

Synthesis, spectroscopy and structure of new push–pull ferrocene complexes containing heteroaromatic rings (thiophene and furan) in the conjugation chain

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Abstract

Six new ferrocene based donor acceptor complexes containing thiophene and furan in the conjugation chain have been synthesized by conventional methods and characterized by NMR, electronic absorption spectral and electrochemical methods. X-ray single crystal structures of three thiophene derivatives, $[(C_5H_5)-Fe-(C_5H_4CH=CH-C_4H_3S)]$ (**1a**), $[(C_5H_5)-Fe-(C_5H_4-CH=CH-C_4H_2S-CHO)]$ (**2a**) and $[(C_5H_5)-Fe(C_5H_4-CH=CH-C_4H_2S-CH=C(CN)_2)]$ (**3a**) have also been determined. Electronic absorption spectral and electrochemical studies suggest that π -donor acceptor interactions are facile in thiophene derivatives when compared to their benzene analogues. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ferrocene; Thiophene; Furan; Nonlinear optics; Electronic absorption spectra; Cyclic voltammetry

1. Introduction

There is a flurry of interest in the development of new materials with large optical non-linearities [1–3]. This is mainly due to the variety of applications they find in the fields such as optical information processing, optical computing and telecommunications. Tremendous efforts [4–6] devoted to the synthesis of organic materials with large second-order optical non-linearities revealed that molecular structures with both large differences between ground state and excited state dipole moments and large transition dipole moments will have large second-order optical non-linearities. Molecules that possess π -donor acceptor interactions suitably fulfil these requirements. Even though, much effort was focused on the synthesis of such organic compounds, organometallic compounds have received less attention. M.L.H. Green [7] and others [8,9] have examined few

ferrocenyl compounds for NLO properties. Our investigations [10] as well as Humphreys laboratories [11,12] have resulted in a huge array of ruthenium acetylides containing aryl or hetero aryl conjugators. These ruthenium acetylides exhibit substantial optical non-linearities. Experimental and theoretical studies on organic chromophores indicated that the presence of hetero-aromatics in the conjugation chain is highly beneficial for the observation of large non-linear optical properties [13]. To the best of our knowledge, hetero-aromatics substituted ferrocenyl ethylene complexes are not yet reported. So we have initiated a program dealing with the synthesis of ferrocenyl ethylene complexes that incorporates hetero-aromatics such as thiophene and furan. Here, we present results in the synthesis, structure and spectroscopy of the ferrocene based donor-acceptor compounds with thiophene or furan in the conjugation chain and dicyanovinyl acceptor group. For comparison we have also synthesized the benzene analogues. Detailed solvatochromic and electrochemical studies have been performed on these organometal-

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lic complexes to assess the π -donor acceptor interactions.

2. Results and discussions

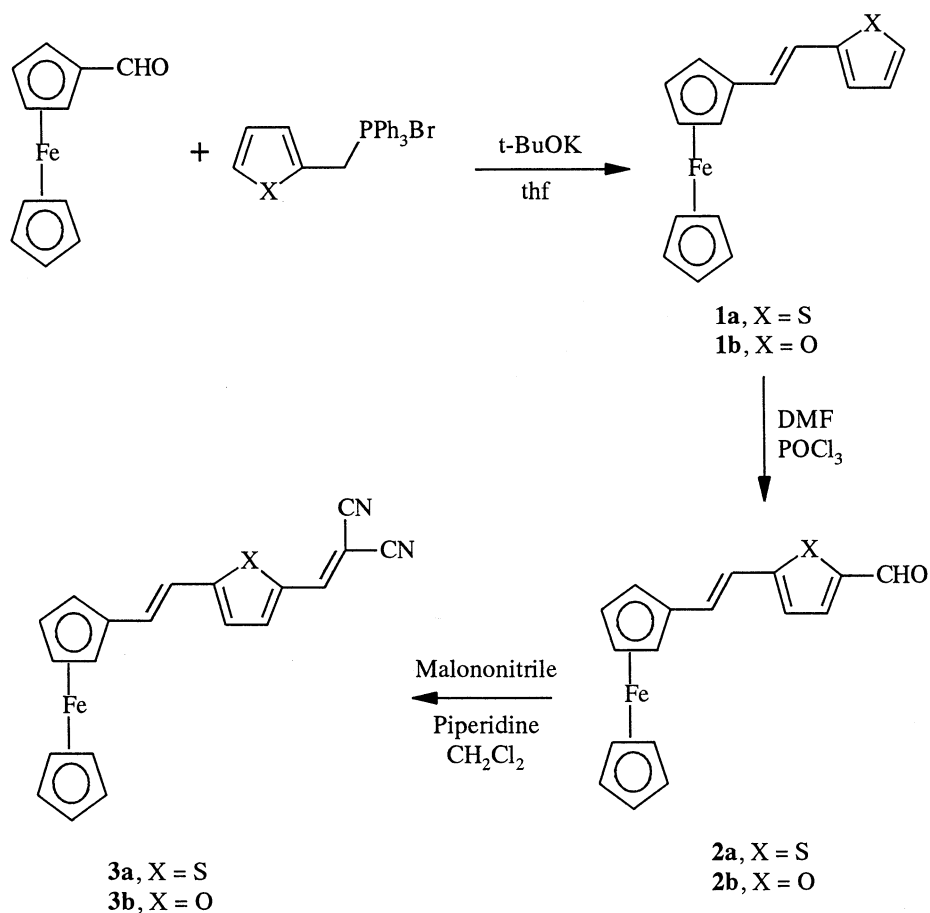
2.1. Synthesis and spectra

The thiophene and furan derivatives (**1a** and **2a**) were prepared by the Wittig reactions of the thienyl or furanyl methyl triphenyl phosphonium bromide with ferrocene carboxaldehyde. Formylation at the 5th position of the hetero-aromatic ring was achieved by using Vilsmeier reagent. Finally, Knoevenagel condensation of the aldehydes with malononitrile in the presence of piperidine yielded the dicyanovinyl derivatives (Scheme 1). The phenylene derivative **2c** 1-ferrocenyl-2-(4-benzenecarboxaldehyde)ethylene is a known compound [14], but for this study, it was prepared in good yield by the Wittig reaction of ferrocenyl methyl phosphonium bromide with excess terephthalaldehyde (four equivalents) (Scheme 2). It is interesting to note that the reaction of the above reagents in an equimo-

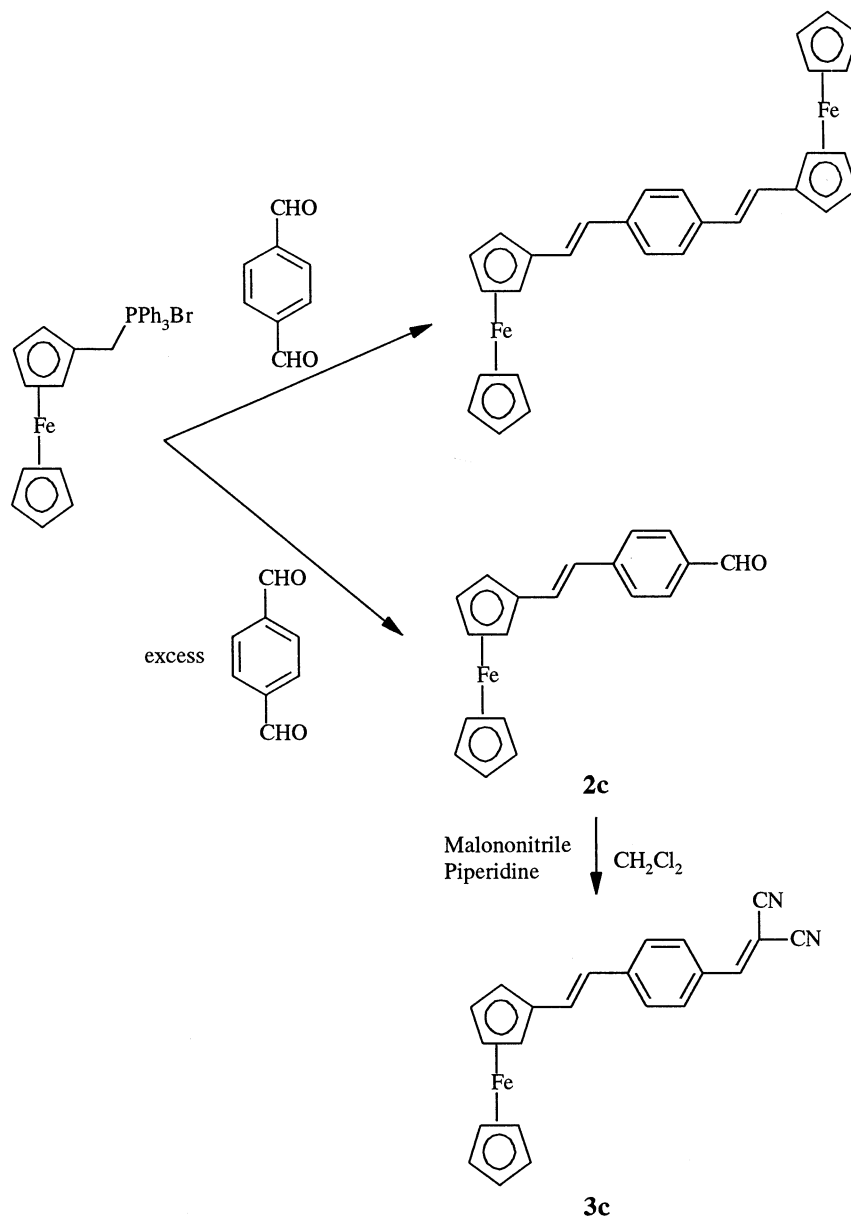
lar ratio gives rise to the diferrocenyl derivative **4** [15].

The ferrocenyl derivatives were characterized by IR and ^1H -NMR spectroscopy, EI MS and elemental analyses. The results are in accordance with the proposed molecular formulations. The molecular structures of the thiophene derivatives were further confirmed by the single crystal X-ray diffraction measurements (*vice supra*). All of the compounds studied exhibit ^1H - and ^{13}C -NMR signals associated with the ferrocenyl and aromatic fragments (Tables 1 and 2). The ethylene bridge signals for **1a** and **2a** indicated the presence of *cis* and *trans* isomers.

No attempt was made to separate the isomers. However, the isomeric mixtures were successfully converted into the *trans* isomer by heating in toluene for 4–6 h. Subsequently, the vinyl protons appear as doublets with coupling constant of ca. 16 Hz in accord with the expected *trans* stereochemistry. The ferrocenyl groups give rise to three separate signals as expected with the unsubstituted C_5H_5 (Cp) ring giving a sharp singlet around 4.10 ppm. The mono substituted C_5H_4 (Cp) ring exhibits an unsymmetrical pair



Scheme 1.



Scheme 2.

of triplets corresponding to the spectrum of an A_2B_2 pattern. These signals appear at low field of the unsubstituted C_5H_5 singlet, showing that the aryl/heteroaryl rings considerably shield all the four ring protons. This shielding is more pronounced in the thiophene and furan derivatives in comparison to the benzene analogues. The effect of the electron withdrawing acceptor group is also witnessed in the 1H chemical shifts of the substituted C_5H_4 ring. Thus, the signals corresponding to them appear in comparatively low field for **3a** and **3b**.

2.2. Structure of the complexes **1a**, **2a** and **3a**

The structure of the ferrocenyl complexes **1a**, **2a** and **3a** were determined by using single crystal X-ray diffraction method. The molecular structures of the complexes were displayed in Figs. 1–3. Table 3 provides the crystal parameters and other experimental details. The selected bond lengths and angles were presented in Table 4. The complexes possess ca. eclipsed ferrocenyl geometry. The variation in the Fe–C bond distances are small, 1.993(6)–2.050(4) and

Table 1
¹H Spectral data^a

No.	Cp	Cp'	Vinyl	H-3	H-4	Others
1a	4.12	4.25(m) 4.40(m)	6.66 (15.9) 6.81 (15.8)	6.94 (m)	6.94 (m)	7.11(5-H)
1b	4.12	4.28(m) 4.50(m)	6.61 (16.2) 6.79 (16.1)	6.30 (3.3)	6.43 (m)	7.49(5-H)
2a	4.17	4.38(m) 4.60(m)	7.00 (15.9) 7.10 (15.9)	7.20 (3.8)	7.81 (4.2)	9.87(CHO)
2b	4.16	4.39(m) 4.60(m)	6.71 (16.1) 7.18 (16.1)	6.59 (3.6)	7.40 (3.7)	9.56(CHO)
3a	4.19	4.45(m) 4.68(m)	7.09 (15.9) 7.25 (15.9)	7.29 (4.2)	7.81 (4.2)	8.30(CH=)
3b	4.17	4.46(m) 4.60(m)	6.78 (16.0) 7.34 (16.0)	6.74 (3.8)	7.43 (3.8)	7.86(CH=)
3c	4.14	4.40(m) 4.63(m)	6.90 (16.2) 7.36 (16.2)	7.73(8.4, H-2)	8.00(8.5, H-3)	8.21(CH=)

^a Chemical shifts in ppm, within parenthesis are multiplicities, assignment or coupling constant values in case of doublets.Table 2
¹³C Spectral data^a

No.	Cp	Cp'	Vinyl	C-2	C-3	C-4	C-S	Others
1a	69.22	66.73 69.04 82.92	119.30 126.87	143.58	123.07	124.26	127.52	–
1b	69.97	67.62 69.86 83.90	112.42 126.64	154.74	107.41	115.2	142.4	–
2a	70.14	68.35 70.76 82.53	119.00 126.22	141.61	133.58	138.98	153.70	183.32
2b	70.18	68.39 70.82 82.33	113.54 125.36	152.42	109.75	133.76	159.92	177.10
3a	71.36	68.75 70.33 83.20	118.48 126.59	133.65	136.30	142.90	142.90	152.16 156.66 115.60 114.92
3b	70.42	68.85 71.55 81.93	112.66 128.99	141.92	112.42	137.21	162.10	148.13 162.10 115.19 115.95
3c	70.20	68.46 70.79 80.42	125.00 134.06	127.26	130.42	132.39	145.85	164.22 115.30 130.71 114.40

^a Chemical shifts in ppm.

is more effective in **3a**. In **3a**, the Fe–C distance associated with the unsubstituted cyclopentadienyl ring is 2.006, while that with the substituted cyclopentadienyl ring is 2.036. Effects of the substituents on the geometry of the cyclopentadienyl rings are also apparent in the ring C–C distances and C–C–C angles. Thus, the distances involving C(1) are some what longer than the remaining C–C distances. Both the

cyclopentadienyl rings are planar within experimental error and they are also parallel to each other. The thiophene rings are coplanar with the parent cyclopentadienyl rings as indicated by the dihedral angles (8.9, 16.1 and 9.9°, respectively for **1a**, **2a** and **3a**) between the respective thiophene and cyclopentadienyl rings. A slight tilting observed for **2a** may arise from crystal packing effects.

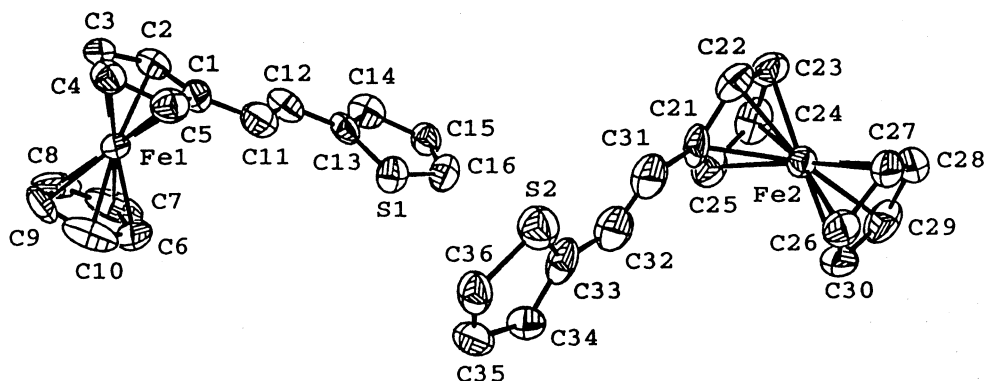


Fig. 1. Molecular structure of **1a** with atom numbering scheme.

2.3. Electronic absorption spectra

The solution electronic absorption spectral studies of compounds designed to possess NLO properties are important for two specific reasons. Firstly, it is necessary to know the transparency region. Secondly, the solvatochromic behaviour of the sample is generally considered as indicative of high molecular hyperpolarisability, β , and hence of potential bulk NLO properties. The compound *Z*-[1-ferrocenyl-2-(4-nitrophenyl)-ethylene] provides an example of an organometallic species which displays marked solvatochromism and also a high powder SHG [7]. The electronic absorption spectra of the present complexes were recorded in dichloromethane and data are presented in Table 5. In general, ferrocenyl compounds show two prominent bands. The band in the UV region is described to possess d-d character while the visible band is believed to be due to an MLCT excitation. All the compounds studied exhibit the above two bands. The higher wavelength band exhibits appreciable bathochromic shift as more electron withdrawing acceptor groups are introduced. Thus, the absorption maxima of the dicyanovinyl derivatives top among the complexes. Within the series the thiophene derivative possess MLCT absorption in low energy (Fig. 4). This further corroborates the idea that replacing phenyl groups in the conjugation chain by less aromatic heterocyclic rings such as thiophene will facilitate the π -donor acceptor interactions.

The solvatochromism of the dicyanovinyl complexes were investigated in detail in ten solvents of differing dielectric properties and the data are presented in Table 6. Higher bathochromic shift is observed in dichloromethane. A drastic change in the spectral pattern is noticed when the spectrum is recorded both in dimethyl formamide and dimethyl sulfoxide. In dimethyl formamide, for thiophene and furan com-

plexes the MLCT band is shifted to higher wavelength and located at around 700 nm, while the benzene analogue experiences normal effect. In dimethyl sulfoxide, **3a** and **3c** show shifts for MLCT and d-d bands, thus pointing to the possibility of some chemical modification. In contrast to the belief that the less aromatic furan derivative exhibits little solvatochromism. On going from hexane to dichloromethane a maximum shift of 24 nm is observed for the thiophene derivative, **3a** and the furan derivative **3b** possess fewer shifts.

2.4. Electrochemistry

The electrochemical properties of the ferrocenyl compounds were examined in dichloromethane solution by cyclic voltammetry, and the pertinent data are presented in Table 7. The compounds **1a** and **1b** with no acceptor groups showed oxidation potentials almost same as parent ferrocene (FcH). Electron withdrawing substituents on the aryl/heteroaryl rings significantly affect the oxidation potentials. Thus, for instance **2b** and **3b** exhibit 71 and 99 mV anodic shifts, respectively

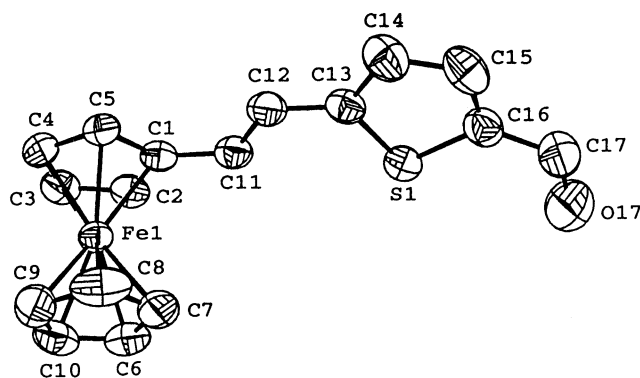
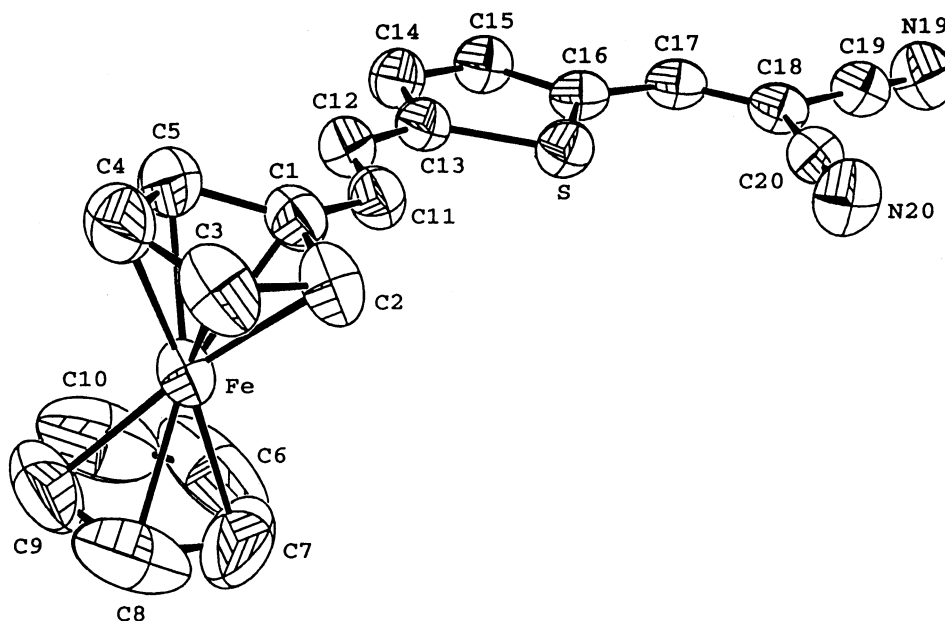


Fig. 2. Perspective view of **2a** with atom numbering scheme.

Fig. 3. Molecular structure of **3a** with atom numbering scheme.

in oxidation potentials relative to unsubstituted derivative **1b**. A similar effect is observed for the thiophene derivatives also. Tremendous shift is realised for the dicyanovinyl derivatives in accordance with its superior electron withdrawing ability. On comparing the benzene and heteroaryl (thiophene and furan) derivatives the later compounds exhibit large anodic

shifts in oxidation potentials. This probably suggests that in the heteroaryl derivatives the π -donor acceptor interactions are more pronounced. The ΔE_p values of the standard ferrocene and the compounds used in this study fall in the same range (Table 7). Thus, the ferrocene oxidation in all the compounds may be termed as reversible or quasi-reversible. An additional

Table 3
Crystallographic data for **1a**, **2a** and **3a**

Compound	1a	2a	3a
Empirical formula	C ₁₆ H ₁₄ SFe	C ₁₇ H ₁₄ OSFe	C ₂₀ H ₁₄ N ₂ SFe
Formula weight	294.19	322.20	370.25
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> 2 ₁ / <i>a</i>
Unit cell dimensions			
<i>a</i> (Å)	19.375(4)	8.1167(9)	12.5914(16)
<i>b</i> (Å)	5.9820(23)	10.0537(23)	7.7549(9)
<i>c</i> (Å)	22.641(3)	17.8006(23)	17.287(4)
<i>V</i> (Å ³)	2617.1(12)	1422.0(4)	1683.3(5)
<i>Z</i>	8	4	4
<i>D</i> _{calc.} (mg m ^{−3})	2.987	1.505	1.461
μ (Mo–K α), (m ^{−1})	2.563	1.191	1.015
Min/max transmission	0.932/1.000	0.862/1.000	0.933/1.000
<i>F</i> (000)	2432	664	762
Crystal size (mm ³)	0.09 × 0.13 × 0.38	0.31 × 0.31 × 0.63	0.38 × 0.44 × 0.47
2 θ range	2.06–50.00	2.06–50.00	2.06–50.00
Index ranges	−23 ≤ <i>h</i> ≤ 22, 0 ≤ <i>k</i> ≤ 7, 0 ≤ <i>l</i> ≤ 26	−9 ≤ <i>h</i> ≤ 9, 0 ≤ <i>k</i> ≤ 11, 0 ≤ <i>l</i> ≤ 21	−14 ≤ <i>h</i> ≤ 14, 0 ≤ <i>k</i> ≤ 14, 0 ≤ <i>l</i> ≤ 14
Reflections collected	4736	2582	3121
Unique data/restraints/parameters	4589/0/325	2499/0/181	2967/0/217
<i>R</i> _p , <i>R</i> _w	0.049, 0.052	0.031, 0.035	0.036, 0.041
Largest remaining peak/hole (e Å ^{−3})	0.640/−0.350	0.320/−0.290	0.290/−0.270

Table 4
Selected bond distances and angles in **1a**, **2a** and **3a**

	1a		2a	3a
	Molecule 1	Molecule 2		
<i>Bond distance</i>				
Fe–C(1)	2.046(7)	2.035(7)	2.040(3)	2.035(3)
Fe–C(2)	2.033(7)	2.045(7)	2.032(3)	2.032(3)
Fe–C(3)	2.037(7)	2.032(7)	2.041(3)	2.050(4)
Fe–C(4)	2.038(8)	2.036(8)	2.039(3)	2.034(4)
Fe–C(5)	2.028(8)	2.026(8)	2.032(3)	2.028(4)
Fe–C(6)	1.997(8)	2.029(7)	2.030(3)	1.993(6)
Fe–C(7)	1.994(9)	2.041(7)	2.032(3)	1.994(6)
Fe–C(8)	2.009(10)	2.045(7)	2.031(3)	2.019(4)
Fe–C(9)	2.025(9)	2.036(8)	2.038(3)	2.016(4)
Fe–C(10)	2.021(9)	2.036(7)	2.041(3)	2.009(5)
C(1)–C(11)	1.483(12)	1.514(13)	1.448(4)	1.449(4)
C(11)–C(12)	1.250(13)	1.212(14)	1.329(4)	1.330(5)
C(12)–C(13)	1.478(12)	1.481(13)	1.446(4)	1.439(4)
C(16)–C(14)	–	–	1.440(5)	1.413(4)
C(17)–C(18)	–	–	–	1.349(5)
<i>Bond angle</i>				
C(1)–C(11)–C(12)	124.6(8)	125.2(10)	124.9(3)	126.5(3)
C(22)–C(12)–C(13)	125.5(8)	127.9(10)	126.2(3)	125.3(3)

irreversible wave at a highly cathodic potential is observed in compounds with dicyanovinyl groups. This may be attributed to the reduction processes of the dicyanovinyl group.

3. Conclusions

A new series of push–pull ferrocene complexes incorporating hetero aromatics such as thiophene and furan in the conjugation chain have been successfully synthesized and characterized thoroughly by spectral, structural and electrochemical studies. Electronic spectral and electrochemical studies point out that π -donor acceptor interactions are more pronounced in the thiophene derivatives when compared to the corresponding furan and benzene analogues. It is realised that the introduction of more strong electron withdrawing groups will enhance the π -donor acceptor interactions and hence the optical non-linearities. Work in this direction is in progress in our laboratory

4. Experimental

The general procedures pertaining to the synthesis of the compounds reported in this paper and their physical measurements are identical to those previously published [10]. Compounds (2-thienylmethyl) triphenyl phosphonium bromide [16], (2-furylmethyl) triphenyl phosphonium bromide [16], (5-bromo-2-thienylmethyl) triphenyl phosphonium bromide [16] and ferrocene car-

boxaldehyde [17] were prepared by adopting reported methods.

4.1. 2-(2-Ferrocenyl-vinyl)-thiophene (**1a**)

The compound (2-thienylmethyl)triphenyl phosphonium bromide (4.39 g, 10 mmol) was dissolved in dry THF and cooled to 0°C. Potassium *t*-butoxide (1.35 g, 12 mmol) was added as a solid through a side arm while stirring the solution vigorously. This generated a deep red coloration. After stirring at 0°C for another 30 min, the solution was brought to room temperature (r.t.) and ferrocene carboxaldehyde (2.14 g, 10 mmol) added in a few batches. The reaction mixture was heated to reflux for 4 h. When the tlc revealed no further reaction it was quenched with ice water and extracted with diethyl ether. The ether layer was washed with brine solution and dried over anhydrous MgSO_4 . Evaporation of the ethereal solution and subjecting the residue to column chromatography in silica using dichloromethane/hexane (1:4) as eluant provided **1a** in an 82% yield. MS (EI): m/e 294 (100%, M^+). Anal. calc. for $\text{C}_{16}\text{H}_{14}\text{SFe}$: C 65.32, H 4.80%. Found: C 65.23, H 4.88%.

4.2. 2-(2-Ferrocenyl-vinyl)-furan (**1b**)

Following the above method (2-furylmethyl) triphenyl phosphonium bromide and ferrocene carboxaldehyde afforded **1b** as a brick red powder in an 80% yield. MS (EI): m/e 278 (100%, M^+). Anal. calc. for $\text{C}_{16}\text{H}_{14}\text{OFe}$: C 69.10, H 5.07%. Found: C 69.08, H 4.90%.

4.3. (E)-5-(2-Ferrocenyl-vinyl)-thiophene-2-carbaldehyde (**2a**) and (E)-5-(2-ferrocenyl-vinyl)-furan-2-carbaldehyde (**2b**)

Essentially the same procedure was applied to prepare **2a** and **2b**; consequently only the synthesis of **2a** is described in detail. Vilsmeier reagent was prepared by mixing dimethyl formamide (20 ml) and phosphorus oxychloride (1.4 ml, 15 mmol) at 0°C. This was added dropwise over 0.5 h to an ice-cooled dimethyl formamide solution (20 ml) of **1a** (2.94 g, 10 mmol) with vigorous stirring. After the addition was over, the mixture was allowed to warm to r.t. and then heated at 60°C for 6 h. The reaction was quenched with the addition of water and subsequently treated with 50 ml of 10% aqueous sodium hydroxide solution. The dark brown suspension was extracted with dichloromethane and thoroughly washed with brine solution. The dichloromethane extracts were combined, dried over anhydrous magnesium sulfate and evaporated to dryness to obtain the crude aldehyde. This was purified by column chromatography using dichloromethane/hexane

Table 5

Electronic absorption data for the ferrocenyl compounds^a

Compound	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ ($M^{-1} \text{ cm}^{-1} \times 10^{-3}$)
1a	325	22.56
	460	1.44
1b	314	22.47
	454	1.00
2a	370	17.52
	505	3.55
2b	360	19.99
	486	3.27
2c	342	26.10
	480	3.60
3a	442	20.64
	574	7.50
3b	443	17.10
	566	6.62
3c	383	19.60
	535	4.76

^a Data measured for dichloromethane solutions of concentration 5×10^{-5} M.

(4:1) as eluant. Yield: 87%. MS (EI): m/e 322 (45%, M^+). Anal. calc. for $C_{17}H_{14}OSFe$: C 63.37, H 4.38%. Found: C 63.08, H 4.38%.

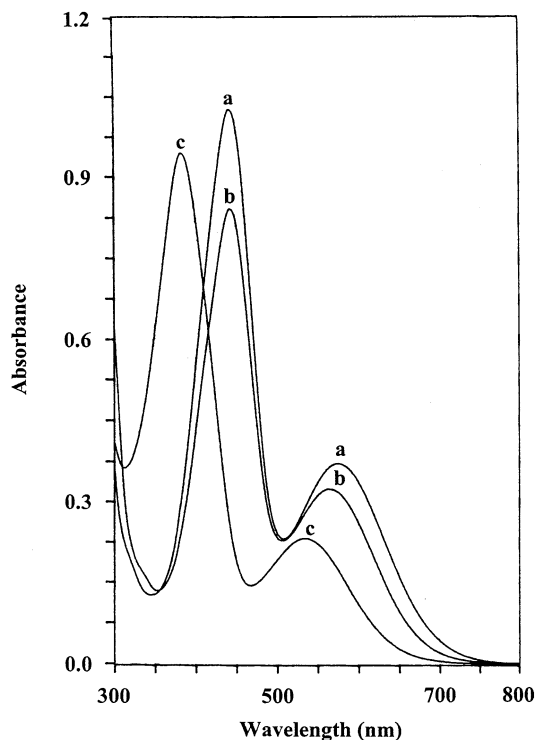
Fig. 4. Electronic absorption spectra of (a) **3a**, (b) **3b** and (c) **3c**.

Table 6

Solvatochromic data for the dicyanovinyl derivatives **3a–c**^a

Solvent	3a		3b		3c	
<i>n</i> -Hexane	550	430	548	432	514	370
Ethyl acetate	555	434	549	434	517	374
1,4-Dioxane	555	434	550	434	515	373
Acetonitrile	559	436	550	437	518	375
Acetone	560	437	551	437	518	374
Tetrahydrofuran	562	437	552	438	519	375
Methanol	564	437	556	438	520	374
Dichloromethane	574	442	565	443	535	383
Dimethyl formamide	716	437	700	430	520	376
Dimethyl sulfoxide	723	678	721	674	690	367

^a Data measured for dichloromethane solutions of concentration 5×10^{-5} M.

Table 7

Cyclic voltammetric data^a

Compound	E_f (V)	Δe_p	Others
1a	0.270	98	–
1b	0.257	91	–
2a	0.323	88	–
2b	0.328	90	–
2c	0.306	90	–
3a	0.350	92	–1.252
3b	0.356	95	–1.330
3c	0.334	97	–1.334
Ferrocene	0.264	82	–

^a Conditions: sample concentration, 10^{-3} M; electrolyte, NBu_4ClO_4 (0.1 M); solvent, dichloromethane; scan rate, 60 mV).

4.4. 4-(2-Ferrocenyl-vinyl)-benzaldehyde (**2c**) [14]

It was prepared in a 75% yield from ferrocenyl methyl phosphonium bromide and four equivalents of terephthalaldehyde as described for **1a**.

4.5. 2-[5-(2-Ferrocenyl-vinyl)-thiophen-2-ylmethylene]-malononitrile (**3a**)

The aldehyde **2a** (0.483 g, 1.5 mmol) and malononitrile (0.112 g, 1.7 mmol) were dissolved in dichloromethane (20 ml) and stirred at r.t. for 2 h. Piperidine (two drops) was added and the stirring continued for a further 12 h. Volatile materials were driven off under reduced pressure and the resulted green residue was chromatographed on silica using dichloromethane/hexane (3:2) mixture as eluant. Gray green crystalline **3a** was thus obtained in an 81% yield. MS (EI): m/e 370 (100%, M^+). Anal. calc. for $C_{20}H_{14}N_2SFe$: C 64.88, H 3.81, N 7.57%. Found: C 64.65, H 4.02, N 6.77%.

4.6. 2-[5-(2-Ferrocenyl-vinyl)-furan-2-ylmethylene]-malononitrile (**3b**)

It was obtained in a 55% yield from **2b** by following a procedure similar to that of **3a**. MS (EI): m/e 354 (100%, M^+). Anal. calc. for $C_{20}H_{14}ON_2Fe$: C 67.32, H 3.98, N 7.91%. Found: C 67.32, H 3.80, N 7.69%.

4.7. 2-[4-(2-Ferrocenyl-vinyl)-benzylidene]-malononitrile (**3c**)

Synthesized as above from **2c** in a 65% yield. MS (EI): m/e 364 (100%, M^+). Anal. calc. for $C_{22}H_{16}N_2Fe$: C 72.55, H 4.43, N 7.69%. Found: C 71.47, H 4.29, N 7.35%.

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