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 $\pi-\pi^*$ 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](image)

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

<table>
<thead>
<tr>
<th>Dye #</th>
<th>Toluene (33.9)</th>
<th>THF (37.4)</th>
<th>CHCl₃ (39.1)</th>
<th>Acetone (42.2)</th>
<th>EtOH (51.9)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \pi \rightarrow \pi^* ) MLCT</td>
<td>( \pi^* \rightarrow \pi ) MLCT</td>
<td>( \pi \rightarrow \pi^* ) MLCT</td>
<td>( \pi \rightarrow \pi^* ) MLCT</td>
<td>( \pi \rightarrow \pi^* ) MLCT</td>
</tr>
<tr>
<td>1a</td>
<td>325</td>
<td>394</td>
<td>392</td>
<td>395</td>
<td>392</td>
</tr>
<tr>
<td>1b</td>
<td>329</td>
<td>515</td>
<td>320</td>
<td>514</td>
<td>322</td>
</tr>
<tr>
<td>1c</td>
<td>343</td>
<td>487</td>
<td>336</td>
<td>488</td>
<td>328</td>
</tr>
<tr>
<td>1d</td>
<td>363</td>
<td>509</td>
<td>358</td>
<td>503</td>
<td>362</td>
</tr>
</tbody>
</table>

*The solvent parameters \( E_T \) in kcal. Mol\(^{-1}\).*

![Fig. 1. MLCT transition in different solvents.](image)
In general, the electronic absorption of these dyes show one band between 325 and 395 nm assigned to $\pi-\pi^*$ 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.\textsuperscript{[3]} and other experimental findings\textsuperscript{[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 $\pi-\pi^*$ transition for 1a showed a red shit 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 $\pi^*$orbital and the difference in dipole moment between ground and excited is small. However, the lower energy band from MLCT, unlike $\pi-\pi^*$, 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\textsuperscript{[3]}. Compounds 1b-1d showed red as well as blue shift from both transition ($\pi-\pi^*$ 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](image)

**Experimental**

**General Procedure**

Typical procedure for the synthesis of dyes 1a-1d: To a refluxed solution of ferrocenecaboxaldehyde (10ml) and the active methylene (10 ml) in ethanol (50ml), piperdine (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 were 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_{2}Fe Cal. C, 64.18; H, 3.82; N, 10.68% v_{max} (KBr/cm^{-1}) 2185, 2170 (CN), 1630 (C=C), 1101, 992, 814. ^{1}H-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, H3, 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_{2}NFe Cal.: C, 61.07; H, 4.41; N, 4.75 %. v_{max}
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(KBr/cm\(^{-1}\)) 2222 (CN), 1730 (C=O), 1600 (C=C), 1105, 990, 815. \(\text{^1H-NMR: } \delta \) 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, \(J = 3.5 \text{ Hz} \), CH3O), 4.27 (s, 5H, C\(_5\)H\(_5\)).

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

Red crystals, yield 88%; m.p. 120-122°C. Anal. Found; C, 61.05; H, 5.36; N, 4.12. C\(_{20}\)H\(_{17}\)NFe Calc.: C, 61.19; H, 5.20; N, 4.28 %. \(\nu_{\text{max}}\) (KBr/cm\(^{-1}\)) 2022 (CN), 1615 (C=C), 1100, 997, 811. \(\text{^1H-NMR: } \delta \) 7.49 (d, 2H, \(J = 8.1 \text{ Hz} \)), 7.34 (s, 1H, -CH=C), 7.21 (d, 2H, \(J = 8.1 \text{ Hz} \)), 4.96 (broad s, 2H, H-2, H4, H-5), 4.52 (broad s, 2H, H-2, H3, H-4), 4.23 (s, 5H, C\(_5\)H\(_5\)), 2.37 (s, 3H, CH\(_3\)).

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

Dark red crystals, yield 55%; m.p. >300°C. Anal. Found; C, 67.87; H, 4.52; N, 11.75. C\(_{20}\)H\(_{15}\)N\(_3\)Fe Calc.: C, 68.04; H, 4.25; N, 11.90%. \(\nu_{\text{max}}\) (KBr/cm\(^{-1}\)) 3100 (NH), 2220 (CN), 1585 (C=C), 1100, 990, 815. \(\text{^1H-NMR: } \delta \) 9.69 broad s, 1H, exchange with D\(_2\)O, 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, C\(_5\)H\(_5\)).

References

تأثير مذيب سلبي لأصباغ الميثان المشتقة من الفروسين

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المستخلص. لوحظ أن مذيب سلبي لأصباغ الميثان المشتقة من الفروسين، والمحضرة بتكاثف أندلود الفروسين مع مركبات الميثيلين النشطة تحت ظروف تكاثف كونفيها، وقد تم توصيف المركبات ودراستها بطيء الأشعة فوق البنفسجية والمرئية في مذيبات مختلفة. أُصدر المركب 1a إزاحة حمراء في قمة الامتصاص في المجال غير المرئي وإزاحة زرقاء للقمة المتمركزة في المجال المرئي، وتزداد الإزاحة بزيادة قطبية المذيب. بينما المركبات الأخرى 11b-1d لها إزاحة حمراء وإزاحت زرقاء. ويعزو السبب في الأثر السلبي للمذيب على هذه المركبات، إلى الاختلاف في القيم القطبي للحالة الأرضية والمثارة، والتدخل المذيب مع المذاب، وكذلك الروابط الهيدروجينية للمستقبل.