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The linear and nonlinear optical properties of organometallic chromophores derived from ferrocene, $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C\text{–}CH_3)]^+[BF_4]^-$ and terthienyl spacers. Crystal structure of 2-[(*E*)-2-ferrocenylethenyl]-5-(2-thienyl)thiophene

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Abstract

Several chromophores based on ferrocene, $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C\text{–}CH_3)]^+$ and terthiophene or dithienylbenzo[*c*]thiophene have been synthesized. Both thienyls have been shown to act as good donor end groups in their own right but contrary to our expectations the benzo[*c*]thiophene merocyanine has a lower hyperpolarizablity (344×10^{-30} esu) than its thienyl congener (650×10^{-30} esu). The structure of 2-[(*E*)-2-ferrocenylethenyl]-5-(2-thienyl)thiophene has been determined by single crystal X-ray diffraction. The terminal thienyl (thp) group is disordered over two orientations about the bithienyl $C(sp^2)$–$C(sp^2)$ bond such that the two sulfur atoms in either thp ring are positioned *trans*/*cis* in the ratio 0.628(4):0.372(4). The integrity of the alkenyl –C=C– remains with a bond length of 1.332(2) Å and the –C–C– lengths adjacent are 1.453(4)/1.441(4) Å. Twisting of the rings from planarity occurs along the Fc–C=C–(thp)–(thp) axis: the angle which the ethenylthiophene $\text{–C=C–}C_4H_2S$ moiety makes with the C_5H_4 is 11.2(2)°, and with the major orientation of the disordered terminal thienyl group, 16(1)°. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Nonlinear optics; Thiophene; Ferrocene; Crystal structures; Merocyanine

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1. Introduction

The continuing impact of ferrocene five decades after its initial discovery, is testament to the important properties of this remarkable compound [1]. We are interested in its moderate donor ability in the context of nonlinear optical (NLO) studies and indeed many organometallic compounds are receiving increasing attention in this area. The flexible nature of their substitution and oxidation states [2] has enabled metal complexes to be utilized as donors (D) or acceptors (A) in the well established D–π–A motif and some very high second order hyperpolarizabilities (*β*-values) have been obtained [3]. Currently we are investigating ferrocene-containing chromophores which also incorporate the cationic acceptor moiety $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C\text{–}CH_3)]^+BF_4^-$ (**1**), originally synthesized by Rosenblum and coworkers [4]. This condenses readily with aldehydes to form diiron alkenylidyne complexes [5] and we recently published a study in which the effect of varying the nature of bithienyl linkers separating **1** and ferrocene was explored [6] (Fig. 1). The *β*-values for the complexes ranged from 429×10^{-30} esu for bithophene itself to 867×10^{-30} esu for (*E*)-1,2-dithienylethene (measured at 1064 nm in dichloro-

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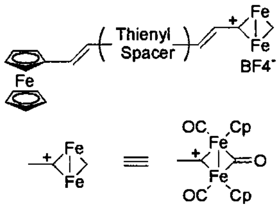

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Fig. 1. Schematic representations of $[Fe_2(\mu\text{-}Cp)_2(\mu\text{-}CO)(CO)(\mu\text{-}C\text{–}R)]^+BF_4^-$ (**1**) and the bithienyl bridged chromophores.

methane), and a pattern was established in which spacer length and minimal loss of aromaticity (benzene versus thiophene) upon charge transfer (CT) were found to be of paramount importance in obtaining large β-values. We report here further results which elucidate an important point in the design of such chromophores.

2. Results and discussion

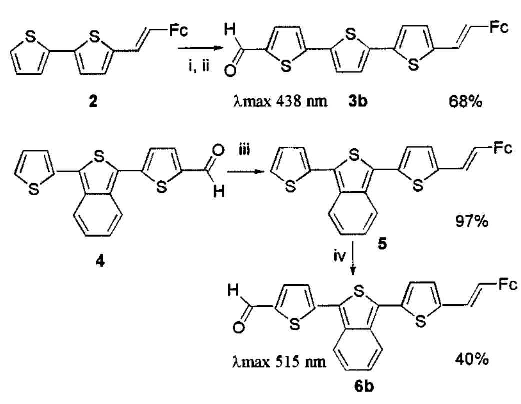
It is well known that increasing the length of a π-spacer often leads to enhanced second harmonic response in NLO chromophores and for the thienyl series shown in Fig. 1, we have already reported the mono- [7] and bithienyl versions [6]. In order to extend these results we have synthesized the terthiophene analogue but have found the quaterthiophene member of the series to be difficult to access due to the insolubility of quaterthienyl aldehydes. Therefore in a different approach to further increase the NLO response whilst still utilizing oligothienyl spacers we have sought to change the aromatic nature of the bridge.

On excitation, a D–π–A system containing a thiophene linker (or any other aromatic spacer), will attain the associated quinoid structure with corresponding loss of resonance energy. It has been recognized that the proquinoid benzo[*c*]thiophene can achieve a benzenoid structure at the expense of the appended thiophene and gain in overall energy [8]. Indeed, studies carried out on polybenzo[*c*]thiophene have found that it exhibits a very low energy gap ($E_{gap} \sim 1.0$ eV, cf. polythiophene $E_{gap} \sim 2.1$ eV [9]) [8]. Similarly Yashimata has developed a number of conducting polymer precursors built around other ring systems with this marked propensity to impose a quinoid geometry on the structure of the π-conjugated polymer backbone [10]. In these compounds pyrazines or thiadiazoles are associated with the thienyl residues but whilst some of these polymers have very small band gaps (0.30 eV) they can be relatively unstable with respect to repeated redox cycling [11]. The analogue of terthiophene, dithienylbenzo[*c*]thiophene has been synthesized and cyclic voltammetry shows a peak anodic potential of 0.800 V/SCE for the compound [8]. This is > 200 mV lower than terthiophene itself [12] and whilst the polymer produced from it is not as strongly conducting (band gap = 1.70 eV) as Yashimata's pyrazine examples or polybenzo[*c*]thiophene itself, it does have the advantage of stability and ease of synthesis.

In order to affirm our assumptions about terthiophene and dithienobenzo[*c*]thiophene and validate the choice of these π-bridges we have performed a theoretical study to calculate their polarizabilities. Low level molecular modeling (MM2) has been undertaken on terthiophene and dithienobenzo[*c*]thiophene previously to determine their preferred conformations [8] and we have extended these results by optimizing both terthiophene and dithienobenzo[*c*]thiophene at a higher level using the Hartree–Fock (HF) and B3LYP (DFT) methods with the 3-21g* basis set, using both the JAGUAR [13] and GAUSSIAN 98 [14] programs.

As expected [8] the calculated structures show that the terminal thienyl residues are inverted with respect to the central thiophene (cf. Scheme 1). The two lowest lying molecular conformers in which the terminal thiophenes are displaced slightly (dihedral angles ca. ± 5 to 10°) to either the same side (conformer A) or opposite sides of the central thienyl residue (conformer B) were found to be of almost equivalent energy (less than 0.5 kcal mol^{-1} difference). The polarizabilities were calculated for each of these conformations using both the HF and B3LYP (DFT) methods and the results are summarized in Table 1.

The HF method is expected to underestimate the polarizabilities and the B3LYP (DFT) method is expected to produce overestimates [15]. The relative magnitude of the data generated by each method concurs with this and shows that benzo[*c*]thiophene is calculated to be more highly polarizable than terthiophene. These results lead us to believe that inclusion of the benzo[*c*]thiophene residue in a π-bridge would enhance its conductive properties as a more effective CT conduit



Scheme 1. Reagents and conditions: (i) $[FcCH_2PPh_3]I$, KO^{t}Bu, THF, 30 min; (ii) BuLi, DMF, THF; (iii) BuLi, $ZnCl_2$, THF, 5-iodo-2-thiophene aldehyde neopentylglycol acetal, $Pd(PPh_3)_4$; and (iv) Aq. 6.0 M. HCl, reflux, 1 h.

and improve the NLO response of the chromophores. Both systems were therefore synthesized and compared.

2.1. Synthesis of chromophores **7a**, **b** and **8a**, **b**

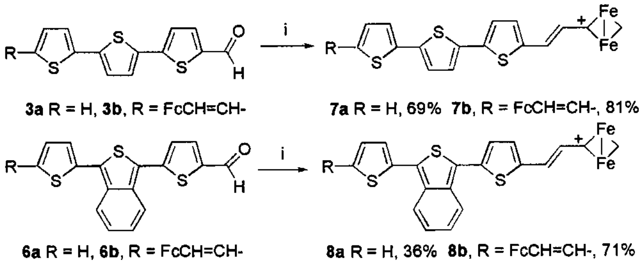
Established procedures were used to convert terthiophene and dithienylbenzo[*c*]thiophene to monoaldehydes **3a** [16] and **6a** [17]. Wittig condensation of **4** with [$FcCH_2PPh_3$]I [18] afforded **5** in good yield solely as the *E*-isomer which was elaborated to the aldehyde **6b** by reaction with BuLi followed by DMF quench and aqueous work-up. Compound **3b** was made in an analogous manner but yields were very poor for both steps (due to solubility problems associated with terthiophene itself) and so Negishi [19] coupling methodology was employed. Thus Wittig reaction of bithienyl aldehyde and [$FcCH_2PPh_3$]I followed by isomerization of the mixture of configurational isomers afforded **2**. This was crystallized from dichloromethane–hexane to give X-ray quality crystals. Cross-coupling of **2** with 5-iodo-2-thiophene aldehyde neopentylglycol acetal (formed from 2-thiophene aldehyde neopentylglycol acetal by lithiation and iodine quench [20]) under palladium catalyzed conditions followed by cleavage of the acetal afforded **3b** in more acceptable overall yield (68%) (Scheme 1). We attempted to synthesize the quaterthiophene analogues of **3** but without pendant solubilizing groups they proved too insoluble to manipulate successfully. It is known that the unstable benzo[*c*]thiophene is stabilized by aromatic groups in the 1,3-positions [13] but the 1,3-dialdehyde is also accessible and relatively stable [21]. We attempted to condense this with one equivalent of [$FcCH_2PPh_3$]I in order to make the monothienyl aldehyde analogue but the product was extremely unstable and decomposed within minutes of workup.

Table 1
Calculated polarizabilities for terthiophene and dithienobenzo[*c*]thiophene

	Polarizability [a]	
	HF [b]	B3LYP (DFT) [b]
Terthiophene (conformer A)	157.076	187.646
Terthiophene (conformer B)	156.734	187.418
Dithienobenzo[*c*]thiophene (conformer A)	163.429	236.157
Dithienobenzo[*c*]thiophene (conformer B)	173.306	236.121

[a] Atomic units.

[b] Values were calculated using the 3-21g* basis set, Hartree–Fock optimized geometry in the JAGUAR and GAUSSIAN98 programs.



Scheme 2. Reagents and conditions: (i) **1**, CH_2Cl_2, reflux, 18 h.

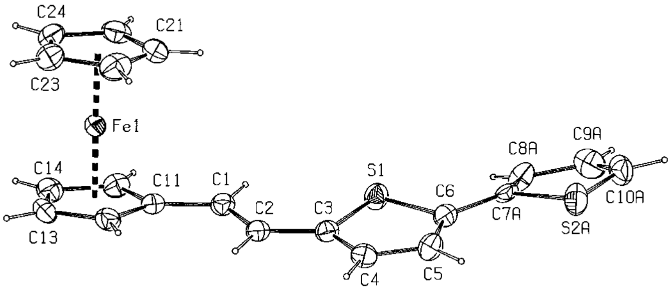


Fig. 2. An ORTEP diagram of **2**. Displacement ellipsoids are drawn at the 30% probability level.

The ferrocene-containing aldehydes **3b** and **6b** condensed readily with **1** in refluxing dichloromethane within 12 h to afford the cationic merocyanines **7b** and **8b**. Purification by precipitation of dichloromethane solutions of the salts from diethyl ether gave the materials as highly colored dark blue–green solids in good to excellent yields, exhibiting the expected NMR and IR spectroscopic data. Compound **7b** gave a satisfactory analysis and **8b** analyzed for 0.75 moles of CH_2Cl_2 of crystallization which could clearly be seen in the NMR spectra. These compounds are soluble in polar organic solvents to give solutions which are reasonably air stable in the absence of light (Scheme 2). Aldehydes **3a** and **6a** were more problematic. 2-Terthienyl aldehyde (**3a**) is relatively insoluble in dichloromethane and so condensation required extended periods of time (72 h) with associated decomposition of **7b**. The product could not be completely freed from insoluble **3a** and the unknown decomposition products even after purification by repeated reprecipitations and attempted crystallization. Compound **6a** afforded **8a** after 12 h at reflux but the chromophore was unstable under these conditions and extensive decomposition took place during condensation. This is reflected in the low yield and once again the compound could not be obtained in a pure state. Spectroscopic measurements on **7a** and **8a** confirmed the proposed structures but microanalysis was inconclusive.

2.2. X-ray structure of **2**

An ORTEP [22] diagram of the molecular structure of compound **2** is presented in Fig. 2. Selected bond lengths and angles are summarized in Table 2 and crystal data and structure refinement are presented in

Table 2
Selected molecular dimensions (Å, °) for compound **2**

Bond lengths [a] (Å)				*Bond angles* (°)			
Fe1–C11	2.041(3)	C1–C2	1.332(4)	C1–C2–C3	126.9(3)	C2–C3–C4	127.9(3)
Fe1–C12	2.035(3)	C1–C11	1.453(4)	C2–C1–C11	126.6(3)	C3–C4–C5	113.8(3)
Fe1–C13	2.041(3)	C2–C3	1.441(4)	C1–C11–Fe1	125.3(2)	C4–C5–C6	113.5(3)
Fe1–C14	2.042(3)	C3–S1	1.738(3)	C12–C11–Fe1	69.24(16)	C5–C6–S1	110.5(2)
Fe1–C15	2.029(3)	C3–C4	1.359(4)	C15–C11–Fe1	69.06(16)	C3–S1–C6	92.2(13)
Fe1–C21	2.032(3)	C4–C5	1.408(4)	C1–C11–C12	127.3(3)		
Fe1–C22	2.035(3)	C5–C6	1.358(4)	C1–C11–C15	126.1(2)		
Fe1–C23	2.041(3)	C6–S1	1.728(3)	C12–C11–C15	106.6(2)		
Fe1–C24	2.045(3)	C6–C7A	1.471(6)	S1–C3–C2	122.0(2)		
Fe1–C25	2.038(3)	C6–C7B	1.455(9)	S1–C3–C4	110.0(2)		

[a] The important bond length ranges in the cyclopentadienyl rings are from 1.406(4) to 1.428(4) Å for the substituted ring and 1.399(4) to 1.427(4) Å for the unsubstituted ring.

Table 4. The plate-like crystal of 2-[(*E*)-2-ferrocenylethenyl]-5-(2-thienyl)thiophene (**2**) diffracted strongly as expected for a typical ferrocene derivative with 74% of the data 'observed' in the 2–26° range (see Section 4) and the data obtained allowed us to determine the details of its conformation unequivocally as well as to evaluate the disorder present (elucidated at the intermediate stages of refinement) in the terminal thienyl group. The ferrocenyl derivative **2** adopts the *E*-configuration about the C1=C2 double bond with a –C=C– bond length of 1.332(4) Å and two C_{ar}–C_{sp^2} distances of 1.453(4) Å for C1–C11 and 1.441(4) Å for C2–C3. The C11–C1–C2/C1–C2–C3 angles are 126.6(3)/126.9(3)° and greater than the 120° expected for ethenyl systems suggesting that these C–C–C angles expand due to the H···H repulsion about the C1–C11 bond. The C11–C1=C2–C3 torsion angle is almost planar 179.6(3)°, but the related angles C2–C1–C11–C15 and C1=C2–C3–C4 are 168.7(3)° and − 177.7(3)° indicating that the twisting of the –C=C– and the ferrocenyl moiety is primarily about the C_{ar}–C_{sp^2}, C11–C1 bond.

There is no significant difference in the Fe–C distances between the substituted ring 2.029(3)–2.042(3) Å and the unsubstituted ring 2.032(3)–2.045(3) Å. The two rings are essentially eclipsed with a range of C1n···Cg1···Cg2···C2n angles between − 3.5(2) and − 4.3(2)°, where Cg1 and Cg2 are the centroids of the substituted and unsubstituted C_5 rings. The Fe1···Cg1 and Fe1···Cg2 distances are 1.6438(14) and 1.6485(15) Å, respectively, and the Cg1···Fe1···Cg2 angle is 178.65(8)°. The system is approximately planar with a small twisting between the ferrocenyl moiety and the two thienyl rings about C1–C11 and C6–C7A/B, respectively. The angle which the central ethenylthiophene –C=C–C_4H_2S moiety makes with the substituted cyclopentadienyl ring is 11.2(2)°, and with the major orientation of the disordered thienyl group, 16(1)°. The intramolecular contact of significance is C1–H1···S1, with H···S 2.78 Å and C–H···S 108°. The important intermolecular interactions of significance are weak C–H···π (arene) interactions.

2.3. NMR and linear optical properties

2.3.1. Infrared and NMR spectroscopic data

The IR and ^{13}C-NMR spectroscopic details for the carbonyl stretching frequencies and the μ-carbon chemical shift values (ppm) for compounds **7** and **8** are recorded in Table 3 along with data for **1** and the mono- and bithienyl members of the series. π-Excessive heteroaromatics are known to act as donors in their own right [23] and in compounds **7a** and **8a** the thienyls act as donating end groups whilst in **7b** and **8b** they are part of the spacer between the $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C\text{–})]^+$ acceptor and ferrocene. The IR absorbances for **7** and **8** do not differ significantly but are considerably shifted from the values for **1** indicating delocalization of the positive charge away from the μ-carbyne onto the organic ligand. The ^{13}C-NMR μ-carbyne shift is a more sensitive indicator of the amount of charge residing in the iron cluster. The peaks corresponding to the μ-carbyne in **7** and **8** are considerably shifted up field in comparison to the extremely low field μ-carbyne shift in **1** (δ 499). The figures suggest compounds **8** are more highly delocalized than **7** and this indicates that dithienylbenzo[*c*]thiophene is both a stronger donor and a more effective π-bridge than terthiophene. The ferrocene donor appears to make little difference for **7** (**7a**: δ 416; **7b**: δ 415) but does have a slight effect in **8** (**8a**: δ 405; **8b**: δ 399). The J_{HH} couplings for the alkenes separating the diiron cluster from the thiophene groups are 13.0 (**7a**), 13.8 (**7b**), 12.0 (**8a**) and 12.2 (**8b**) Hz indicating an *E*-configuration. Their magnitudes suggest that there is reduced bond length alternation in the C1–C4 segment with **8** having a more delocalized π-system than **7**.

Table 3
Spectroscopic data: infrared (CO region), ^{13}C-NMR (μ-carbyne) and UV–vis (LMCT and MLCT) absorption

No	IR-bands [a] (cm^{-1})	^{13}C-NMR [b] δ (ppm)	λ (nm) ε, M^{-1} cm^{-1}) [c] MLCT		λ (nm) ([c] LMCT	
			CH_2Cl_2	CH_3CN	CH_2Cl_2	CH_3CN
1	2046, 2012, 1853	499 [d]	–	–	–	–
7a	2028, 2001, 1828	416	–	–	658 (28 550)	619 (30 720)
8a	2027, 2000, 1837	405	–	–	720 (35 390)	707 (38 350)
Mono-Th [e]	2029, 1979, 1838	409	768 (20 310)	685 (21 770)	573 (33 230)	547 (30 630)
Bi–Th [f]	2031, 1996, 1842	413	777 (10 500)	670 (15 600)	606 (27 400)	577 (31 650)
7b	2032, 2003, 1843	415	772 (21 900)	692 (25 000)	660 (39 500)	636 (43 800)
8b	2026, 1997, 1836	399	773 (33 300)	685 (21 000)	880 (46 900)	791 (46 800)

[a] Recorded in dichloromethane.

[b] Recorded in d_2-dichloromethane.

[c] Molar concentrations were all ca. 1×10^{-5} M.

[d] Recorded in *d*-chloroform.

[e] Monothiophene spacer [7].

[f] Bithiophene spacer [6].

2.3.2. UV–vis spectra

The data for the UV–vis absorption spectra are also collected in Table 3. Compounds **7a** and **8a** have one principle low energy band attributed to the π–π* or ligand to metal charge transfer (LMCT) band for the thiophene-containing portion of the molecule. The band due to **8a** has a higher intensity and is seen at a lower energy than for **7a** and both exhibit negative solvatochromism. The ferrocenyl derivatives have two strong overlapping bands in this region. The spectra are shown in Fig. 3 along with those of the mono- and bithienyl analogues for comparative purposes. Based on the work of Sarkar and coworkers [24], we have characterized the peaks as the π–π*/LMCT band and the metal to ligand CT (MLCT) band centered on ferrocene. It is evident that the position of the MLCT band is relatively immobile in this series (ca. 770 nm in CH_2Cl_2 and 690 nm in CH_3CN) and deconvolution of the complex peaks in **7b** and **8b** was achieved by a curve (Lorenzian) fitting analysis based on the estimated position and intensity of this band by analogy with the mono- and bithienyl members of the series.

For measurements made in dichloromethane the difference in energy for the LMCT band between the mono- and bithienyl compounds is −0.63 kJ and between the bithienyl chromophore and the terthienyl analogue the difference is −0.92 kJ. However, going from the terthiophene to the dithienylbenzo[*c*]thiophene compounds there is a much larger difference in energy for this band of −2.57 kJ reflecting its much smaller HOMO–LUMO gap. There is the expected general trend in the intensity of absorbance for the complexes as they increase in length but the dithienylbenzo[*c*]thiophene compound has a very much more intense absorption than its terthienyl congener suggesting that the associated π–π* transition is much more efficient.

2.4. Nonlinear optical properties

The HRS technique [25] was used to obtain the hyperpolarizability (β) of compounds **7b** and **8b** at 1300 nm using the external reference method and they were found to be 650 and 344×10^{-30} esu, respectively. The largest reported β-value for an organometallic compound was for a zinc porphyrin complex [26]. However, β-values for organometallic chromophores are generally in the range of $50–700 \times 10^{-30}$ esu [2] and our complexes fall well within these limits.

The relative magnitudes of the hyperpolarizabilities for the complexes were contrary to our expectations with the terthienyl complex (**7b**) having the higher value and we were initially puzzled by this finding. However, consideration of the linear spectroscopic evidence outlined above which suggests that the ground state of **8b** is more highly delocalized than **7b** and the transition to the first excited state is a more efficient, lower energy process provides a clue to this apparent anomaly. A large dipole moment change on excitation is necessary for high β-values and we suggest that the more highly delocalized system in **8b** does not experience the prereq-

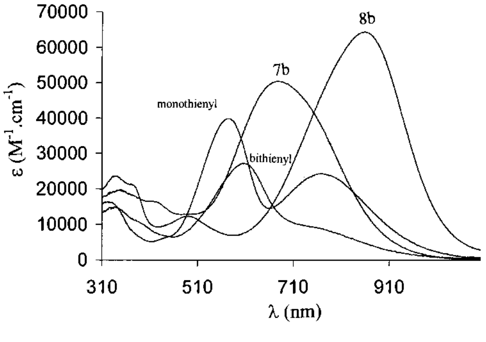


Fig. 3. UV–vis absorption spectra recorded in CH_2Cl_2 at ca. 1×10^{-5} M concentration.

uisite extensive reorganization of charge necessary for a large dipole moment change and consequent large hyperpolarizability.

3. Conclusions

The linear optical and NMR spectroscopic data show that the terthienyl moieties may act as reasonable donors in their own right with benzo[*c*]thiophene being a better donor having the more delocalized structure. Unfortunately, the effective lowering of the gap between the ground and excited states in the ferrocene dithienylbenzo[*c*]thiophene chromophore relative to its terthienyl congener has negative consequences for the hyperpolariziblity. It may be the case that a less highly polarizable bridge is necessary for high β-values when a strong donor and acceptor (e.g. $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C\text{–}CH_3)]^+$) are present.

4. Experimental

4.1. General methods

All reactions were performed under N_2 atmosphere. Tetrahydrofuran was distilled freshly from sodium benzophenone ketyl. $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C\text{–}CH_3)]^+BF_4^-$ (**1**) was prepared according to the literature procedure [4]. All other chemicals and reagents were used as received without further purification. Melting points (m.p.) were recorded on an electrothermal digital melting point apparatus and are uncorrected. ^1H-NMR spectra were obtained on a Varian INOVA-300 MHz spectrometer or a Varian INOVA-500 MHz spectrometer. ^{13}C-NMR spectra were obtained on a Varian INOVA-300 MHz spectrometer or a Varian INOVA-500 MHz spectrometer operating at 75 and 126 MHz, respectively. FTIR spectra were obtained on a Perkin–Elmer Paragon 1000 spectrometer as either a solution in CH_2Cl_2 (windows: KBr, path length 0.1 mm) or in a KBr pellet. UV–vis spectra were obtained on a UnicamUV2 spectrometer.

4.2. 2-[(E)-2-Ferrocenylethenyl]-5-(2-thienyl)thiophene (2)

5-Thienyl-2-thiophenecarboxaldehyde (0.194 g, 1.0 mmol) was added to a suspension of ferrocenylmethyl triphenylphosphonium iodide (1.00 g, 2.1 mmol) in CH_2Cl_2 (10 ml) and sat. aq. KOH (5.40 g, 100 mmol) was introduced. The mixture was stirred for 3 h after which it was quenched with water (50 ml) and extracted with CH_2Cl_2 (2 × 50 ml). The organic extracts were combined and washed with water (3 × 50 ml) and brine (1 × 50 ml) followed by drying over $MgSO_4$ before removal of the solvent. The residue was washed through a plug of alumina in a Büchner funnel with Et_2O and the solvent removed. The red solid was dissolved in CH_2Cl_2 (30 ml) and a single crystal of iodine was added. The mixture was heated at reflux for 1 h and cooled before washing with sat. aq. sodium thiosulfate solution (1 × 50 ml) followed by water (1 × 50 ml). The solution was dried over $MgSO_4$ before removal of the solvent in vacuo and purification by column chromatography on silica gel with 10:90 Et_2O–petroleum ether (40:60) as the eluant to give the title compound as a red solid (0.214 g) in 62% yield. The solid was recrystallized from CH_2Cl_2–hexane to afford red needles. M.p. 167.5–169.0 °C. ^1H-NMR (300 MHz, $CDCl_3$): $\delta = 7.20$ (dd, 1H, $J = 5.0$, 1.1 Hz, ThC3″-H), 7.16 (dd, 1H, $J = 1.1$, 3.5 Hz, ThC5″-H), 7.04 (d, 1H, $J = 3.7$ Hz, ThC3′-H), 7.00 (dd, 1H, $J =$ 3.5, 5.0, Hz, ThC4″-H), 6.83 (d, 1H, $J = 3.7$ Hz, ThC4′-H), 6.77 (d, 1H, $J = 15.8$ Hz, FcCHC*H*Th), 6.65 (d, 1H, $J = 15.8$ Hz, FcC*H*CHTh), 4.43 (m, 2H, Fcα-H), 4.29 (m, 2H, Fcβ-H), 4.15 (s, 5H, Fc). ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 142.9$, 138.0, 135.1, 128.1, 127.5, 125.5, 124.4, 124.4, 123.6, 119.4, 83.1, 69.6, 69.5, 67.1. IR (CH_2Cl_2, cm^{-1}): 1624 (5), 1509 (3), 1473 (1), 1106 (8), 1043 (7), 1028 (6), 1002 (5), 944 (10). IR (KBr, cm^{-1}): 1638 (10), 1557 (4), 1417 (3), 1102 (1), 1042 (1), 1030 (1), 1001 (1), 940 (2), 931 (1), 798 (4), 695 (6). UV–vis: λ (λ_{max}) (nm): (CH_2Cl_2), 469 (373); (MeCN) 459 (370). The structure has also been established by single crystal X-ray diffraction.

4.3. 1-[(E)-(2-(5-Ferrocenylethenyl)thienyl)]-2-thienylbenzo[c]thiophene (5)

1,3-Di(2-thienyl)benzo[*c*]thiophene-5-carbaldehyde (0.300 g, 0.92 mmol) was added to a solution of the ylid formed from ferrocenylmethyl triphenylphosphonium iodide (1.739 g, 3.60 mmol) in dry THF (50 ml) and KO^{t}Bu (0.560 g, 5.00 mmol). The mixture was stirred at room temperature (r.t.) for 30 min and quenched with water (50 ml) before being extracted with CH_2Cl_2 (3 × 50 ml). The combined extracts were washed with water (1 × 50 ml) and dried over $MgSO_4$ before removal of the solvent in vacuo and purification by column chromatography on silica gel with 10:90 CH_2Cl_2–petroleum ether (40:60) as the eluant to give the title compound as a dark red solid (0.455 g) in 97% yield. ^1H-NMR (300 MHz, $CDCl_3$): $\delta = 7.94$–8.40 (m, 2H, benzo[*c*]thiophene), 7.39 (d, 1H, $J = 3.0$ Hz, Th), 7.38 (d, 1H, $J = 2.5$ Hz, Th), 7.23 (d, 1H, $J = 2.5$ Hz, Th), 7.14–7.18 (m, 2H, benzo[*c*]thiophene), 6.96 (d, 1H, $J = 3.0$ Hz, Th), 6.84 (d, 1H, $J = 15.5$ Hz, FcCH=C*H*), 6.74 (d, 1H, $J = 15.5$ Hz, FcC*H*=CH), 4.45 (m, 2H, Fcα-H), 4.31 (m, 2H, Fcβ-H), 4.18 (s, 5H, Fc). ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 143.8$, 135.9, 135.7, 135.3, 133.4, 128.1, 127.7, 127.4, 126.4, 126.0, 125.8, 125.7, 125.6, 125.1, 125.0, 122.0, 121.9, 119.3, 83.1, 69.5, 69.5, 67.1. IR (CH_2Cl_2, cm^{-1}): 1639 (2), 1621 (2), 1607 (2), 1378 (1), 1192 (1), 1105 (10), 1042 (7), 1026 (7), 1001 (7), 952 (6), 930 (5), 925 (5). IR (KBr, cm^{-1}): 1639 (9), 1560 (10), 1415 (8), 1105 (1), 1041 (1), 1025 (1), 952 (1), 931 (1), 839 (2), 812 (3), 788 (3), 739 (4), 693 (4), 643 (4). UV–vis: λ_{max} (nm): (CH_2Cl_2) 469; (MeCN) 467. Anal. Found: C, 65.95; H, 4.14. Calc. for $C_{28}H_{20}FeS_3$: C, 66.14; H, 3.94%.

4.4. *1-[(E)-(2-(5-Ferrocenylethenyl)thienyl)]-2-thienylbenzo[c]thiophene–5-carbaldehyde* ***(6b)***

1-[(*E*)-(2-(5-ferrocenylethenyl)thienyl)]-2-thienylbenzo[*c*]thiophene (**5**) (0.120 g, 0.24 mmol) was dissolved in THF (10 ml) and cooled to −78 °C. BuLi (0.15 ml, 2.0 M in hexanes, 0.30 mmol) was added dropwise and the reaction was stirred for 1 h at this temperature. Dimethyl sulfoxide (0.10 ml) was added and the mixture allowed to warm to r.t. Dilute HCl (0.5 M., 10 ml) was added and the mixture was extracted with CH_2Cl_2 (2 × 50 ml). The combined organic portions were washed with water (3 × 50 ml) and dried over $MgSO_4$ before removal of the solvent in vacuo and purification by column chromatography on silica gel with 50:50 CH_2Cl_2–Et_2O as the eluant to afford the title compound as a dark red solid (0.120 g) in 40% yield. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.05 (m, 2H, benzo[*c*]thiophene), 7.75 (d, 1H, J = 4.0 Hz, Th), 7.43 (d, 1H, J = 4.2 Hz, Th), 7.29 (d, 1H, J = 3.7 Hz, Th), 7.24 (m, 2H, benzo[*c*]thiophene), 6.98 (d, 1H, J = 3.7 Hz, Th), 6.84 (d, 1H, J = 14.6 Hz, FcCHC*H*Th), 6.77 (d, 1H, J = 14.6 Hz, FcC*H*CHTh), 4.47 (2H, m, Fcα-H), 4.33 (2H, m, Fcβ-H), 4.18 (s, 5H, Fc). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 182.5, 146.2, 145.1, 141.9, 137.3, 136.8, 135.6, 132.6, 131.3, 128.6, 127.1, 126.8, 125.7, 125.4, 125.3, 124.4, 122.5, 121.7, 119.0, 82.8, 69.7, 69.6, 67.2. IR (CH_2Cl_2, cm^{-1}): 1657 (10), 1620 (1), 1608 (1), 1385 (1), 1339 (1), 1228 (4), 1106 (1), 1057 (3). IR (KBr, cm^{-1}): 1654 (10), 1616 (3), 1556 (2), 1441 (3), 1424 (5), 1335 (1), 1281 (1), 1226 (3), 1106 (1), 1054 (2), 1027 (1), 946 (2), 790 (3), 739 (2). UV–vis: λ_{max} (nm) (CH_2Cl_2): 515; (MeCN) 499. Anal. Found: C, 61.80; H, 4.14. Calc. for $C_{28}H_{20}FeOS_3 \cdot H_2O$: C, 61.99; H, 4.06%.

4.5. *2-[(E)-(2-(5-Ferrocenylethenyl)bithienyl)]-thiophene-2-aldehyde* ***(3b)***

2-[(*E*)-2-Ferrocenylethenyl]-5-(2-thienyl)thiophene (**2**) (0.070 g, 0.20 mmol) was dissolved in THF (10 ml) and cooled to −78 °C. BuLi (0.15 ml, 2.0 M in hexanes, 0.30 mmol) was added dropwise and the reaction was stirred for 1 h at this temperature. Dry $ZnCl_2$ (0.055 g, 0.40 mmol) was introduced in one portion as a solid and the mixture was allowed to warm to r.t. followed by stirring for 30 min. 2-(5′-Iodothienyl)-5,5-dimethyl-dioxane (0.200 g, 0.60 mmol) and palladium tetrakis-triphenyl phosphine (0.025 g) were added in one portion and the reaction was stirred at r.t. for 12 h. The mixture was quenched with water (1 × 10 ml) and extracted with CH_2Cl_2 (1 × 30 ml). The organic extracts were combined and washed with water (1 × 30 ml) followed by drying over $MgSO_4$. The solvent was removed in vacuo and purification by column chromatography on silica gel with CH_2Cl_2 as the eluant gave the protected terthienyl aldehyde as a red solid (0.101 g) in 88% yield. This was heated at reflux in HCl (20 ml, 6.0 M) for 1 h to cleave the acetal and a red solid was separated by filtration. This was purified by column chromatography on silica gel with 50:50 CH_2Cl_2–Et_2O as the eluant to give the required product as a red solid (0.065 g) in 77% yield. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 9.86 (s, 1H, CHO), 7.68 (d, 1H, J = 4.2 Hz, Th), 7.28 (d, 1H, J = 3.9 Hz, Th), 7.24 (d, 1H, J = 3.9 Hz, Th), 7.12 (d, 1H, J = 3.9 Hz, Th), 7.10 (d, 1H, J = 3.9 Hz, Th), 6.87 (d, 1H, J = 3.7 Hz, Th), 6.78 (d, 1H, J = 15.9 Hz, Th), 6.70 (d, 1H, J = 15.9 Hz, Th), 4.48 (m, 2H, Fcα-H), 4.32 (2H, m, Fcβ-H), 4.16 (s, 5H, Fc). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 183.0, 147.6, 144.6, 142.3, 140.3, 138.0, 134.9, 134.4, 128.9, 127.7, 126.0, 125.7, 124.9, 124.6, 119.5, 83.3, 70.1, 70.0, 67.6. IR (CH_2Cl_2, cm^{-1}): 1697 (5), 1601 (10), 1564 (1), 1565 (2), 1556 (1), 1105 (1). IR (KBr, cm^{-1}): 1692 (5), 1593 (10), 1576 (9), 1448 (5), 1417 (6), 1217 (1) 1167 (2), 1103 (2), 815 (3), 799 (6). UV–vis: λ_{max} (nm): (CH_2Cl_2) 438; (MeCN) 427. Anal. Found: C, 60.21; H, 3.97. Calc. for $C_{25}H_{18}FeOS_3 \cdot 0.66H_2O$: C, 60.24; H, 3.88%.

4.6. *General procedure for the condensation of* $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C\text{–}CH_3)]^+[BF_4]^-$ ***(1)*** *with aldehydes* ***3*** *and* ***6***

Following the procedure of Casey [5], **1** (one equivalent) and the required aldehyde (two equivalents) were stirred at reflux in CH_2Cl_2 (5–10 ml). The reactions were monitored by IR spectroscopy for the disappearance of the ν_{CO} bands of the starting material which took approximately 18 h. The volume of the solvent was reduced in vacuo to half the original amount and the product was isolated by precipitation by the addition of Et_2O (50–100 ml). The precipitate was collected by filtration and redissolved in a minimum volume of CH_2Cl_2 before being re-precipitated by the addition of Et_2O (100 ml). This was repeated and the solid was dried under high vacuum.

4.6.1. *Preparation of* $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}(E)\text{-}C\text{–}CH{=}CH\text{-}2\text{-}(terthiophene)]^+[BF_4]^-$ ***(7a)***

Experimental procedures and work-up were as described above. Experimental details: **3a** (0.110 g, 0.40 mmol), **1** (0.100 g, 0.23 mmol). Obtained as a dark blue solid. Yield: 0.112 g, 69% based on **1**. ^{1}H-NMR (500

MHz, CD_2Cl_2): $\delta = 9.43$ (bd, 1H, $J = 13.0$ Hz, μ-CC*H*=CHTh), 8.15 (b, 1H, Th), 7.94 (bd, 1H, $J = 13.0$ Hz, μ-CC*H*=C*H*Th), 7.53 (b, 1H, Th), 7.44 (b, 1H, Th), 7.31 (m, 2H, Th), 7.15 (b, 1H, Th), 7.06 (b, 1H, Th), 5.30 (bs, 10H, Cp). ^{13}C-NMR (126 MHz, CD_2Cl_2): $\delta = 415.9$ (μ-CCH), 255.5 (μ-CO), 208.1 (tCO), 152.9, 149.8, 146.1, 155.9, 139.1, 138.8, 137.3, 135.5, 135.2, 130.1, 128.9, 128.4, 126.9, 125.5, 125.2, 91.9. IR (CH_2Cl_2, cm^{-1}): 2028 (CO, 10), 2001 (CO, 5), 1828 (CO, 4); (KBr, cm^{-1}): 2025 (CO, 10), 1989 (CO, 3), 1839 (CO, 6), 1541 (6), 1532 (6), 1502 (6), 1433 (9), 1376 (6), 1336 (3), 1214 (7), 1184 (9), 1147 (6), 1083 (8), 1052 (8), 856 (1), 836 (1), 794 (6), 730 (2), 643 (1), 585 (2). UV–vis: λ_{max} (nm) (ε, M^{-1} cm^{-1}) (CH_2Cl_2): 416 (14 740), 658 (28 550); (MeCN), 412 (16 800), 619 (30 720).

4.6.2. *Preparation of* $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}(E)\text{-}C\text{-}CH{=}CH\text{-}2\text{-}(1,3\text{-di}(2\text{-theinyl})\text{benzo}[c]\text{thiophene})]^+[BF_4]^-$ ***(8a)***

Experimental procedures and work-up were as described above. Experimental details: **6a** (0.130 g, 0.40 mmol), **1** (0.100 g, 0.23 mmol). Obtained as a dark blue–green solid. Yield: 0.062 g, 36% based on **1**. ^{1}H-NMR (500 MHz, CD_2Cl_2): $\delta = 9.46$ (d, 1H, $J = 12.0$ Hz, μ-CC*H*=CHTh), 8.25 (b, 1H, Th), 8.14 (d, 1H, $J = 8.5$, Hz, Th), 7.98 (d, 1H, $J = 12.0$ Hz, μ-CCH=C*H*Th), 7.70 (b, 1H, Th), 7.59 (bm, 2H, Th), 7.54 (bm, 2H, Th), 7.36 (b, 1H, Th), 7.32 (b, 1H, Th), 7.26 (b, 1H, Th), 5.29 (bs, 10H, Cp). ^{13}C-NMR (126 MHz, CD_2Cl_2): $\delta = 404.8$ (μ-CCH), 256.3 (μ-CO), 208.1 (tCO), 152.9, 148.6, 145.6, 138.3, 138.1, 136.8, 136.5, 134.8, 129.1, 129.0, 128.9, 128.8, 128.2, 126.9, 126.6, 125.8, 123.2, 122.5, 91.2. IR (CH_2Cl_2, cm^{-1}): 2027(6), 2000 (2), 1837 (4), 1606 (1), 1534 (6), 1496 (4), 1325 (3), 1316 (3), 1219 (5), 1184 (10), 1146 (6), 1067 (7), 935 (1); (KBr, cm^{-1}): 2014 (7), 1987 (5), 1826 (4), 1636 (3), 1570 (6), 1534 (8), 1494 (4), 1420 (10), 1314 (3), 1243 (6), 1221 (5), 1182 (9), 1145 (7), 1084 (6), 1062 (7), 933 (1), 840 (1), 790 (1), 726 (1), 704 (1), 632 (2), 544 (2). UV–vis: λ_{max} (nm) (ε, M^{-1} cm^{-1}) (CH_2Cl_2): 459 (12 150), 720 (35 390); (MeCN) 417 (11 100), 707 (38 350).

4.6.3. *Preparation of* $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}(E)\text{-}C\text{-}CH{=}CH\text{-}2\text{-}(5\text{-}(2\text{-ferrocenylethene})\text{terthiophene})]^+[BF_4]^-$ ***(7b)***

Experimental procedures and work-up were as described above. Experimental details: **3b** (0.040 g, 0.082 mmol), **1** (0.035 g, 0.080 mmol). Obtained as a dark blue–green solid. Yield: 0.052 g, 71% based on **1**. ^{1}H-NMR (300 MHz, CD_2Cl_2): $\delta = 9.12$ (d, 1H, $J = 13.8$ Hz, μ-CC*H*=CHTh), 8.23 (d, 1H, $J = 3.1$ Hz, Th), 7.97 (d, 1H, $J = 13.8$ Hz, μ-CCH=C*H*Th), 7.60 (d, 1H, $J = 3.8$ Hz, Th), 7.47 (d, 1H, $J = 4.4$ Hz, Th), 7.25 (d, 1H, $J = 3.8$ Hz, Th), 7.18 (d, 1H, $J = 3.8$ Hz, Th), 6.67 (m, 2H, FcC*H*=CH, Th), 6.64 (d, 1H, $J = 15.5$ Hz, FcCH=C*H*), 5.36 (s, 10H, Cp), 5.02 (m, 2H, Fcα-H), 4.84 (2H, m, Fcβ-H), 4.52 (s, 5H, Fc). ^{13}C-NMR (126 MHz, CD_2Cl_2): $\delta = 414.5$ (μ-CCH), 255.6 (μ-CO), 208.1 (tCO), 152.6, 149.8, 145.9, 145.8, 143.8, 141.6, 138.9, 136.8, 135.8, 129.6, 128.7, 128.6, 127.0, 125.5, 122.8, 120.5, 93.2, 91.7, 74.9, 74.8, 68.8. IR (CH_2Cl_2, cm^{-1}): 2032 (CO, 9), 2003 (CO, 2), 1843 (CO, 4), 1605 (3), 1534 (4), 1509 (4), 1488 (3), 1180 (10), 1147 (7), 1056 (8), 1048 (7); (KBr, cm^{-1}): 2020 (CO, 5), 1987 (2), 1830 (3), 1576 (9), 1508 (4), 1426 (10), 1214 (2), 1184 (4), 1143 (3), 1084 (3), 1045 (4), 792 (1), 649 (2), 583(2). UV–vis: λ (nm) (ε, M^{-1} cm^{-1}): (CH_2Cl_2) 660 (39 500), 772 (21 900); (MeCN) 636 (43 800), 692 (25 000). Anal. Found: C, 52.90; H, 3.35. Calc. for $C_{40}H_{29}Fe_3O_3S_3BF_4$: C, 52.86; H, 3.19%.

4.6.4. *Preparation of* $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}(E)\text{-}C\text{-}CH{=}CH\text{-}2\text{-}(5\text{-}((E)\text{-}1\text{-}(5\text{-}(2\text{-ferrocenylethenyl}))\text{thienyl})\text{-}2\text{-thienylbenzo}[c]\text{thiophene})]^+[BF_4]^-$ ***(8b)***

Experimental procedures and work-up were as described above. Experimental details: **6b** (0.100 g, 0.18 mmol), **1** (0.060 g, 0.14 mmol). Obtained as a dark blue–green solid. Yield: 0.102 g, 81% based on **1**. ^{1}H-NMR (500 MHz, CD_2Cl_2): $\delta = 9.28$ (d, 1H, $J = 12.2$ Hz, μ-CC*H*=CHTh), 8.08 (m, 3H, Th), 7.85 (d, 1H, $J = 12.2$ Hz, μ-CCH=C*H*Th), 7.42 (m, 2H, Th), 7.36 (bs, 1H, Th), 7.25 (bs, 1H, Th), 6.80 (bs, 1H, Th), 6.78 (d, 1H, $J = 15.6$ Hz, FcC*H*=CH, Th), 6.70 (d, 1H, $J = 15.6$ Hz, FcCH=C*H*), 5.18 (s, 10H, Cp), 4.51 (m, 2H, Fcα-H), 4.38 (2H, m, Fcβ-H), 4.15 (s, 5H, Fc). ^{13}C-NMR (126 MHz, CD_2Cl_2): $\delta = 399.4$ (μ-CCH), 257.0 (μ-CO), 208.3 (tCO), 152.8, 148.4, 147.3, 145.2, 138.5, 138.1, 138.0, 136.3, 132.8, 130.5, 129.3, 129.0, 126.9, 126.8, 125.7, 123.5, 122.9, 119.4, 92.7, 91.1, 71.1, 70.7, 67.9. IR (CH_2Cl_2, cm^{-1}): 2026 (CO, 5), 1997 (CO, 1), 1836 (CO, 3), 1606 (1), 1534 (4), 1496 (2), 1422 (10), 1406 (5), 1326 (2), 1310 (2), 1229 (3), 1198 (2), 1183 (6), 1150 (6), 1114 (4), 1068 (5), 932 (1); (KBr, cm^{-1}): 2013 (CO, 7), 1984 (CO, 2), 1826 (CO, 4), 1531 (5), 1494 (4), 1406 (8), 1369 (5), 1325 (5), 1310 (5), 1241 (7), 1228 (7), 1183 (10), 1145 (9), 1063 (9), 930 (2), 842 (1), 788 (1), 724 (1), 548 (2). UV–vis: λ (nm) (ε, M^{-1} cm^{-1}): (CH_2Cl_2) 773 (33 300), 880 (46 900); (MeCN) 685 (21 000), 791 (46 800). Anal. Found: C, 54.22; H, 3.35. Calc. for $C_{44}H_{31}Fe_3O_3S_3BF_4\cdot0.75CH_2Cl_2$: C, 54.29; H, 3.34%.

4.7. *X-ray data collection*

Details of the X-ray experimental conditions, cell data, data collection and refinement for **2** are summarized in Table 4. Molecule **2** crystallized in the monoclinic system and the space group was determined to be $P2_1/a$ from the systematic absences and subsequent successful refinement. The crystal diffracted quite

Table 4
Crystal data and structure refinement for **2**

Empirical formula	$C_{20}H_{16}FeS_2$
Formula weight	376.3
Temperature (K)	273(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/a$
Unit cell dimensions	
a (Å)	14.2312(10)
b (Å)	8.1445(12)
c (Å)	15.8655(12)
β (°)	114.307(4)
Absorption coefficient (mm^{-3})	1.144
F(000)	776
V (Å^3)	1675.9(3)
Z	4
Calculated density (Mg m^{-3})	1.491
Crystal size (mm)	$0.34 \times 0.27 \times 0.05$
Theta range for data collection (°)	2–26
Index ranges	$-17 \leq h \leq 1$, $-1 \leq k \leq 10$, $-18 \leq l \leq 19$
Reflections collected/unique	4215/3278 [$R_{int} = 0.024$]
Completeness to $2\theta = 26°$ (%)	100
Max/min transmission	0.945, 0.697
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3278/27/255
Goodness-of-fit on F^2	1.01
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.038$, $wR_2 = 0.076$
R indices (all data)	$R_1 = 0.064$, $wR_2 = 0.085$
Largest difference peak and hole (e Å^{-3})	0.24 and -0.34
Largest shift/error max	<0.001

The data were collected on a Siemens P4 diffractometer. The crystal structure was solved and refined using SHELXS97 and SHELXL97 on a Pentium 400 computer.

strongly (74% of the measured data could be labeled as 'observed' in the 2–26° θ range ($I > 2\sigma(I)$). The structure was solved by direct methods using SHELXS97 [27] which revealed most of the non-hydrogen atoms of the ferrocenyl core and the ligand 'backbone' and refined using the SHELXL97 [27] suite of programs. The remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. The terminal thienyl group is disordered 0.628(4)/0.372(1) over two orientations such that the major orientation has the two sulfurs on neighboring thienyl units *trans* to one another and the minor conformation has the two sulfurs *cis* to one another Hydrogen atoms (visible in difference maps at an intermediate stage of the refinement) were included at geometrically idealized positions, but restrained to ride on the carbon atom to which they were bonded (C–H 0.93 Å). Refinement was by full-matrix least-squares calculations on F, initially with isotropic and later with anisotropic thermal parameters for all non-hydrogen atoms. The minor component of disorder in the thienyl ring was treated with *soft* restraints.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 156287 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] N.J. Long, Metallocenes: An Introduction to Sandwich Complexes, Blackwell Science, Oxford, 1998.

[2] (a) N.J. Long, Angew. Chem. Int. Ed. Engl. 34 (1995) 21;
(b) T. Verbiest, S. Houbrechts, M. Kauranen, K. Clays, A. Persoons, J. Mater. Chem. 7 (1997) 2175;
(c) I.R. Whittall, A.M. McDonagh, M.G. Humphrey, Adv. Organomet. Chem. 42 (1998) 291;
(d) J. Heck, S. Dabek, T. Meyer-Friedrichsen, H. Wong, Coord. Chem. Rev. 190–192 (1999) 1217.

[3] D.N. Prasad, D.J. Williams, Introduction to Nonlinear Optical Effects in Molecules and Polymers, Wiley, New York, 1991.

[4] M. Nitay, W. Priester, M. Rosenblum, J. Am. Chem. Soc. 100 (1978) 3620.

[5] (a) C.P. Casey, M.S. Konings, R.E. Palermo, R.E. Colborn, J. Am. Chem. Soc. 107 (1985) 5296;
(b) C.P. Casey, M.S. Konings, S.R. Marder, J. Organomet. Chem. 345 (1988) 125.

[6] R.D.A. Hudson, A.R. Manning, I. Asselberghs, R. Van Boxel, A. Persoons, J.F. Gallagher, J. Organomet. Chem. 619 (2001) 141.

[7] T. Farrel, T. Meyer-Friedrichsen, T. Murphy, J. Heck, A.R. Manning, Eur. J. Inorg. Chem., in press.

[8] S. Musmanni, J.P. Ferraris, J. Chem. Soc. Chem. Commun. 2 (1993) 172.

[9] (a) T. Hattori, W. Hayes, K. Wong, K. Kaneto, K. Yoshino, J. Phys. C. 17 (1984) L803;
(b) T.C. Chung, J.H. Kaufmann, A.J. Heeger, F. Wudl, Phys. Rev. B 30 (1984) 702.

[10] (a) C. Kitamura, S. Tanaka, Y. Yashimata, J. Chem. Soc. Chem. Commun. 13 (1994) 1585;

(b) S. Tanaka, Y. Yashimata, Synth. Met. 55–57 (1993) 1251;
(c) S. Tanaka, Y. Yashimata, Synth. Met. 69 (1995) 599;
(d) M. Karikomi, C. Kitamura, S. Tanaka, Y. Yashimata, J. Am. Chem. Soc. 117 (1997) 6791.

[11] S. Tanaka, C. Kitamura, Y. Yashimata, Chem. Mater. 8 (1997) 570.

[12] J.P. Ferraris, G.D. Skiles, Polymer 28 (1987) 179.

[13] JAGUAR version 3.5, Schröedinger inc., Portland, OR.

[14] GAUSIAN98, Gausian inc., Pittsburg, PA.

[15] W. Kochs, M. Holthausens, A Chemists Guide to Density Functional Theory, Wiley, New York, 2000 (184pp.).

[16] A.K. Mohanakrishnan, M.V. Lakshmikantham, C McDougal, M.C. Cava, J.W. Baldwin, R.M. Metzger, J. Org. Chem. 63 (1998) 3105.

[17] J.P. Parakka, M.P. Cava, Tetrahedron 51 (1995) 2229.

[18] (a) P.L. Pauson, W.E. Watts, J. Chem. Soc. (1963) 2990;
(b) Org. Synth. Col. Vol. V. [Ed. H.E. Baumgarten], Wiley, New York (1973) 434.

[19] E. Erdik, Organozinc Reagents in Organic Synthesis, CRC Press, Boca Raton, FL, 1996.

[20] J.F. Gallagher, R.D.A. Hudson, A.R. Manning, Acta Crystallogr. C 57 (2001) 28.

[21] D. Lorcy, K.D. Robinson, Y. Okuda, J.L. Atwood, M.P. Cava, J. Chem. Soc. Chem. Commun. 5 (1993) 345.

[22] P. McArdle, J. Appl. Crystallogr. 28 (1995) 65.

[23] A. Berlin, S. Bradamante, R. Ferraccioli, G.A. Pagani, F. Sannicolò, J. Chem. Soc. Perkin Trans. 1 (1987) 2631.

[24] K.N. Jayaprakash, P.C. Ray, I. Matsuoka, M.M. Bhadbhade, V.G. Puranik, P.K. Das, H. Nishihara, A. Sarkar, Organometallics 18 (1999) 3851.

[25] (a) G. Olbrechts, R. Strobbe, K. Clays, A. Persoons, Rev. Sci. Instrum. 69 (1998) 2233;
(b) G. Olbrechts, K. Wostyn, K. Clays, A. Persoons, Opt. Lett. 24 (1999) 403.

[26] S.M. LeCours, H.W. Guan, S.G. DiMangno, C.H. Wang, M.J. Therien, J. Am. Chem. Soc. 118 (1996) 1495.

[27] G.M. Sheldrick, SHELXS97 and SHELXL97, University of Göttingen, Germany, 1997.