

Organometallic dyes: Part 1. Synthesis of orange to cyan dyes based on donor–conjugated–acceptor chromogenes using ferrocene as the donor group

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A novel series of organometallic donor–conjugated–acceptor dyes derived from ferrocene as the donor group have been synthesized via the Knoevenagel reaction of ferrocene carboxaldehyde and various active methylene compounds to give a range of dyes ranging from orange to blue–green in color. The most bathochromic dye is that derived from dialkyl thiobarbituric acid and the least is that derived from the tetralone. The dyes showed an unusual negative solvatochromism as the solvent polarity increased. All dyes synthesized are expected to have some non-linear optical properties, as evidenced from the pronounced solvatochromism. Copyright © 2001 John Wiley & Sons, Ltd.

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1 INTRODUCTION

There is considerable interest in the synthesis of new materials with large second-order optical non-linearity because of their potential applications in optical data storage, telecommunications and optical signals processing.^{1–4} First and second hyperpolarizabilities can be observed with molecules that possess electron donor and acceptor groups connected by a conjugated π -electron bridge that allows the possibility of intramolecular charge

transfer.^{5–8} The non-linear optical properties are usually enhanced by one of the following modifications: (a) increasing the donor group releasing ability; (b) increasing the accepting ability of the acceptor group; (c) lengthening the conjugated system. Although increasing the conjugated system causes a pronounced bathochromic shift, it results in a remarkable decrease in the solubility of the dye in common organic solvents. Modification (a) is self-evident, but modification (b) needs further investigation. In a previous publication⁹ we reported the synthesis of varieties of (D– π –A) systems based on the dimethylamino group as the donor element with various acceptors.

Currently, there is much interest in the technological uses of metallocenes.^{10–13} The sandwich structure of ferrocene renders it completely different from conventional aromatic molecules. In medicine, ferrocene is ideal for use in drug design because of its low toxicity;¹⁴ ferrocene derivatives have been proposed as hematinics for the treatment of iron deficiency anemia.¹⁵ Although the preparation of some non-linear molecules containing ferrocene as the donor group, such as **1**, **2**, **3** and **4** (Fig. 1), have been accomplished,^{16–20} these reported ferrocenyl derivatives contain long conjugated systems and result in low solubility in common organic solvents.

In this report the synthesis and spectroscopic studies of some new (D– π –A) chromogenes, based on ferrocene as the donor element and with a relatively low π -conjugated system with various acceptors, will be discussed.

2 RESULTS AND DISCUSSION

2.1 Dye synthesis

Dyes **5a–d** were prepared (Fig. 2) via the

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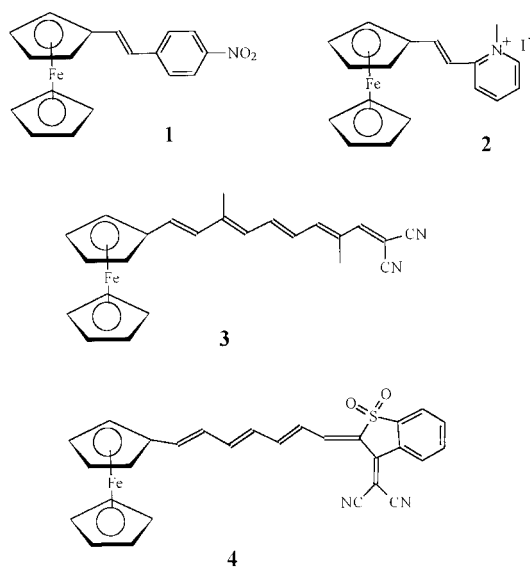


Figure 1

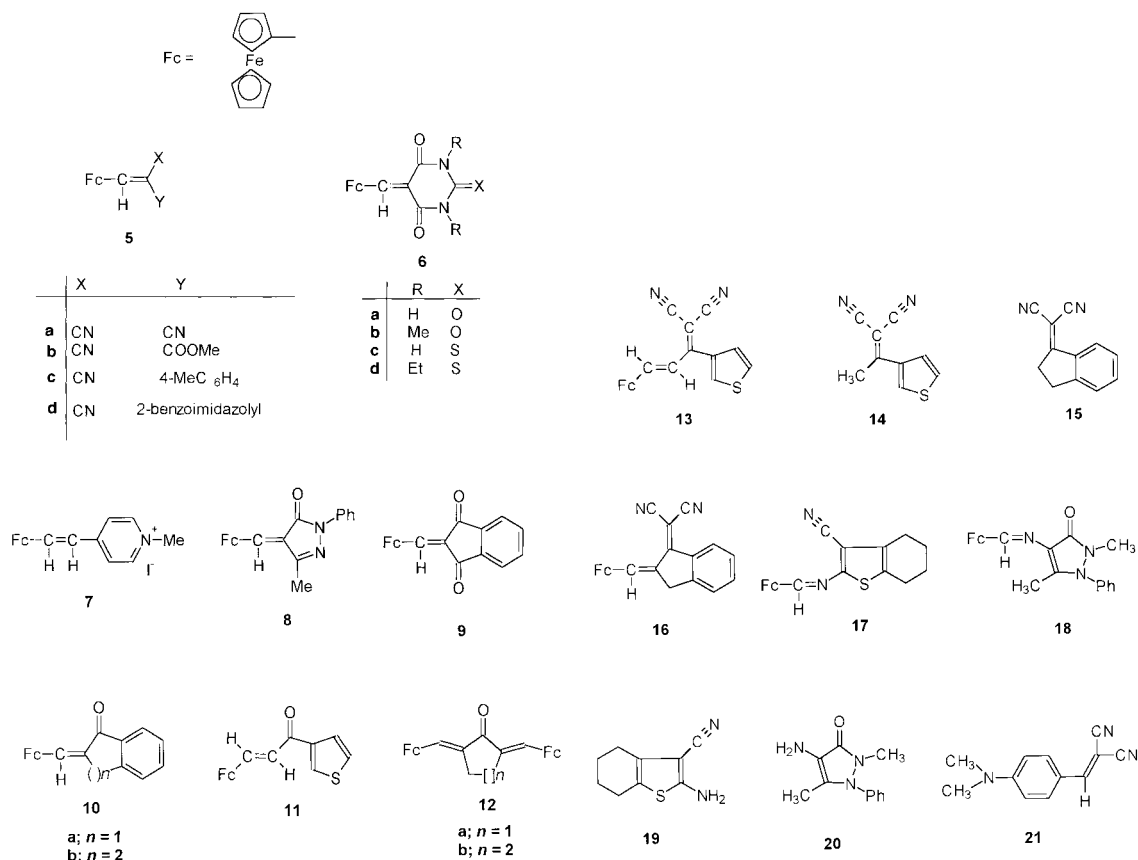


Figure 2

Knoevenagel²¹ condensation of ferrocene carboxaldehyde (Fc-CHO) and the appropriate active methylene compounds. The ¹H NMR spectra of dye **5a**, which was obtained from malononitrile as an active methylene component, showed a singlet at δ 7.70 integrating for the one olefinic proton. The two ortho protons of the substituted cyclopentadienyl (Cp) moiety appeared as a broad singlet at δ 5.01 and the other protons showed a broad singlet centered at δ 4.85. The five protons of the unsubstituted Cp ring exhibited a singlet at δ 4.33. The IR spectrum of compound **5a** showed absorptions at 2185 and 2170 cm⁻¹ for the two cyano groups. Compound **5b** was obtained exclusively as the Z-isomer, as evidenced by its ¹H NMR spectrum, which exhibited a singlet at δ 8.20 attributed to the olefin proton and a doublet at δ 4.33 with $J = 2.5$ Hz for the methoxy protons, due to the long-range coupling with the olefinic protons. This was further substantiated by a nuclear Over-

Table 1 Selected ^1H NMR and IR data of ferrocenyl dyes

Dye	$\delta \text{H}_{\text{olef}}$	$\delta(\text{H}2 + \text{H}5)$	$\delta(\text{H}3 + \text{H}4)$	$\nu_{\text{max}}/\text{cm}^{-1}$ C=C/C=N
5a	7.70	5.01	4.85	1630
5b	8.20	5.04	4.74	1600
5c	7.34	4.96	4.52	1615
5d	8.39	5.01	4.68	1585
6a	8.47	5.34	5.00	1580
6b	8.45	5.32	4.90	1565
6c	8.48	5.38	5.08	1613
6d	8.46	5.34	4.97	1620
7	7.75	4.80	4.62	1600
8	7.80	4.81	4.62	1620
9	7.88	5.44	4.85	1601
10a	7.60	4.67	4.52	1640
10b	7.70	4.57	4.45	1610
11	7.76	4.59	4.49	1590
12a	7.44	4.60	4.51	1625
12b	7.62	4.55	4.43	1605
13	7.71	4.98	4.61	1625
16	8.10	4.41	4.32	1605
17	8.38	4.85	4.59	1627
18	9.96	4.80	4.62	1616

hauser enhancement (NOE) experiment; when the signal at a δ 8.20 proton was irradiated the signal at δ 4.33 showed a positive enhancement. The dye series **6a–d** was prepared from barbituric and thiobarbituric acids and their *N,N*-dialkylated derivatives.

The introduction of the cyclic barbituric and thiobarbituric acid derivatives causes a low-field shift of the signal of the ortho proton (Ha) of the substituted Cp when compared with dye **5a**, and the same effect was also observed for the other protons (Hb) of the Cp moiety (Table 1). This low-field shift is attributed to the electron-withdrawing nature of the moiety ($-\text{CH}=\text{acceptor}$), which decreases the electron density on the Cp ring, hence making the protons less deshielded. On the other hand, a high diamagnetic anisotropy effect of the carbonyl group of both the barbituric and thiobarbituric acid moieties was observed for the olefinic proton (H_{olef}) when comparing the values for the dye series **6a–d** (Table 1) with that for dye **5a**. Dyes **7** and **8** were also prepared by Knoevenagel condensations of the *N*-methyl-4-methylpyridinium iodide salt and 3-methyl-1-phenylpyrazol-5-one respectively.

Dyes **9**, **10a** and **10b** and **11** were prepared *via* an aldol condensation of the appropriate ketone and Fc-CHO. The diferrocenylidene cycloalkanones

(**12a** and **12b**) were prepared *via* an aldol condensation of two equivalents of Fc-CHO and one equivalent of either cyclopentanone or cyclohexanone respectively. Dye **13** was prepared from the dicyanomethylene derivative **14** using toluene as solvent.

Recently, we have reported the synthesis of new methine dyes from 1-dicyanomethyleneindane (**15**). Dye **16** was prepared by condensation of **15** with Fc-CHO in THF. Schiff bases **17** and **18** were prepared by condensation of 2-amino-3-cyano-octahydrothiophene (**19**) and 4-aminophenazone (**20**) respectively. The ^1H NMR spectra of the Schiff bases **17** and **18** exhibited two singlets at δ 9.96 and δ 8.38 integrated for one proton each, which are attributed to the olefinic protons.

2.2 Electronic absorption spectroscopic properties

The UV–visible spectral data in chloroform, acetonitrile and acetone are summarized in Table 2. The molar absorption coefficient was measured in acetone.

All the ferrocenyl dyes synthesized showed two bands in chloroform; the first band is strong and lies in the UV region, and the second band appeared in the visible region with medium intensity. Recently, Marder and coworkers described the origin of the color for some metallocene-based dyes.²² They assigned the high-energy band to be as a result of the transition from the π orbital of the bridge to the lowest unoccupied molecular orbital (LUMO) of the acceptor. On the other hand, the low-energy band was assigned to the transition from the highest occupied molecular orbitals (HOMOs) of the metal (corresponding to the degenerate d_{z^2} , $d_{x^2-y^2}$ and d_{xy} orbitals) to the LUMO of the acceptor.

Unlike the rest of the dyes synthesized, **5a**, **10a** and **11** exhibited a third band appearing as a shoulder in the region 390–396 nm.

In a previous paper²³ we proposed that the relative intensity of an acceptor in the chromophores based on conjugated donor–acceptor systems can be estimated from the values of the absorption maximum. A stronger acceptor would produce a bathochromic shift, and so on.

The ferrocenyl dyes synthesized can be classified into four main series: (a) the cyano derivatives, which are exemplified by dyes **5a–d**, **13** and **16**; (b) the barbituric and thiobarbituric acid derivatives **6a–d**; (c) the chalcones series, **9**, **10a** and **10b**, **11** and **12a** and **12b**; and finally (d) the Schiff bases **17** and **18**.

Table 2 UV–visible spectral data of ferrocenyl dyes in various solvents

Dye	$\lambda_{\text{max}}(\text{CHCl}_3)$		$\lambda_{\text{max}}(\text{CH}_3\text{CN})$		$\lambda(\epsilon_{\text{max}}/\text{dm}^3\text{cm}^{-1}/\text{mol}^{-1})$ (acetone)	
	Band 1	Band 2	Band 1	Band 2	Band 1	Band 2
5a	334, 392	531	339, 393	499	345 (16 376), 395 (4945)	521 (4913)
5b	322	521	317, 379	515	331 (10 881)	517 (2023)
5c	328	495	325	487	334 (35 000)	485 (3714)
5d	362	518	350	506	349 (17 000)	503 (2613)
6a	350	571	346	546	343 (13 125)	544 (2779)
6b	352	558	347	545	345 (26 275)	546 (5363)
6c	377	584	368	572	364 (22 882)	567 (4591)
6d	378	581	368	567	374 (16 521)	575 (3700)
7	363	453, 574	350	464, 520	347 (6331)	460 (1900)
8			400	499	395 ^a	487 ^a
9	361	575	356	566	341 (25 000)	566 (6250)
10a	333, 396	516	330, 392	507	335 (17 295), 395 (3320)	506 (2807)
10b	330	508	329	496	333 (40 256)	493 (5471)
11	323	504	319	501	334 (34 326), 383 (9660)	495 (7938)
12a	359	539	350	530	350 (46 692)	525 (12 356)
12b	342	520	321	503	338 (42 813)	505 (10 515)
13	335, 390	535		525	341 ^a	532 ^a
16	332	541	345	580	335 ^a	550 ^a
17	381	504	376	499	375 (13 500)	501 (3000)
18	335	472	359	460	362 ^a	475 ^a

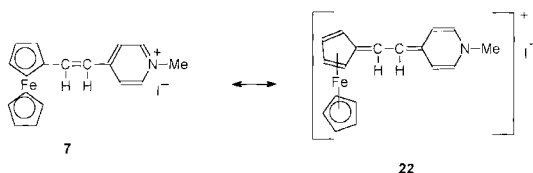
^a Poor solubility.

In the cyano derivatives, the parent dicyanomethylene derivative **5a** showed an absorption band at 531 nm in chloroform, which is the most bathochromic shift as well as the most hyperchromic shift of the visible band compared with the other members of the cyano derivatives (**5b–d**). On the other hand, the introduction of an extra C=C double bond, as in dye **16**, produced a further bathochromic shift. The observed sequence in producing bathochromic shifts in this series is **16** > **5a** > **5b** > **13** > **5d** > **5c**. The ferrocenyl moiety as a donor is far stronger than *N,N*-dimethylamino, as demonstrated by comparing the absorption maximum of the ferrocenyl dye **5a** and its *N,N*-dimethylamino analogue **21**, which absorbs some 112 nm less than dye **5a** in chloroform. The parent dyes of the second series are the unsubstituted barbituric and thiobarbituric acids; they showed absorption bands in chloroform at 571 nm and 584 nm respectively. The *N,N*-dialkylation of the parents dyes **6a** and **6c** causes some bathochromic shifts in polar solvents. The sequence **6d** > **6c** > **6b** > **6a** for producing a bathochromic shift was observed. The third series of dyes was the chalcones, **9**, **10a** and **10b**, **11** and **12a** and **12b**. Usually the chalcones range in color from yellow to red. Ferrocenyl chalcone (**9**) is blue in both the solid

state and in solution. The analation of the α,β -unsaturated ketone system causes a bathochromic shift, as can be noticed when comparing dyes **11** and **10a** and **10b**. Moreover, the decrease in the ring size causes a bathochromic shift of the resulting chalcone, as seen in dyes **10a** and **10b**. A pronounced increase in the visible band of chalcone dyes was achieved by synthesis of the bis ferrocenyl derivatives **12a** and **12b**. The fourth series of ferrocenyl dyes were Schiff bases. Schiff base **17** showed an absorption band at 504 nm in chloroform, and dye **18** showed a hypsochromic shift of 32 nm compared with **17** in chloroform.

2.3 Solvatochromism and non-linear properties

In general, all the dyes showed an unusual negative solvatochromism with increasing solvent polarity. For example, dye **5a** showed an absorption band at 531 nm in chloroform that was displaced to 499 nm in acetonitrile. The most negative solvatochromic shift was observed for compound **7**; this is due to the contribution of the resonance hybrid (**22**) to the excited state (Scheme 1). On the other hand, the smallest solvatochromic effect was observed for chalcone (**11**).



Scheme 1

It has been reported that preliminary information on non-linear optical properties of polar molecules can be deduced from measuring the absorption spectra in different solvents differing in their dielectric constants.^{24,25} This method is referred to as the two-level model. In the light of this model and the absorption spectral data given in Table 2, the new ferrocenyl methine dyes showed pronounced solvatochromism and they are expected to show some non-linear optical properties.

3 EXPERIMENTAL

Melting points were recorded on a Thomas–Hoover capillary melting apparatus without correction. IR spectra were taken as KBr disks on a Nicolet Magna 520 FTIR spectrometer. NMR spectra were obtained with a Bruker DPX 400 (400 MHz) spectrometer using CDCl₃ solutions. Microanalyses were carried out using a Perkin Elmer 240B analyzer. UV–visible spectra were recorded on a Shimadzu 260 spectrometer for solutions.

3.1 1-Dicyanomethyleneindan (15)

Anhydrous sodium acetate (6.5 g, 0.076 mol) was added to a stirred solution of 1-indanone (10 g, 0.075 mol) and malononitrile (5.1 g, 0.075 mol) in absolute ethanol (100 ml) at 25 °C. The reaction mixture was stirred for 2 h, diluted with water and acidified to pH 3–4 with hydrochloric acid. The solid formed was filtered off, and washed with water followed by small amount of ethanol. The crude product was recrystallized from ethanol to give **15** as an off-white powder (11.5 g, 84%), m.p. 146–148 °C. Anal. Found: C, 80.3; H, 4.23; N, 15.9. Calc. for C₁₂H₈N₂: C, 80.0; H, 4.44; N, 15.6%. $\nu_{\max}$ (KBr/cm⁻¹) 2222 (CN), 1570; ¹H NMR: δ 7.1–8.4 (m, 4H, aromatic protons), 3.3 (t, 2H, CH₂), 3.1 (t, 2H, CH₂).

3.2 2-Amino-3-cyano-4,5-tetramethylenethiophene (19)

Malononitrile (6.68 g, 0.1 mol), cyclohexanone (9.82 g, 0.1 mol), sulfur (3.2 g, 0.1 mol) and ethanol (25 ml) were stirred while diethylamine (10 ml) was added portionwise so the mixture temperature remained below 40 °C; a yellow solid precipitated before completion of the addition. The mixture was stirred for 4 h at 40–50 °C; the mixture was cooled and the solid filtered off. The white solid was recrystallized from an ethyl acetate/ethanol (3:7) mixture; white flakes, yield 89%; m.p. 146–148 °C. Anal. Found: C, 62.02; H, 3.67; N, 15.95. Calc. for C₉H₆N₂S: C, 62.10; H, 3.44; N, 16.08%. $\nu_{\max}$ (KBr/cm⁻¹) 3430, 3330, 3220 (NH), 2210 (CN). ¹H NMR: δ 4.61 (broad s, 2H, NH₂, exchanged with D₂O), 2.50 (m, 4H, 2 × CH₂), 1.81 (m, 4H, 2 × CH₂).

3.3 3-Methyl-3-(thiophen-3-yl)propene-1,1-dicarbonitrile (14)

To a warm solution of 3-acetylthiophene (10 g, 0.079 mol) and malononitrile (5.24 g, 0.079 mol) in ethanol (50 ml), diethylamine (5 ml) was added portionwise and the solution was refluxed for 3 h. After cooling to room temperature the reaction mixture was poured into water (150 ml) containing a few drops of concentrated hydrochloric acid. The precipitated product formed was collected by filtration and washing with a small amount of cooled ethanol (10 ml); yellow crystals, yield 65%; m.p. 187–189 °C. Anal. Found: C, 61.98; H, 3.63; N, 16.11. Calc. for C₉H₆N₂S: C, 62.10; H, 3.44; N, 16.08%. $\nu_{\max}$ (KBr/cm⁻¹) 2210, 2201 (CN). ¹H NMR: δ 7.58 (s, 1H, H-2), 7.48 (d, 1H, *J* = 5.2 Hz, H-5), 7.11 (d, 1H, *J* = 5.1 Hz, H-4), 1.27 (s, 3H, CH₃).

3.4 General procedure for the preparation of dyes 5a–d, 6a–d and 7

To a refluxed solution of FC-CHO (10 mmol) and the active methylene (10 mmol) in ethanol (50 ml), Piperidine (1 ml) was added. After the addition the solution became darker; the reflux was continued for 6 h, then the solution was left to cool to room temperature and the products were precipitated. The precipitates were filtered and washed with cold water and finally with ethanol, dried and recrystallized from ethanol.

3.5 1,1-Dicyanovinyl-2-ferrocene (5a)

Deep-red crystals, yield 50%; m.p. 231–233 °C. Anal. Found: C, 64.06; H, 4.01; N, 10.49. Calc. for $C_{14}H_{10}FeN_2$: C, 64.18; H, 3.82; N, 10.68%. $\nu_{\max}$ (KBr/cm⁻¹) 2185, 2170 (CN), 1630 (C=C), 1101, 992, 814. ¹H NMR: δ 7.70 (s, 1H, —CH=C), 5.01 (broad s, 2H, H-2, H-4, H-5), 4.85 (broad s, 2H, H-2, H-3, H-4), 4.33 (s, 5H, C_5H_5).

3.6 (Z)- 1-Cyano-1-methoxycarbonylvinylferrocene (5b)

Red crystals, yield 89%; m.p. 80–82 °C. Anal. Found: C, 60.88; H, 4.65; N, 4.51. Calc. for $C_{15}H_{13}FeNO_2$: C, 61.07; H, 4.41; N, 4.75%. $\nu_{\max}$ (KBr/cm⁻¹) 2222 (CN), 1730 (C=O), 1600 (C=C), 1105, 990, 815. ¹H NMR: δ 8.20 (s, 1H, —CH=C), 5.04 (broad s, 2H, H-2, H-4, H-5), 4.74 (broad s, 2H, H-2, H-3, H-4), 4.33 (d, 3H, J = 3.5 Hz, CH_3O), 4.27 (s, 5H, C_5H_5).

3.7 1-Cyan-1-[4-tolueyl]vinylferrocene (5c)

Red crystals, yield 88%; m.p. 120–122 °C. Anal. Found: C, 61.05; H, 5.36; N, 4.12. Calc. for $C_{20}H_{17}FeN$: C, 61.19; H, 5.20; N, 4.28%. $\nu_{\max}$ (KBr/cm⁻¹) 2022 (CN), 1615 (C=C), 1100, 997, 811. ¹H NMR: δ 7.49 (d, 2H, J = 8.1 Hz), 7.34 (s, 1H, —CH=C), 7.21 (d, 2H, J = 8.1 Hz), 4.96 (broad s, 2H, H-2, H-4, H-5), 4.52 (broad s, 2H, H-2, H-3, H-4), 4.23 (s, 5H, C_5H_5), 2.37 (s, 3H, CH_3).

3.8 1-Cyano-1-[2-benzoimidazolyl]vinylferrocene (5d)

Dark-red crystals, yield 55%; m.p. >300 °C. Anal. Found: C, 67.87; H, 4.52; N, 11.75. Calc. for $C_{20}H_{15}FeN_3$: C, 68.04; H, 4.25; N, 11.90%. $\nu_{\max}$ (KBr/cm⁻¹) 3100 (NH), 2220 (CN), 1585 (C=C), 1100, 990, 815. ¹H NMR: δ 9.69 (broad s, 1H, exchange with D_2O , NH), 8.39 (s, 1H, —CH=C), 7.87 (broad s, 1H, H-4 benzoimidazolyl), 7.57 (broad s, 1H, H-6 benzoimidazolyl), 7.29 (broad s, 2H, H-5, H-7 benzoimidazolyl), 5.01 (broad s, 2H, H-2, H-4, H-5), 4.68 (broad s, 2H, H-2, H-3, H-4), 4.27 (s, 5H, C_5H_5).

3.9 5-Ferrocenylidenebarbituric acid (6a)

Deep-blue crystals, yield 71%; m.p. 240–242 °C. Anal. Found: C, 55.32; H, 3.91; N, 8.46. Calc. for $C_{15}H_{12}FeN_2O_3$: C, 55.60; H, 3.70; N, 8.64%. $\nu_{\max}$ (KBr/cm⁻¹) 3220 (NH), 1760, 1670 (C=O), 1580 (C=C), 1100, 996, 810. ¹H NMR: δ 8.47 (s, 1H, —CH=C), 5.99 (broad s, 2H, exchange with D_2O , 2 $\times$ NH), 5.34 (broad s, 2H, H-2, H-4, H-5), 5.00 (broad s, 2H, H-2, H-3, H-4), 4.30 (s, 5H, C_5H_5).

3.10 5-Ferrocenylidene(1,3-dimethylbarbituric acid) (6b)

Deep-blue crystals, yield 64%; m.p. 212–214 °C. Anal. Found: C, 57.83; H, 4.72; N, 7.71. Calc. for $C_{17}H_{16}FeN_2O_3$: C, 58.00; H, 4.55; N, 7.95%. $\nu_{\max}$ (KBr/cm⁻¹) 1725, 1660 (C=O), 1565 (C=C), 1103, 992, 810. ¹H NMR: δ 8.45 (s, 1H, —CH=C), 5.32 (broad s, 2H, H-2, H-4, H-5), 4.90 (broad s, 2H, H-2, H-3, H-4), 4.27 (s, 5H, C_5H_5), 3.40 (s, 3H, CH_3N), 3.37 (s, 3H, CH_3N).

3.11 5-Ferrocenylidenethiobarbituric acid (6c)

Deep-blue crystals, yield 66%; m.p. > 300 °C. Anal. Found: C, 52.83; H, 3.4; N, 8.01. Calc. for $C_{15}H_{12}FeN_2O_2S$: C, 52.98; H, 3.52; N, 8.24%. $\nu_{\max}$ (KBr/cm⁻¹) 3221 (NH), 1696, 1650 (C=O), 1613 (C=C), 1115 (C=S), 1107, 994, 811. ¹H NMR: δ 8.48 (s, 1H, —CH=C), 5.38 (broad s, 2H, H-2, H-4, H-5), 5.08 (broad s, 2H, H-2, H-3, H-4), 4.33 (s, 5H, C_5H_5), 3.48, 3.78 (broad, 2H, exchange with D_2O , 2 $\times$ NH).

3.12 5-Ferrocenylidene(1,3-diethylthiobarbituric acid) (6d)

Deep-blue crystals, yield 61%; m.p. 164–166 °C. Anal. Found: C, 57.36; H, 4.88; N, 76.84. Calc. for $C_{19}H_{20}FeN_2O_2S$: C, 57.57; H, 5.05; N, 7.07%. $\nu_{\max}$ (KBr/cm⁻¹) 1680, 1660 (C=O), 1620 (C=C), 1115 (C=S), 1101, 992, 809. ¹H NMR: δ 8.46 (s, 1H, —CH=C), 5.36 (broad s, 2H, H-2, H-4, H-5), 4.97 (broad s, 2H, H-2, H-3, H-4), 4.31 (s, 5H, C_5H_5), 4.31 (q, 4H, CH_2N), 1.32 (t, 6H, CH_3CH_2N).

3.13 (E)-4-(2-Ferrocenylvinyl)-1-methylpyridinium iodide (7)

Red crystals, yield 55%; m.p. 160–162 °C. Anal.

Found: C, 49.87; H, 4.26; N, 3.12. Calc. for $C_{18}H_{18}FeIN$: C, 50.17; H, 4.18; N, 3.25%. $\nu_{\max}$ (KBr/cm $^{-1}$) 1600 (C=C), 1102, 991, 810. 1H NMR: δ 9.95 (broad s, 1H), 9.12 (broad s, 2H), 7.87 (s, 1H, —CH=C), 4.80 (broad s, 2H, H-2, H-4, H-5), 4.62 (broad s, 2H, H-2, H-3, H-4), 4.28 (s, 5H, C_5H_5).

3.14 4-Ferrocenylidene(3-methyl-1-phenylpyrazolon-2-one) (8)

Dark-red crystals, yield 53%; m.p. > 300 °C. Anal. Found: C, 68.35; H, 4.65; N, 7.41. Calc. for $C_{21}H_{18}FeN_2O$: C, 68.15; H, 4.86; N, 7.57%. $\nu_{\max}$ (KBr/cm $^{-1}$) 1620 (C=C), 1108, 996, 812. 1H NMR: δ 7.87 (s, 1H, —CH=C), 7.48 (m, 5H, aromatic protons), 4.80 (broad s, 2H, H-2, H-4, H-5), 4.62 (broad s, 2H, H-2, H-3, H-4), 4.20 (s, 5H, C_5H_5), 1.9 (s, 3H, CH_3).

3.15 2-Ferrocenylideneindan-1,3-dione (9)

Dark-blue crystals, yield 85%; m.p. 221–223 °C. Anal. Found: C, 70.06; H, 3.92. Calc. for $C_{20}H_{14}FeO_2$: C, 70.22; H, 4.09%. $\nu_{\max}$ (KBr/cm $^{-1}$) 1685 (C=O), 1601 (C=C), 1100, 996, 815. 1H NMR: δ 7.90 (d, 2H, $J = 3.74$ Hz, H-4, H-7), 7.77 (d, 2H, $J = 3.74$ Hz, H-4, H-6), 7.88 (s, 1H, —CH=C), 5.44 (broad s, 2H, H-2, H-4, H-5), 4.85 (broad s, 2H, H-2, H-3, H-4), 4.20 (s, 5H, C_5H_5).

3.16 General procedure for the preparation of chalcones 10a, 10b, 11, 12a and 12b

To a well-stirred solution of Fc-CHO (10 mmol) and the appropriate ketone (10 mmol) in ethanol (30 ml) was added dropwise a solution of NaOH (30 ml, 10%) at 60 °C over a period of 20 min. After the addition was completed the solution was left to stir at room temperature for 12 h, then poured into ice-cold water (200 ml) and stirred for 2 h. The precipitated chalcone was filtered off and washed with copious amounts of water until the wash was neutral; then it was washed with cold ethanol and dried. The solid products were recrystallized from ethanol.

3.17 2-Ferrocenylidene(1-indanone) (10a)

Dark-red crystals, yield 98%; m.p. 160–162 °C. Anal. Found: C, 72.98; H, 4.63. Calc. for

$C_{20}H_{16}FeO$: C, 73.22; H, 4.88%. $\nu_{\max}$ (KBr/cm $^{-1}$) 1690 (C=O), 1640 (C=C), 1108, 995, 815. 1H NMR: δ 7.91 (d, 1H, $J = 7.5$ Hz, H-7), (d, 1H, $J = 7.5$ Hz, H-6), 7.56 (d, 1H, $J = 7.4$ Hz, H-4), 7.42 (dd, 1H, $J_{54} = J_{56} = 7.24$ Hz, H-5), 7.60 (s, 1H, —CH=C), 4.67 (broad s, 2H, H-2, H-4, H-5), 4.52 (broad s, 2H, H-2, H-3, H-4), 4.17 (s, 5H, C_5H_5).

3.18 2-Ferrocenylidene(1-tetralone) (10b)

Red crystals, yield 70%; m.p. 120–130 °C. Anal. Found: C, 73.58; H, 5.11. Calc. for $C_{21}H_{18}FeO$: C, 73.67; H, 5.26%. $\nu_{\max}$ (KBr/cm $^{-1}$) 1665 (C=O), 1610 (C=C), 1108, 995, 815. 1H NMR: δ 8.11 (d, 1H, $J = 7.6$ Hz, H-8), 7.47 (d, 1H, $J_{76} = 7.5$, $J_{78} = 14$ Hz, H-7), 7.36 (dd, 1H, $J_{65} = 7.8$, $J_{67} = 15.7$ Hz, H-6), 7.26 (dd, 1H, $J = 6.5$ Hz, H-5), 7.70 (s, 1H, —CH=C), 4.57 (broad s, 2H, H-2, H-4, H-5), 4.45 (broad s, 2H, H-2, H-3, H-4), 4.18 (s, 5H, C_5H_5).

3.19 3-Ferrocenyl-1-(3-thienyl)propenone (11)

Red crystals, yield 93%; m.p. 135–137 °C. Anal. Found: C, 63.23; H, 4.28. Calc. for $C_{17}H_{14}FeOS$: C, 63.40; H, 4.35%. $\nu_{\max}$ (KBr/cm $^{-1}$) 1655 (C=O), 1590 (C=C), 1101, 992, 815. 1H NMR: δ 8.11 (broad s, 1H), 7.76 (s, 1H, —CH=C), 7.65 (broad s, 1H), 7.36 (broad s, 1H), 6.99 (d, 1H, $J = 15.14$ Hz, C=CH—C=O), 4.59 (broad s, 2H, H-2, H-4, H-5), 4.49 (broad s, 2H, H-2, H-3, H-4), 4.18 (s, 5H, C_5H_5).

3.20 2,5-Diferrocenylidenecyclopentanone (12a)

This compound was prepared as described for **10a** except that two molar equivalents of Fc-CHO were used.

Dark-red crystals, yield 77%; m.p. 200–202 °C. Anal. Found: C, 68.25; H, 4.91. Calc. for $C_{27}H_{24}Fe_2O$: C, 68.13; H, 5.04%. $\nu_{\max}$ (KBr/cm $^{-1}$) 1690 (C=O), 1625, 1610 (C=C), 1110, 990, 813. 1H NMR: δ 7.44 (s, 1H, —CH=C), 4.60 (broad s, 2H, H-2, H-4, H-5), 4.51 (broad s, 2H, H-2, H-3, H-4), 4.17 (s, 5H, C_5H_5), 2.81 (broad s, 4H, $2 \times CH_2$).

3.21 2,6-Diferrocenyldenecyclohexanone (12b)

This compound was prepared as described for **10a** except that two molar equivalents of Fc-CHO were used.

Red crystals, yield 55%; m.p. 150–152 °C. Anal. Found: C, 68.58; H, 5.18. Calc. for $C_{28}H_{26}Fe_2O$ C, 68.63; H, 5.31%. $\nu_{\max}$ (KBr/cm⁻¹) 1665 (C=O), 1605 (C=C), 1105, 996, 811. ¹H NMR: δ 7.26 (s, 1H, —CH=C), 4.55 (broad s, 2H, H-2, H4, H-5), 4.43 (broad s, 2H, H-2, H3, H-4), 4.17 (s, 5H, C₅H₅), 2.73 (broad s, 4H, 2 × CH₂-3, 5), 1.83 (broad s, 2H, CH₂-4).

3.22 Ferrocenyl-2-(thiophen-3-yl)buta-1,3-diene-1,1-dicarbonitrile (13)

Fc-CHO (0.5 g, 2.34 mmol) and 3-thienylethylidenemalononitrile **14** (0.41 g, 2.34 mmol) were refluxed in dry toluene before diethylamine (0.17 g, 2.34 mmol) was added; the reaction mixture was refluxed for 6 h, then cooled to room temperature and the toluene was evaporated under reduced pressure. The product was chromatographed on silica gel using a chloroform/petroleum ether (4:1) mixture, to give dye **13** as dark-black crystals, 88%, m.p. 150 °C. Anal. Found: C, 64.53; H, 3.82, N, 7.32. Calc. for $C_{20}H_{15}FeN_2S$ C, 64.74; H, 4.04; N, 7.55%. $\nu_{\max}$ (KBr/cm⁻¹) 2219 (CN), 1625 (C=C), 1101, 993, 810. ¹H NMR: δ 8.11 (broad s, 1H), 7.71 (s, 1H, —CH=C), 7.41 (broad s, 1H), 7.11 (broad s, 1H), 7.00 (broad s, 1H), 4.98 (broad s, 2H, H-2, H4, H-5), 4.61 (broad s, 2H, H-2, H3, H-4), 4.17 (s, 5H, C₅H₅).

3.23 2-Ferrocenyldiene-1-dicyanomethyleneindan (16)

A mixture of Fc-CHO (0.85 g, 3.97 mmol) and 1-dicyanomethyleneindane (**15**) (0.71 g, 3.97 mmol) in dry tetrahydrofuran (25 ml) was stirred at room temperature for 10 min, then diethylamine (0.29 g, 3.97 mmol) was added. The reaction mixture was stirred for another 3 h at room temperature. The reaction mixture was poured into crushed ice (50 g) and the separated solid dye was collected and recrystallized from a dichloromethane–toluene mixture. Black crystals, yield 60%; m.p. 280 °C. Anal. Found: C, 73.11; H, 4.38; N, 7.21. Calc. for $C_{23}H_{17}FeN_2$: C, 73.26; H, 4.51; N, 7.42%. $\nu_{\max}$ (KBr/cm⁻¹) 2219 (CN), 1605, 1585 (C=C), 1110,

997, 819. ¹H NMR: δ 8.01 (s, 1H, —CH=C), 7.1–7.91 (m, 4H, aromatic protons), 4.41 (broad s, 2H, H-2, H4, H-5), 4.32 (broad s, 2H, H-2, H3, H-4), 4.11 (s, 5H, C₅H₅), 3.5 (broad s, 4H, CH₂).

3.24 General procedure for the preparation of Schiff bases **17** and **18**

A solution of Fc-CHO (10 mmol) and the amine (10 mmol) in ethanol (30 ml) was refluxed for 5 h. The precipitated products that formed on cooling to room temperature were filtered and washed with ethanol (3 × 15 ml) and dried. The solids obtained were recrystallized from ethanol.

3.25 3-Cyano-2-ferrocenyliminomethyl-4,5-tetramethylenethiophene (17)

Dark-red crystals, 81%; m.p. 150 °C. Anal. Found: C, 64.14; H, 4.93; N, 7.35. Calc. for $C_{20}H_{18}FeN_2S$: C, 64.22; H, 4.81; N, 7.49%. $\nu_{\max}$ (KBr/cm⁻¹) 2219 (CN), 1627 (C=N), 1100, 997, 820. ¹H NMR: δ 8.38 (s, 1H, —CH=N), 4.85 (broad s, 2H, H-2, H4, H-5), 4.59 (broad s, 2H, H-2, H3, H-4), 4.26 (s, 5H, C₅H₅), 2.66 (broad s, 4H, 2 × CH₂), 1.86 (broad s, 4H, 2 × CH₂).

3.26 4-Ferrocenyliminomethyl-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (18)

Black powder, 88%; m.p. 288 °C. Anal. Found: C, 68.13; H, 5.36; N, 10.32. Calc. for $C_{22}H_{21}FeN_3O$: C, 68.21; H, 5.26; N, 10.52%. $\nu_{\max}$ (KBr/cm⁻¹) 1665 (C=O), 1616 (C=N), 1110, 1000, 831. ¹H NMR: δ 9.96 (s, 1H, —CH=N), 7.69 (m, 5H, aromatic protons), 4.80 (broad s, 2H, H-2, H4, H-5), 4.62 (broad s, 2H, H-2, H3, H-4), 4.28 (s, 5H, C₅H₅), 4.12 (s, 3H, CH₃N), 2.18 (s, 3H, CH₃ C=C).

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