3-dithiole moiety by one electron, leading overall to the formation of the dicationic state. This assignment is supported by the fact that both the first and the second oxidations of **12** in CH_2Cl_2 are electrochemically reversible. Furthermore, the redox potentials of this two-electron process are scan-rate dependent, consistent with the behavior of ferrocene, for which the redox potential is independent of the scan rate. However, the second oxidation is reversible at 739 mV with a ΔE_p value $E^{1/2}{}_{Ox}$ (2) − $E^{1/2}_{Ox}$ (1) = 739 − 505 = 234 mV, v = 100 mV. Comparing the redox potentials for **1**, **6a**, and **12** shows that the oxidation peak potential (E^1_{pa}) of **6a** in CH_2Cl_2 is more positive than that of **1** or **12** following the trend **12** < **1** < **6a**. This might be attributed to the electron-withdrawing effect of the CO group and is in agreement with the electrochemical data in Table 4 and Fig. 4. In contrast, the anodic peak potential (E^1_{pa}) of **12** is less than that of **1** by 51 mV. This must result from the extended conjugation between the two donor moieties. Based on these observations and other reported data, oxidation of the Fc moiety in **12** should be easier than that of the parent ferrocene.

Electron spectroscopy

As can be seen in Figs. 5 and 6, the UV–Vis spectra of the ferrocene carbonyls in comparison to the parent ferrocene (**1**) in ethanol as the solvent are mainly dominated by the absorption of the ferrocene moieties in the region of 275–300 nm. It is known that in the region 300–500 nm, no intense absorption is observed for the parent ferrocene. This might be attributed to the weak absorption intensity of ferrocene itself. The absorptions of the investigated carbonyls were observed as listed in Table 5. Upon

Table 3 Cyclic voltammetric data (CV) of compounds **10**, **11**, and **12,** scan rate 10–600 mV

No.	Scan rate (mV)	E^1_{pa}/mV	E^1_{pc}/mV	E^2_{pa}/mV	E^2_{pc}/mV	ΔEp^1 (E_{pa}–E_{pc})/mV	ΔEp (E^2–E^1)/mV
10	10	540	481	1,110	–	59	570
	100	637	398	–	–	239	–
	300	711	312	–	–	399	–
11	100	779	681	885	–	98	105
	300	779	676	891	–	103	112
	600	773	662	907	–	111	134

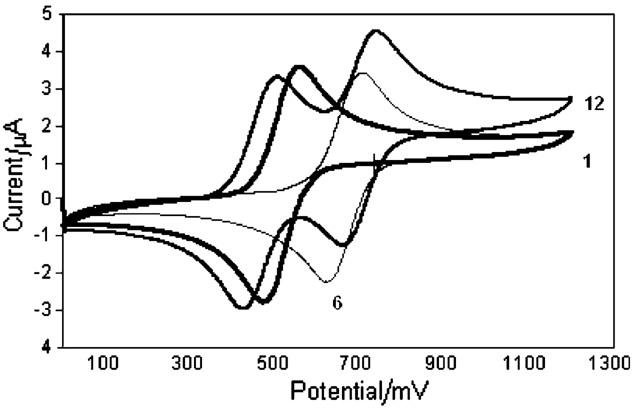


Fig. 4 Cyclic voltammetry (CV) of compounds **1**, **6a**, and dithiafulvalene **12** in CH_2Cl_2 at scan rate 100 mV

Table 4 Cyclic voltammetric data (CV) of ferrocene (**1**) and **6a**, scan rate 100 mV

No.	Compound	$E^{1/2}_{ox}$/mV	$E^{1/2}_{red}$/mV	ΔE ($E_{ox}-E_{red}$)/mV
1	Ferrocene	556	473	83
6a	Fc-CH=CHCOCH$_3$	714	620	94

No.	Compound	E^{1}_{ox}/mV	E^{1}_{red}/mV	E^{2}_{ox}/mV	E'^{2}_{red}/mV	ΔE ($E'^2-E'^1$)/mV
12	Fc-DTF	505	426	739	661	234

comparison of the λ_{max} values of **1** and ferrocene carbonyl compounds, an associated absorption peak appeared in the region of 300–400 and 400–500 nm. An increase in the absorption intensities was also recognized. This means that ground-state intramolecular electronic interactions are observed in all ferrocene carbonyl compounds (Table 5).

It should be mentioned that intermolecular interactions are observed in all investigated ferrocene carbonyl compounds as judged 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 (**1**), and its intensity shows a linear dependence on concentration.

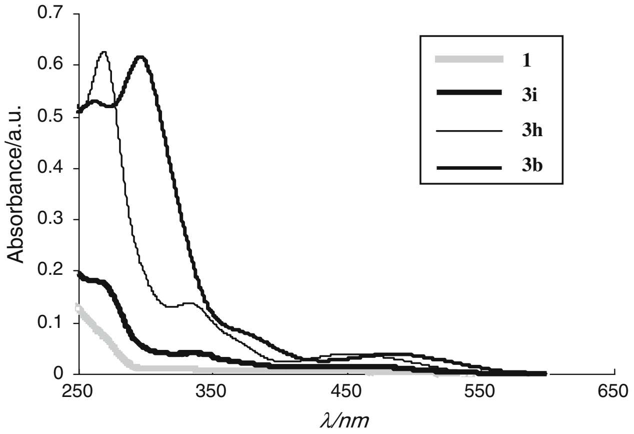


Fig. 5 UV–Vis spectra of **1**, **3b**, **3h**, and **3i** in EtOH (4.05×10^{-5} M)

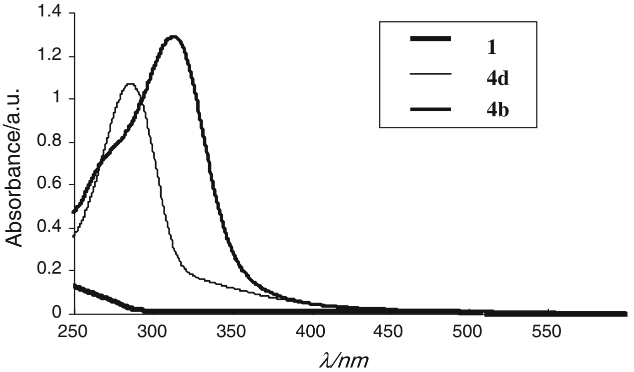


Fig. 6 UV–Vis spectra of **1**, **4b**, and **4d** in EtOH (4.05×10^{-5} M)

Table 5 Absorption maxima in the electronic spectra of both ferrocene (**1**) and ferrocene-carbonyl compounds in EtOH (4.05×10^{-5}M)

Compound no.	λ_{max}/nm (log ε)
1	440 (2.01), 326 (1.77), 315 (3.6)
3b	495 (4.17), 429 (4.02), 297 (5.39), 264 (5.33)
3f	464 (3.78), 342 (4.20), 264 (4.86)
3g	462 (4.18), 400 (3.98), 335 (4.74), 269 (5.4)
4b	314.5 (5.71)
4d	286.5 (5.63)

The absorption intensities of these compounds differ only slightly with the change of substituents between the ferrocene and carbonyl group. The lowest energy bands in ethanol as the solvent related to the ferrocene carbonyl compounds are summarized in Table 5. The appearance of weak broad absorption bands in the 400–550 nm regions indicates the existence of charge-transfer interaction in these compounds.

Conclusion

In conclusion, a number of 1- and 1,1′-disubstituted carbonyl ferrocenes were synthesized by means of Friedel–Crafts reaction, and their structures were confirmed by spectral analyses. Some Fc-π-exTTF and Fc-π-exDTF derivatives were accomplished by the Wittig–Horner reaction of the respective phosphonate ester **9** with different alkanoylferrocenes. Electrochemical studies of the ferreocenylketones and these new conjugated hybrids **10**, **11**, and **12** were performed using cyclic voltammetry at ambient temperature using TBAP as the supporting electrolyte. The CV exhibited good donor properties, showing a one-electron quasi-reversible oxidation potential. The oxidation-potential values, and to a larger extent, the reduction-potential values processes, are strongly influenced by the scan rate. Increasing the scan rate from 20 to 600 mV leads to an increase in the oxidation potential. Comparison of ferrocene with the Fc-DTF or Fc-extended TTF showed that the oxidation peak potential (E_{pa}) belongs to the ferrocene moiety in CH_2Cl_2, and it is more positive than that of ferrocene (**1**) due to the electron-withdrawing effect of the CO group in compounds **3a**–**3i**, **4a**–**4i**, **6a**, and **11**. In contrast, the anodic peak potential (E^1_{pa}) of **12** is less than that of **1** by 51 mV due to the conjugation between the two donor moieties. A comparison of the absorption bands of ferrocene carbonyl compounds with ferrocene showed a red-shift and increase in the absorption intensities.

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, 1-5-1). ^{1}HNMR and ^{13}C-NMR spectra were recorded at room temperature on a Varian Nuclear Magnetic Resonance Spectrometer (500 MHz). Chemical shifts are denoted in δ units (ppm), relative to TMS as internal standard, J values are given in hertz (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 (Hitatshi). Cyclic voltammetry was measured on a cyclic voltammogram spectrometer (model CS-1090/model CS-1087, Cypress System). Column chromatography was performed on silica gel 60 (230–400 Mesh ASTM). Solvents were distilled before use. Thiophene-2-carboxylic acid chloride and furan-2-carboxylic acid chloride are commercially available and used without further purification. Benzoyl chloride and phenylpropionyl chlorides were prepared [19] and distilled before use. The synthesis of 1-alkyl/arylcarbonylferrocenes **3a**–**3h** was achieved according to literature procedures providing benzoylferrocene (**3a**), mp 111–112 °C, lit. mp 112 °C [19]; 1-(2-thenoyl)ferrocene (**3b**), mp 121–123 °C, lit. mp 124–126 °C [23]; 1-(2-furoyl)ferrocene (**3c**), mp 79–81 °C, lit. mp 80 °C [23]; 1-(2-pyrroyl)ferrocene (**3d**), mp 163 °C, lit. mp 163 °C [23]. 1,1′-Di(2-thenoyl)ferrocene (**4b**) was obtained with mp 158–160 °C, lit. 166–168 °C [16–23].

1-(2-(N-methylpyrroyl)ferrocene (**3e**, $C_{16}H_{15}FeNO$)
This compound was obtained by reaction of 0.54 g **3d** (2.01 mmol) with 4.37 g methyl iodide (30.8 mmol) in the presence of 125 mg NaH (2.6 mmol) in 20 cm^3 dry THF as dark red crystals in 22% yield. IR (KBr): ν = 3,100m, 2,950w, 1,570s, 1,540s, 1,455s, 1,410s, 1,310s, 1,250m, 1,220m, 1,125s, 1,100s, 1,070s, 1,000s, 880s, 850s, 820s, 785s, 760s, 605s, 570s cm^{-1}; ^{1}HNMR ($CDCl_3$): δ 7.13 (d, J = 4 Hz, 1pyrrole-H), 6.82 (m, lpyrrole-H), 6.14 (t, J = 4 Hz, 1pyrrole-H), 4.94 (s, 2ferrocene-H), 4.49 (t, J = 2 Hz, 2ferrocene-H), 4.20 (m, 5ferrocene-H), 3.94 (s, NCH_3) ppm; EI-MS: *m/z* (%) = 293 (M$^+$, 100).

1-(2-Indolyl)ferrocene (**3f**, $C_{19}H_{15}FeNO$)
This compound was obtained following the method described in **3a**–**3d** as dark red crystals in 10% yield. IR (KBr): ν 3,324s (NH), 3,090m, 1,615m, 1,587s, 1,517s, 1,454s, 1,400s, 1,342s, 1,267s, 1,133s, 1,062s, 1,031s, 1,000s, 823s, 777s, 744s, 669m, 485s cm^{-1}. ^{1}HNMR ($CDCl_3$): δ 9.19 (s, NH), 7.76–7.75 (d, J = Hz, 1indole-H), 7.46–7.45 (d, J = Hz, 1aromatic-H), 7.38–7.34 (m, 2aromatic-H), 7.18 (m, 1aromatic-H), 5.24 (s, 2ferrocene-H), 4.73 (s, 2ferrocene-H), 4.34 (s, 5ferrocene-H) ppm; EI-MS: *m/z* (%) = 329 (M$^+$, 18).

1,1′-(2-Difuroyl)ferrocene (**4c**, $C_{20}H_{14}FeO_4$)
This compound was obtained after chromatography using $CHCl_3$ in the third fractions as dark red crystals in 21% yield, mp 104–106 °C. IR (KBr): ν 3,100s, 1,730m, 1,619s, 1,606s, 1,563s, 1,479s, 1,442s, 1,375s, 1,334s, 1,295s, 1,220s, 1,155s, 1,079s, 1,051s, 1,020s, 975s, 912s, 881s, 813s, 767s, 599s, 501s cm^{-1}; ^{1}HNMR: δ = 7.5 (s, 2furan-H), 7.27 (s, 2furan-H), 6.54 (d, J = 1 Hz, J = 2 Hz, 2furan-H), 5.16 (d, J = 2 Hz, 4ferrocene-H), 4.55 (d, J = 2 Hz, 4ferrocene-H) ppm; ^{13}C NMR: δ = 183.60 (2 CO), 153.41 (furan, C-2, C-2′), 145.64 (furan, C-5, C-5′), 117.15, 112.13 (furan-C-3, C-4, C-3′, C-4′), 79.10 (ferrocene-C-1, C-1′), 74.23, 72.45 (ferrocene-CH) ppm; FAB-MS: *m/z* (%) = 374 (M$^+$, 54).

1-[4-(2-Furoyl)]-2-furoylferrocene (**5**, $C_{20}H_{14}FeO_4$)
This compound was obtained as the second fractions from the preparation of **4c** as a dark violet-red oil, which solidified after long standing in refrigerator, yield 16%. IR (KBr) ν = 3,139s, 1,774s, 1,706s, 1,631s, 1,565s, 1,461s, 1,378s, 1,290s, 1,186s, 1,155s, 1,056s, 1,038s, 933s, 883s, 840s, 819s, 759s, 593s, 501s cm^{-1}; ^{1}HNMR: δ = 7.75 (m, 1furan-H), 7.66–7.63 (m, 2furan-H), 7.41–7.40 (dd, J = 1 Hz, J = 4 Hz, 1furan-H), 6.69–6.68 (dq, J = 0.5 Hz, J = 1.5 Hz, 1Hfuran-H), 5.29 (quintet, J = 1.5 Hz, J = 3 Hz, 2ferrocene-H), 4.71–4.70 (quintet, J = 1.5 Hz, J = 2 Hz, 2ferrocene-H), 4.22 (s, 5ferrocene-H) ppm; ^{13}CNMR: δ = 185.18 (Fc-CO), 168.66 (furan-CO-furan), 155.35, 151.42, 147.62 (furan, C-2, C-2′, C-4), 120.19, 120.11, 116.88, 112.81 (furan-CH), 77.23 (ferrocene-C), 73.39, 71.09, 70.43 (ferrocene-CH) ppm; FAB-MS: *m/z* (%) = 374 (M$^+$, 18).

1-Ferrocenylbut-1-en-3-one (***6a***) *and 1,3-diferrocenylprop-1-en-3-one* (***6b***)

Following the method described in Ref. [27] the derivatives **6a** and **6b** were synthesized directly in yields of 88 and 92% from the condensation of formylferrocene (**3i**) with acetone or 1-acetylferrocene (**2h**) in the presence of KOH as basic catalyst.

1-Ferrocenylbut-1-en-3-one (**6a**, $C_{14}H_{14}FeO$)

This compound was obtained as dark red crystals in 88% yield, mp 79–80 °C. IR (KBr): v = 3,095m, 1,652s, 1,616s, 1,440m, 1,351s, 1,259s, 1,178s, 1,105s, 1,029s, 1,002s, 968s, 821s, 561s, 497s cm^{-1}; ^{1}HNMR: δ = 7.45–7.41 (d, J = 16 Hz, 1CH = CH), 7.36–7.32 (d, J = 16 Hz, 1CH = CH), 4.51 (s, 2ferrocene-H), 4.45 (s, 2ferrocene-H), 4.15 (s, 5ferrocene-H), 2.29 (s, CH_3) ppm; ^{13}C-NMR ($CDC1_3$) δ 197.86 (CO), 145.11, 124.71 (CH = CH), 78.57 (ferrocene-C), 71.23, 69.74, 68.80 (ferrocene-CH), 27.20 (CH_3) ppm; FAB-MS: *m/z* (%) = 254 (M$^+$, 60)].

1,3-Diferrocenylprop-1-en-3-one (**6b**, $C_{23}H_{20}Fe_2O$)

This compound was obtained as dark red crystals in 92% yield, mp 205–207 °C. IR (KBr): v 3,087s, 2,360m, 1,643s, 1,577s, 1,469s, 1,448s, 1,375s, 1,351m, 1,290s, 1,249s, 1,180m, 1,105s, 1,081s, 1,029s, 1,002s, 977s, 910s, 821s, 744m, 667s, 547s, 511s cm^{-1}; ^{1}HNMR: δ = 7.71-7.68 (d, J = 16 Hz, 1CH = CH), 6.75-6.72 (d, J = 16 Hz, 1CH = CH), 4.87 (s, 2ferrocene-H), 4.60 (s, 2ferrocene-H), 4.56 (s, 2ferrocene-H), 4.47 (s, 2ferrocene-H), 4.20 (s, 5ferrocene-H), 4.18 (s, 5ferrocene-H) ppm; FAB-MS: *m/z* (%) = 424 (M$^+$, 100).

1-Ferrocenyl-2-(benzo-1,3-dithiol-2-ylidenyl)]but-1-ene (**12**, $C_{21}H_{18}FeS_2$)

A mixture of 0.524 g **3** (2 mmol) was stirred in 50 cm^3 dry THF under a stream of nitrogen at −78 °C. A solution of *n*-BuLi (2.3 cm^3, 2.6 M in *n*-hexane) was added portion-wise, and the mixture was stirred for 15 min. A solution of 0.374 g **6a** (1 mmol) in 50 cm^3 dry THF was added portion-wise within 15 min. The temperature of the reaction was raised to room temperature, and the reaction mixture was kept overnight with stirring. The THF was removed under vacuum, the residue was washed with water, extracted with chloroform, and dried (Na_2SO_4). The crude oil product was chromatographed on silica gel using chloroform/*n*-hexane (1/4) to give **12** as dark red crystal in 82% yield. IR (KBr): v = 3,095m, 3,054m, 3,023m, 2,929m, 1,569s, 1,546s, 1,432s, 1,376s, 1,281m, 1,160m, 1,103s, 1,024s, 1,000s, 943s, 815s, 736s, 514s cm^{-1}; ^{1}H-NMR: δ = 7.49–7.44 (m, 2aromatic-H), 7.32–7.28 (m, 2aromatic-H), 6.72–6.64 (d, J = 38 Hz, 1CH = CH), 6.40–6.32 (d, J = 38 Hz, 1CH=CH), 4.66 (s, ferrocene-H), 4.51 (s, 2ferrocene-H), 4.35 (s, 5ferrocene-H), 2.2 (s, CH_3) ppm; ^{13}C NMR: δ = 136.56, 136.18 (thiafulvalene, C=CS_2), 125.84, 125.66, 124.68, 121.46, 121.43, 119.93 (aromatic-C, CH, CH=CH), 70.16, 68.84, 68.07, 68.57, 66.13 (ferrocene-C and CH), 17.38 (CH_3) ppm; FAB-MS: *m/z* = 390 (M$^+$, 20)].

2-(Benzo[d][1,3]dithiol-2-ylidene(furan-2-yl)methyl)-5-(benzo[d][1,3]dithiol-2-ylidene-(ferrocenyl)methyl)furan (***10***) *and* *(5-(benzo[d][1,3]dithiol-2-ylidene(furan-2-yl)-methyl)furan-2-yl)(ferrocenyl)methanone* (***11***)

A solution of 0.374 g **5** (1 mmol) was stirred in 50 cm^3 dry THF under a stream of nitrogen at −78 °C. A solution of *n*-BuLi (1.53 cm^3, 2.6 M) was added portion-wise and the mixture was stirred for 15 min. A solution of 1 mmol ferrocenyl ketones **5** in 50 cm^3 dry THF was added portion-wise within 15 min. The temperature of the reaction was raised to room temperature and the reaction mixture was kept overnight with stirring. The THF was removed under vacuum, the residue was washed with water, extracted with chloroform, and dried (Na_2SO_4). The crude oil was chromatographed on silica gel using chloroform/*n*-hexane (1/4) to give **10** as dark red oil in 12% yield in the early fractions. The polarity of the elutant was increased to be 1:2 to elute **11** in the next fractions as dark red oil in 36% yield.

2-(Benzo[d][1,3]dithiol-2-ylidene(furan-2-yl)methyl)-5-(benzo[d][1,3]dithiol-2-ylidene-(ferrocenyl)methyl)furan (**10**, $C_{34}H_{22}FeO_2S_4$)

Yield 10%; IR ($CHCl_3$): v = 3,056m, 2,927s, 2,863s, 1,623s, 1,567s, 1,488s, 1,467s, 1,446s, 1,386s, 1,361s, 1,315s, 1,226m, 1,199m, 1,122m, 1,055ms 1,012s, 923s, 838s, 744s, 497s cm^{-1}; ^{1}H-NMR: δ = 7.69–7.68 (m, 2furan-H), 7.59–7.58 (d, J = 3.5 Hz, 1furan-H), 7.30–7.25 (m, 2aromatic-H), 7.15–7.14 (m, 2aromatic-H), 7.08–7.05 (m, 4aromatic-H), 6.81–6.80 (d, J = 4 Hz, 1furan-H), 6.61–6.60 (d, J = 4 Hz, 1furan-H), 4.64-4.63 (t, J = 4 Hz, 2ferrocene-H), 4.34–4.33 (t, J = 4 Hz, 2ferrocene-H), 4.16 (s, 5ferrocene-H) ppm; ^{13}C NMR: δ = 157.81, 146.40 (furan-C), 136.43, 135.97 (thiafulvalene C=CS_2), 125.89, 125.82, 125.45, 122.76, 121.41, 121.31, 121.25 (aromatic-C and CH), 118.84, 112.40, 111.21, 106.89 (furan-CH), 69.48, 68.68, 67,91 (ferrocene-C and CH) ppm; FAB-MS: *m/z* = 647 (M^{+1}, 10), 646 (M$^+$, 5).

(5-(Benzo[d][1,3]dithiol-2-ylidene(furan-2-yl)-methyl)-furan-2-yl)(ferrocenyl)methanone (**11**, $C_{27}H_{18}FeO_3S_2$)

Yield 36%; IR ($CHCl_3$): v = 3,058w, 3,006m, 2,364w, 1,612s, 1,569s, 1,508s, 1,473s, 1,448s, 1,376s, 1,295s, 1,218m, 1,186m, 1,149m, 1,106m, 1,054s, 1,029s, 1,002s, 921m, 819s, 744s, 501s cm^{-1}; ^{1}H-NMR: δ = 7.56–7.55 (dd, J = 1 Hz, J = 1 Hz, 1aromatic-H), 7.40 (d, J = 4 Hz, 1aromatic-H), 7.37–7.35 (m, 1aromatic-H), 7.32–7.30 (m, 1aromatic-H), 7.19–7.17 (m, 2aromatic-H), 6.57–6.55 (m, 2furan-H), 6.52–6.51 (dd, $J = 4$ Hz, $J = 1.5$ Hz, 1furan-H), 5.17–5.16 (t, $J = 2$ Hz, 2ferrocene-H), 4.56 (t, $J = 2$ Hz, 2ferrocene-H), 4.18 (s, 5ferrocene-H) ppm; ^{13}C NMR: $\delta = 183.95$ (C=O), 154.24, 152.06, 150.67 (furan-C), 141.87 136.07, 136.46, 126.12, 125.44 (thiafulvalene C=CS_2, aromatic-C), 121.71, 121.34, 118.75 (aromatic-CH), 111.21, 110.43, 109.84, 105.75 (furan-CH), 76.09 (ferrocene-C), 72.33, 70.78, 70.20 (ferrocene-CH) ppm; FAB-MS: $m/z = 510$ (M^+, 2).

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