

Negative Solvatochromism of Ferrocenyl Methine Dyes

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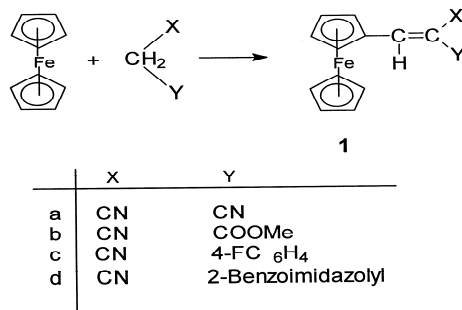
Abstract. A novel solvatochromic ferrocenyl methine dyes has been synthesized by condensation of ferrocen-3-carboxaldehyde with active methylene compounds under Knoevengel conditions and characterized by UV-*vis* in a range of solvents. Compound 1a has a red shift in π - π^* and a blue shift increases with solvent polarity in the MLCT (M \rightarrow A) while 1b-1d variation of red as well as blue shifts from both states. No d-d transition is observed in these compounds. These shifts are interpreted by different dipole moments in the ground and excited state as well as solvent interaction between solute/solvent and H-bonding with the acceptor.

Introduction

We reported the preparation and characterization of new ferrocenyl-based methines with an end capped with different electron-withdrawing groups^[1-3]. Here, we report the synthesis of ferrocenyl methine dyes by the condensation of ferrocen-3-carboxaldehyde with active methylene compounds under Knoevengel conditions to afford a new methine dyes with absorption maximum in the visible region (Scheme 1).

The interest in the use of blue shift organic and organometallic molecules for Second Order Non-Linear Optical (SONLO) devices prompted us to study the electronic structure of these ferrocenyl methines. Solvatochromic effects may give an indication of the magnitude expected for nonlinear optical properties since it reflects the polarizability of a chromophore^[4-6]. The absorption maximum measured in solvents of increasing polarity is given in Table 1. Figure 1 shows MLCT for the four compounds in different solvents (Toluene,

(THF, CHCl₃, acetone and ethanol) while Fig. 2 represents the effect of these solvents for 1a.



Scheme 1

Table 1. Absorption spectral data of methine dyes 1a-1d in various solvents.

Dye #	λ_{max}											
	Toulene (33.9)*		THF (37.4)		CH ₃ Cl (39.1)		Acetone (42.2)		EtOH (51.9)			
	$\pi \rightarrow \pi^*$	MLCT	$\Pi^* \rightarrow \pi$	MLCT	$\pi^* \rightarrow \pi$	MLCT	$\pi \rightarrow \pi^*$	MLCT	$\pi \rightarrow \pi^*$	MLCT		
1a	325		394		392	531	395	521	392	475	4945	4913
1b	329	515	320	514	322	521	331	517	334	517	10881	2023
1c	343	487	336	488	328	495	334	485	326	486	35000	3715
1d	363	509	358	503	362	518	349	503	357	512	17000	2613

*The solvent parameters E_T in kcal. Mol⁻¹.

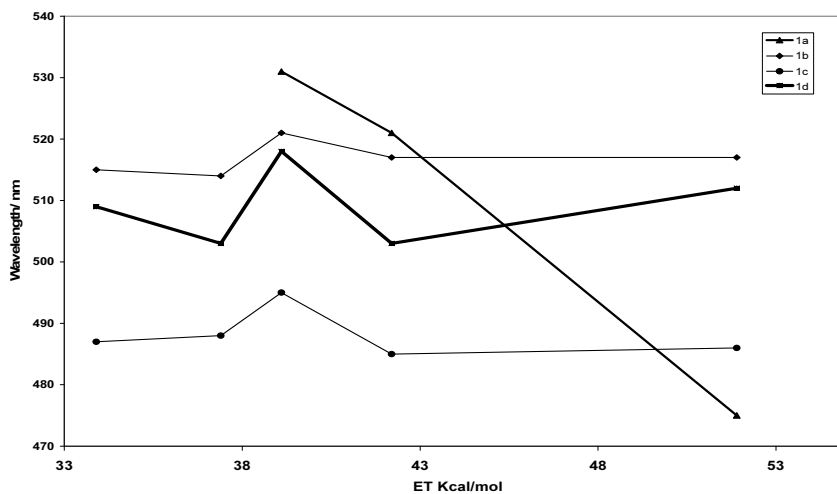


Fig. 1. MLCT transition in different solvents.

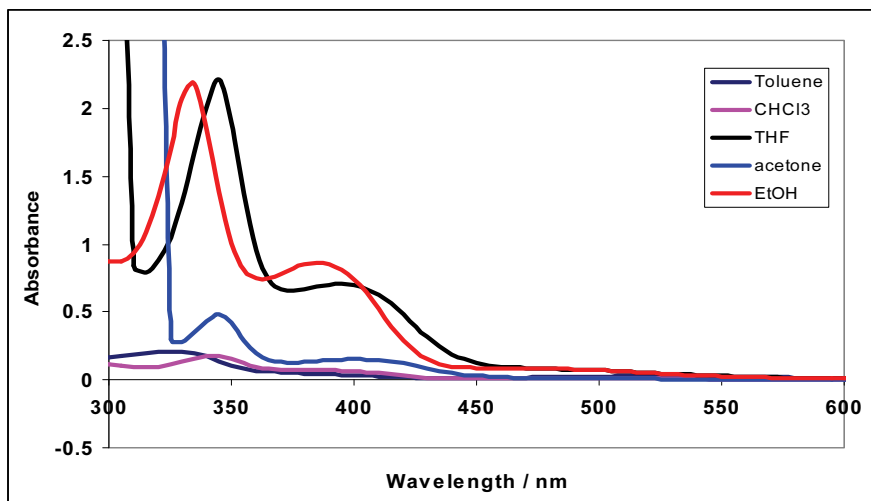
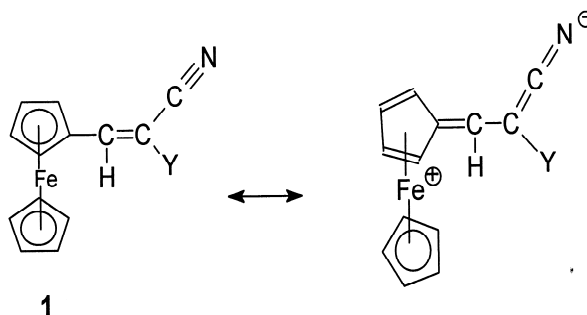


Fig. 2. UV-Vis absorption of 1a in different solvents.

In general, the electronic absorption of these dyes show one band between 325 and 395 nm assigned to π - π^* transition and another one at a longer wavelength between 509-521 nm due to metal-to-ligand charge transfer (MLCT) and no absorption observed for d-d transition unless it is covered by the broad LMCT band. These assignments are based on theoretical results reported by Barlow *et al.*^[3] and other experimental findings^[7-10]. The two bands are strongly influenced by the nature of the acceptor group as well as by the polarity of the solvent. The band from π - π^* transition for 1a showed a red shift on increasing the solvent polarity (δ 70 nm), but the shift is not linear with the solvent polarity indicating that the mesomeric form (Scheme 2) lowers the energy of the π^* orbital and the difference in dipole moment between ground and excited is small. However, the lower energy band from MLCT, unlike π - π^* , showed a clear dependence on the nature of solvent polarity with maximum δ 56 nm blue shifted. These different shifts are not attributed to the solvent polarity alone, but to the interaction of the solute/solvent and the nature of hydrogen bonding ability between solvent/dye as well. From the large shifts observed for 1a, we conclude that it has larger polarizability compared with 1b-1d due cyano electron withdrawing groups. The negative bathochromic shift is certainly due to opposite in sign between the dipole moments of the ground and excited states^[3]. Compounds 1b-1d showed red as well as blue shift from both transition (π - π^* and MLCT).

It can be attributed to weak acceptor groups replacing the cyano moiety and also the small dipole moment difference between ground and excited states and with opposite signs.



Scheme 2

Experimental

General Procedure

Typical procedure for the synthesis of dyes 1a-1d: To a refluxed solution of ferrocenecarboxaldehyde (10ml) and the active methylene (10 ml) in ethanol (50ml), piperidine (1ml) was added. After the addition, the solution became darker and the reflux was continued for six hours, then the solution was left to cool to room temperature and the products were precipitated. The precipitate was filtered and washed with cold water and finally with ethanol, dried and recrystallized from the appropriate solvent.

1,1-Dicyanovinyl-2-Ferrocene (1a)

Deep red crystals, yield 50%; m.p. 231-233 °C. Anal. Found; C, 64.02; H, 3.95; N, 10.47. $C_{14}H_{10}N_2Fe$ Cal. C, 64.18; H, 3.82; N, 10.68%. ν_{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, C₅H₅).

(Z)-1-Cyano-1-Methoxycarbonylvinylferrocene (1b)

Red crystals, yield 98%; m.p. 80-82 °C. Anal. Found; C, 60.88; H, 4.65; N, 4.51. $C_{15}H_{13}O_2NFe$ Calc.: C, 61.07; H, 4.41; N, 4.75 %. ν_{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, H4, H-5), 4.74 (broad s, 2H, H-2, H3, H-4), 4.33 (d, 3H, *J* = 3.5 Hz, CH₃O), 4.27 (s, 5H, C₅H₅).

1-Cyan-1-[4-Toluy] Vinylferrocene (1c)

Red crystals, yield 88%; m.p. 120-122°C. Anal. Found; C, 61.05; H, 5.36; N, 4.12. C₂₀H₁₇NFe Calc.: C, 61.19; H, 5.20; N, 4.28 %. v_{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, H4, H-5), 4.52 (broad s, 2H, H-2, H3, H-4), 4.23 (s, 5H, C₅H₅), 2.37 (s, 3H, CH₃).

1-Cyano-1-[2-Benzoimidazolyl] Vinylferrocene (1d)

Dark red crystals, yield 55%; m.p. >300°C. Anal. Found; C, 67.87; H, 4.52; N, 11.75. C₂₀H₁₅N₃Fe Calc.: C, 68.04; H, 4.25; N, 11.90%. v_{max} (KBr/cm⁻¹) 3100 (NH), 2220 (CN), 1585 (C=C), 1100, 990, 815. ¹H-NMR: δ 9.69 broad s, 1H, exchange with D₂O, (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, H4, H-5), 4.68 (broad s, 2H, H-2, H3, H-4), 4.27 (s, 5H, C₅H₅).

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تأثير مذيّب سلبي لأصباغ الميثان المشتقة من الفروسين

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المملكة العربية السعودية

المستخلص. لوحظ أثر مذيّب سلبي لأصباغ الميثان المشتقة من الفروسين، والمحضرة بتكاثف ألدهيد الفروسين مع مركبات الميثيلين النشطة تحت ظروف تكاثف كروفيناغل. وقد تم توصيف المركبات ودراستها بطيف الأشعة فوق البنفسجية والمرئية في مذيّبات مختلفة. أبدى المركب 1a إزاحة حمراء في قمة الامتصاص في المجال غير المرئي و إزاحة زرقاء للقمة المتمركزة في المجال المرئي، وتزداد الإزاحة بزيادة قطبية المذيّب. بينما المركبات الأخرى 1b-1d لها إزاحة حمراء وإزاحات زرقاء. ويعزى السبب في الأثر السلبي للمذيّب على هذه المركبات، إلى الاختلاف في العزم القطبي للحالة الأرضية والمثارة، وإلى تداخل المذيّب مع المذاب، وكذلك الروابط الهيدروجينية للمستقبل.