Summary

Small functional chromophores are of great importance due to their wide range of applications and are characterized by ease in synthesis and functionalization. Such molecules with inherent “push-pull” character are capable of showing intramolecular charge-transfer (ICT) based functions as well as high second-order nonlinear optical (NLO) behaviour. The latter is of great significance for applications related to telecommunications, optical computing, data storage and information processing. Compared to inorganic counterparts initially employed as NLO materials, the organic materials gained significance due to the architectural flexibility, low cost synthesis and fabrication and ease in fabrication. Organometallic chromophores have attained unique distinction as a consequence of many attractive properties typical of the presence of a “metal centre” possessing polarizable d-electrons and the accompanied diversity of oxidation states. In this investigation, our aim was to synthesize new “push-pull” chromophores of different donor-π-acceptor (D–π–A) designs using ferrocene as a donor unit. In most of these designs, the ICT was influenced by varying the donor and/or acceptor strengths as well as by using intervening π-bridge of variable length. The NLO behaviour of these chromophores has been studied as well as interesting structure-property relationships have been deduced by correlating electronic absorption spectroscopic data with electrochemical as well as theoretical studies. In addition, we have developed the use of ferrocene based representative D–π–A systems for recognition of different analytes, an aspect which is otherwise dominated by organic receptors and is comparatively underappreciated with organometallic compounds. Specifically, in this part of the investigation, we have utilized cyclic voltammetry as an additional channel to corroborate the spectroscopic changes realized upon analyte recognition. We believe that the results obtained in this investigation would significantly add to the existing knowledge of these areas of investigation. The results have been presented in the form of five chapters. While the first chapter of the thesis presents a brief introduction, the contents of the remaining chapters is summarized below.

Chapter 2 Review of literature

In this chapter, a preliminary introduction to nonlinear optics is followed by description of fundamental requirements for different organic and organometallic materials
to show NLO behaviour. A detailed discussion on the NLO behaviour of ferrocene (ferrocene–π–acceptor) based chromophores follows in most of the remaining part. In view of limited reviews available on the subject, in this chapter, we have tried to compile all known ferrocene–π–acceptor based chromophores and the associated second-order NLO behaviour reported till date.

Chapter 3 *Nonlinear optical response of ferrocene based donor–π–acceptor “push-pull” chromophores*

In this Chapter, synthesis of different designs (Figure 1) of ferrocene–π–acceptor chromophores, employing differently substituted donor, acceptor and the intervening π-bridge are reported. This is followed by the evaluation of their linear, nonlinear and electrochemical properties. All the studies were well supported by theoretical calculations carried out using Gaussian 09 software.

**Figure 1.** Structures of chromophores. Group A: ferrocene–π–acceptor; Group B: ferrocene–π/extended π-acceptor; Group C: Acceptor–π–ferrocene–π–acceptor.
Summary

Three groups of chromophores (Figure 1) have been studied in this investigation. Section 3.2 of the thesis presents the synthesis and characterization of all these chromophores. Group A represents ferrocene–π–acceptor type chromophores, while, Groups B and C contain, respectively, ferrocene–π/extended–π–acceptor and acceptor–π–ferrocene–π–acceptor type chromophores. Thus, nine chromophores (1-9) equipped with different acceptors, π-bridge and substitution pattern on ferrocene were selected for the evaluation of linear, NLO, electrochemical properties which were additionally corroborated with theoretical investigations. This set of chromophores constituted an excellent set of chromophores for deducing structure-property relationships as briefly summarized below.

UV-visible absorption spectra of the chromophores 1-4 displayed a weak low energy (LE) peak in the region 455-505 nm, ascribed to the metal-to-ligand charge-transfer (MLCT) along with an intense high energy (HE) band in the region 320-400 nm, attributed to the \( \pi \rightarrow \pi^* \) transition (Figure 2a, Table 1).

![Figure 2](image_url)

**Figure 2.** (a) UV-visible spectra of the chromophores 1-4 in DCM (2.8 \( \times \) 10^{-5} M); (b) B3LYP/6-31G predicted energy level diagram for the chromophores 1-3, where blue and red lines depict the energies of the contributing HOMO (H) and LUMO (L) orbitals, respectively.

The UV-visible absorption bands of the chromophores 1-3 (4 was not included, as it could not be optimized) were rationalized by carrying out time-dependent density functional theory (TD-DFT) calculations on the optimized structures of the chromophores in solvent phase (DCM). The computed data depicted high intensity transitions at 3.78 (327.36 nm), 3.08 (402.29 nm) and 3.23 (383.62 nm) eV for the chromophores 1-3 and showed good agreement with the experimental data (Table 1). The HE bands of the chromophores 1-3...
Chapter 5

corresponds to the transitions between H-2→L and is assigned as \( \pi \rightarrow \pi^* \) transition on the basis of visualisation of the electron density of the frontier molecular orbitals (FMO). Wherein, considerable electron density was located on the \( \pi \)-bridge in H-2, while, the electron density in the L orbitals is mainly localized on the \( \pi \)-bridge and/or thiophene (Figures 3-5). Further, the TD-DFT data revealed the LE bands of 1-3 to be originating from H→L transitions computed with the energies 3.56 (348.17 nm) eV, 2.69 (459.27 nm) and 2.84 (435.09 nm) eV. The contributing H→L (1) and H→L+2 (2 and 3) could be best described as MLCT transitions owing to the fact that the H frontier molecular orbitals of these transitions have considerable electron density localized on the ferrocene unit, while the L or L+2 (in case of 1) have electron density on the acceptor part (Figures 3-5). However, the LE of chromophore 1 possess additional contribution from H→L+2 (Table 1) with energy 2.72 (348.17 nm) eV, conferring it d-d character in addition to the MLCT character.

Table 1. HE and LE absorption bands of 1-4 (in DCM) and corresponding selected data of electronic transitions in 1-3 calculated by TD-DFT calculations using B3LYP/6-31G method with solvent effects (DCM).

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>HE ( \lambda_{\text{exp}}/\varepsilon ) ( (\lambda_{\text{calc}}/f) )</th>
<th>Main contribution (assignment)</th>
<th>LE ( \lambda_{\text{exp}}/\varepsilon ) ( (\lambda_{\text{calc}}/f) )</th>
<th>Main contribution (assignment)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>324/23133</td>
<td>H-2→L (( \pi \rightarrow \pi^* ))</td>
<td>456/1449</td>
<td>H→L (M→L)</td>
</tr>
<tr>
<td></td>
<td>(327.36/0.5218)</td>
<td></td>
<td>(348.17/0.3878)</td>
<td>H→L+2 (d-d)</td>
</tr>
<tr>
<td>2</td>
<td>371/35449</td>
<td>H-2→L (( \pi \rightarrow \pi^* ))</td>
<td>501/7193</td>
<td>H→L (M→L)</td>
</tr>
<tr>
<td></td>
<td>(402.29/0.6425)</td>
<td></td>
<td>(459.27/0.1381)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>347/21716</td>
<td>H-2→L (( \pi \rightarrow \pi^* ))</td>
<td>485/2953</td>
<td>H→L (M→L)</td>
</tr>
<tr>
<td></td>
<td>(383.62/0.5274)</td>
<td></td>
<td>(435.09/0.1310)</td>
<td></td>
</tr>
<tr>
<td>4*</td>
<td>396/18334</td>
<td>( \pi \rightarrow \pi^* )</td>
<td>503/4661</td>
<td>M→L</td>
</tr>
<tr>
<td></td>
<td>351/23232</td>
<td>( \pi \rightarrow \pi^* )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\*Theoretical data for chromophore 4 is not included as it could not be optimized.

Probing the effect of the electron withdrawing substituents on the thiophene ring, it could be seen that to obtain 2, 3 and 4 from 1 by altering the acceptor strength, resulted in a considerable red shift in both the HE as well as LE bands of 2 (HE: \( \Delta \lambda = 47 \) nm; LE: \( \Delta \lambda = 45 \) nm), 3 (HE: \( \Delta \lambda = 23 \) nm; LE: \( \Delta \lambda = 29 \) nm) and 4 (HE: \( \Delta \lambda = 72 \) & 27 nm; LE: \( \Delta \lambda = 47 \) nm) as

\* Concentration: \( 2.8 \times 10^{-5} \) M (DCM); \( \lambda \) and \( \varepsilon \) are presented in units nm and M\(^{-1}\)cm\(^{-1}\), respectively; In TD-DFT data \( f \) refer to oscillator strength; calc. - calculated; exp. - experimental.

232
Summary

compared to 1, as shown in table 1 and figure 2a. Comparing 2 and 3, contrary to the expectation that the cyano group in 3 should induce a larger red shift in the absorption band, compared to the formyl derivative 2, the trend is reversed ($\lambda_{\text{max}}$ of HE bands in 2: 371 nm; 3: 347 nm) and is attributed to the relative field strengths of cyano and formyl groups as the p-orbitals in the –C=O group are more available for participation in CT process than in the CN group. These red shifts could be explained upon comparing (Figure 2b) energies of the FMOs of the chromophores 1-3, which showed that the difference in energies between the contributing H and L orbitals (1: $\Delta E = 3.749$ eV > 3: $\Delta E = 3.184$ eV > 2: $\Delta E = 2.943$ eV) followed the same trend as the increasing strength of the acceptor in the order 1 < 3 < 2.

**Figure 3.** The electron density of frontier molecular orbitals of 1 contributing to UV-visible absorption bands (isosurface value = 0.04).

**Figure 4.** The electron density of frontier molecular orbitals of 2 contributing to UV-visible absorption bands (isosurface value = 0.04).

**Figure 5.** The electron density of frontier molecular orbitals of 3 contributing to UV-visible absorption bands (isosurface value = 0.04).

Further, the absorption bands of the chromophores 1-4 depicted a red shift upon increasing the polarity of solvent used to record the spectra. This positive solvatochromism was in general more in the LE bands (max. $\Delta \lambda = 31$ nm in case of 2) as compared to HE bands. The extent of shift ($\Delta \lambda$) in wavelengths of maximum absorption on moving from the
least polar hexane to the most polar DMSO in the chromophores 1-4 followed the trend 2 > 4 > 3 > 1, which is incidentally the trend of increasing acceptor strength also.

Chromophores 1-4 exhibited a reversible one-electron oxidation wave within the range 0.500 to 0.600 V attributed to the ferrocene/ferrocenium redox couple (Figure 6), which was slightly positively shifted as compared to that of ferrocene due to the influence of the acceptor. Upon increasing the strength of the acceptor from 1 to 4, the redox potential showed an anodic shift (1-2: ΔE_{1/2} = 0.072 V; 1-3: ΔE_{1/2} = 0.083 V; 1-4: ΔE_{1/2} = 0.076 V), indicating the increased electronic interaction between ferrocene and the corresponding acceptor owing to the increased strength of the latter, and consequent inhibition in oxidation of relatively electron deficient ferrocene unit of 2, 3 and 4.

![Figure 6](image_url)

**Figure 6.** The cyclic voltammograms of ferrocene and the chromophores 1-4 (1 x 10^{-4} M) in DCM.

The first hyperpolarizability, β, of the chromophores 1-3 was evaluated using the nanosecond hyper-Rayleigh Scattering (HRS) method at 1064 nm (Table 2). The chromophores 4 (unstable in solution) and 1 (poor signal) could not yield β values. However, 2 showed greater β value as compared to 3 (Δβ = 29 x 10^{-30} esu) which could be attributed to the greater acceptor strength of the formyl group than the corresponding cyano group in 3 as deduced from the absorption and electrochemical data. Further, the β values of the chromophores 2 and 3 were resonantly enhanced as their MLCT transitions (λ_{max} of LE bands in 2: 501 nm; 3: 485 nm) lied in close proximity to the second harmonic wavelength (532 nm) of the incident light. The β values are thus corrected for this resonance enhancement (β_{HRS,0}) by using the simple two-level model and are depicted in table 2.

The spectroelectrochemical study of chromophores 1-4, was carried out by recording the UV-visible absorption spectra of the chromophores as a function of the applied potential. The chromophores 2 and 3 could be completely oxidized when oxidation potential was applied for 800 sec, while chromophore 4 took 1440 sec for complete oxidation to the
corresponding ferrocenium species. The completion of the oxidation process was confirmed from the disappearance of the MLCT band, which reappeared upon subsequent reduction of the oxidized species of 2, 3 and 4 for 640 sec, 800 sec and 960 sec, respectively (Figure 7a shows spectroelectrochemical spectrum of 2 as a representative of the Group A chromophores). In contrast to the chromophores 2, 3 and 4, 1 displayed an increase in the intensity of the MLCT band upon application of an oxidation potential for 1120 sec which upon subsequent reduction decreased to retain the original intensity of the MLCT band (Figure 7b). This behaviour provided a further evidence for its LE band to possess d-d character as also evidenced from the TD-DFT calculations.

Table 2. Quadratic nonlinear optical parameters: first hyperpolarizability, $\beta_{HRS}$, first hyperpolarizability corrected for resonance enhancement, $\beta_{HRS,0}$.

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>$\beta_{HRS}$ ($10^{-30}$ esu)</th>
<th>$\beta_{HRS,0}$ ($10^{-30}$ esu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>83±4</td>
<td>7.0±0.5</td>
</tr>
<tr>
<td>3</td>
<td>54±2</td>
<td>7.0±0.5</td>
</tr>
</tbody>
</table>

Figure 7. UV-visible absorption spectra of chromophores (a) 2 and (b) 1, upon sequential electrochemical oxidation and reduction.

In line with the results obtained for the Group A chromophores, section 3.3 describes the results of Group B ferrocene–π/extended–π–acceptor chromophores (5-7). These chromophores were depicted to be stable upto 300 °C with 6 being stable upto 400 °C by thermogravimetric analysis (TGA). In the UV-visible absorption spectra, the LE and HE bands corresponding to MLCT and $\pi\rightarrow\pi^*$ transitions, respectively, were displayed by chromophores 5-7. The additional HE bands observed in the chromophores 5-7 are also
attributed to the $\pi \rightarrow \pi^*$ transitions as a result of the extended $\pi$-conjugation in these systems. The localization of the electron density over the frontier molecular orbitals of the chromophores involved in the transitions led to the assignment of the bands (Table 3).

Table 3. HE and LE absorption bands of 5-7 (in DCM) and their corresponding selected data of electronic transitions calculated by TD-DFT calculations using B3LYP/6-31G method with solvent effects (DCM).

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>HE</th>
<th>LE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda^{\text{exp.}}$ / $\varepsilon$</td>
<td>Main contribution</td>
</tr>
<tr>
<td></td>
<td>($\lambda^{\text{calc.}}$ / $f$)</td>
<td>(assignment)</td>
</tr>
<tr>
<td>5</td>
<td>409/34474 (420.12/0.8114)</td>
<td>H-2$\rightarrow$L ($\pi \rightarrow \pi^*$)</td>
</tr>
<tr>
<td>6</td>
<td>478/48677 (501.92/0.1762)</td>
<td>H$\rightarrow$L+1 ($\pi \rightarrow \pi^*$)</td>
</tr>
<tr>
<td></td>
<td>341/31523 (391.82/0.1030)</td>
<td>H$\rightarrow$L+1 ($\pi \rightarrow \pi^*$)</td>
</tr>
<tr>
<td>7</td>
<td>526/21565 (476.90/0.3714)</td>
<td>H$\rightarrow$L+1 ($\pi \rightarrow \pi^*$)</td>
</tr>
<tr>
<td></td>
<td>396/14726 (331.14/0.1513)</td>
<td>H$\rightarrow$L+1 ($\pi \rightarrow \pi^*$)</td>
</tr>
</tbody>
</table>

Further, in the chromophores 5-7, increasing the length of the $\pi$-bridge from 5$\rightarrow$6$\rightarrow$7 caused a greater red shift ($\Delta \lambda = 69$ nm, 5$\rightarrow$6; $\Delta \lambda = 48$ nm, 6$\rightarrow$7, Figure 8a, see also Table 3) for the HE transition band, while the LE transition appeared as a shoulder at almost identical wavelength of 568 nm (5), 581 nm (6) and 585 nm (7). The red shifts are suggestive of the decreasing H-L energy gap upon elongation of the $\pi$-bridge length ($\Delta E = 0.53$ eV 5 vs 6; $\Delta E = 0.28$ eV 6 vs 7) in the order 5 > 6 > 7 (Figure 8b).

Moreover, an increase in polarity of the solvents from hexane to DMSO led to a significant red shift in the HE ($\Delta \lambda = 23$ nm for 5; $\Delta \lambda = 16$ nm for 6 and $\Delta \lambda = 28$ nm for 7) and LE ($\Delta \lambda = 39$ nm for 5; $\Delta \lambda = 32$ nm for 6 and $\Delta \lambda = 43$ nm for 7) bands. The positive solvatochromism in these three chromophores followed the trend 5 < 6 < 7, which is also the trend of the increasing conjugation length, being maximum for longest chromophore 7 ($\Delta \lambda_{\text{HE}} = 28$ nm; $\Delta \lambda_{\text{LE}} = 43$ nm).

* Kindly see footnote at page no. 233.
Summary

Figure 8. (a) UV-visible absorption spectra of the chromophores 5-7 in DCM (2.8 x 10^{-5} M); (b) B3LYP/6-31G predicted energy level diagram for the chromophores 5-7, where blue and red lines depict the energies of the contributing H and L orbitals, respectively.

The electrochemical studies on 5-7 revealed that increase in the π-bridge conjugation length of the chromophores led to a cathodic shift (5-6: ΔE_{1/2} = 0.085 V; 6-7: ΔE_{1/2} = 0.030 V) in the reversible redox wave of the ferrocene/ferrocenium couple of the respective chromophore (Figure 9). This cathodic shift indicated a decreased electronic interaction between ferrocene unit and the acceptor, as the positive charge tends to stabilize over the longer π-bridge. Again 7, being the largest chromophore, possess the lowest E_{1/2} value.

Figure 9. The cyclic voltammograms of ferrocene and the chromophores 5-7 (1 x 10^{-4} M) in DCM.

The β values of the chromophores 5-7 (measured in DCM, using HRS method at 1300 nm, Table 4) showed a respective 3- and 5-fold increase in β value of 6 and 7, respectively, as compared to 5. The β values were corrected for the resonance enhancement (β_{HRS,0}) by employing the simple two-level model and are tabulated in table 4.
Further, the spectroelectrochemical studies of the chromophores, as described earlier, showed the disappearance of the MLCT band which depicted the conversion of the non-centrosymmetric ferrocene–π–A (D–π–A) systems into the centrosymmetric ferrocenium-π-acceptor (A’–π–A) systems. The $\beta_{HRS}$ and $\beta_{HRS,0}$ of the corresponding oxidized species were found to be lower as compared to the un-oxidized chromophores (Table 4). This was further corroborated from the quadratic curves which showed the ferrocenium-π-acceptor constructs to have lower nonlinearities as compared to the corresponding ferrocene derivatives (Figure 10, quadratic curve of 6 as a representative has been shown as it possess the highest on/off ratio).

![Figure 10. Quadratic curve of 6](image)

As monosubstituted D–π–A chromophores 5-7 are asymmetrically conjugated π-electron systems, these possess large polarizabilities in the direction of their molecular axis $z$. Thus, the largest component of $\beta$ is $\beta_{zzz}$ which has been calculated for this set of chromophores and listed in table 4. Further, the depolarization ratios of the chromophores 5-7 were measured to be 3.0± 0.1 (5), 3.2± 0.1 (6) and 3.0± 0.1 (7) assigning them as one-dimensional “monomeric chromophores”.

* The experimental depolarization ratio of the reference chromophore Disperse Red 1 is 3.2.

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**Table 4. Quadratic nonlinear optical parameters of 5-7.**

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>$\beta_{HRS}$ $(10^{-30} \text{ esu})$</th>
<th>$\beta_{HRS,0}$ $(10^{-30} \text{ esu})$</th>
<th>$\beta_{ox,HRS}$ $(10^{-30} \text{ esu})$</th>
<th>$\beta_{ox,HRS,0}$ $(10^{-30} \text{ esu})$</th>
<th>$\beta_{zzz}$ $(10^{-30} \text{ esu})$</th>
<th>$\rho^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>24± 1</td>
<td>5.0± 0.2</td>
<td>14± 1</td>
<td>2.6± 0.2</td>
<td>60± 2</td>
<td>3.0± 0.1</td>
</tr>
<tr>
<td>6</td>
<td>75± 5</td>
<td>12± 1</td>
<td>3.2± 0.2</td>
<td>0.50± 0.05</td>
<td>180± 10</td>
<td>3.2± 0.1</td>
</tr>
<tr>
<td>7</td>
<td>120± 10</td>
<td>19± 1</td>
<td>10± 1</td>
<td>1.4± 0.1</td>
<td>300± 30</td>
<td>3.0± 0.1</td>
</tr>
</tbody>
</table>
Similarly, section 3.5 discerns the optical, electrochemical, thermogravimetric and theoretical calculations of the disubstituted A–π–ferrocene–π–A chromophores 8 and 9. TGA depicted the chromophores to be stable up to 200 °C. In line with the monosubstituted (1-7) chromophores, the disubstituted 8 and 9 also display the HE and LE bands at wavelength almost similar to those of their monosubstituted counterparts (Figure 11a). In addition to the intense HE bands at 420 nm (8) and 479 nm (9), additional HE bands were observed in the absorption spectrum of chromophores 8 (387 nm and 313 nm) and 9 (328 nm and 352 nm) which could be attributed to π→π* transitions due to extended conjugation. The assignment of the bands was made on the basis of the TD-DFT calculations as described in the case of Group A chromophores. The insertion of thiophene in the π-bridge of 8 to produce 9, (Figure 11a) led to a significant red shift in the HE (Δλ = 59 nm, 8→9) band and the LE (Δλ = 45 nm, 8→9) band. This red shift is a consequence of a small H-L gap of 9 (ΔE = 2.239 eV) as compared to 8 (ΔE = 2.840 eV) (Figure 11b).

**Figure 11.** (a) UV-visible spectra of the chromophores 8 and 9 in DCM (2.8 x 10⁻⁵ M); (b) B3LYP/6-31G predicted energy level diagram for the chromophores 8 and 9, where blue and red lines depict the energies of the contributing H and L orbitals, respectively.

A characteristic feature of the disubstituted chromophores 8 and 9 was the band splitting for one of their HE bands. The split bands of each of 8 (at 387 and 420 nm) and 9 (at 328 and 352 nm) appeared as twin bands (Figure 11a) of approximately similar extinction coefficients. This is a clear spectral fingerprint of the interaction between the two dipolar moieties in a single chromophore. The appearance of twin bands in 8 and 9 is the consequence of small energy difference between the H and L (ΔE = 2.840 eV (8) and 2.239 eV (9), Figure 11b) and H-1 and L+1 ((ΔE = 3.047 eV (8) and 2.442 eV (9), which facilitates the transitions H→L and H-1→L+1. Further, the increase in the solvent polarity led to a
significant bathochromic shifts in the LE (Δλ = 48 nm for 8; Δλ = 53 nm for 9) and HE (Δλ = 27 and 31 nm for 8; Δλ = 20 nm for 9) absorption bands of the chromophores which was larger for longer conjugated 9 as compared to 8.

It was observed that upon increasing the length of the π-bridge conjugation from 8 to 9 by insertion of thiophene rings resulted in a cathodic shift in the reversible redox wave of the chromophores (ΔE_{1/2} = 0.164 V 8→9, Figure 12). This shift is a result of the charge localization over the longer bridge, leading to a decreased electronic communication between the donor and acceptor.

Further, the experimentally determined values of β (HRS, at 1300 nm in DCM) depicted a 2.5 fold increase upon increasing the π-bridge length from 8 (β = 35± 5 x 10^{-30} esu) to 9 (β = 85± 5 x 10^{-30} esu). Similarly β₀ values for 9 are higher as compared to 8. Further, the β values of the oxidized versions show a significant reduction upon oxidation of 8 (Δβ = 10±3 x 10^{-30} esu; Δβ₀ = 2.2 x 10^{-30} esu) and 9 (Δβ = 67±4 x 10^{-30} esu; Δβ₀ = 7.5±0.4 x 10^{-30} esu) indicating the conversion of ferrocene donor (A-π-D-π-A systems) into the corresponding ferrocenium acceptor (A–π–D⁺–π–A⁻ systems). This conversion was substantiated by the disappearance of the MLCT band in the linear optical spectra obtained from spectroelectrochemical studies and the quadratic curves of the oxidized forms of chromophores 8 and 9. In addition, the close proximity lie between the depolarization ratios obtained for 8 and 9 (2.3±0.1, 8 and 2.4±0.1, 9) and the reported value for purely disubstituted chromophores (ρ = 1.5).

In section 3.6 discussion on the structure dependent relationships of the linear, NLO as well as electrochemical behaviour of the chromophores (2-3 and 5) used in this investigation is presented. The bathochromic shift [3→2→5 (Δλ_{HE} = 24 nm; Δλ_{LE} = 16 nm]
for 3→2 and Δλ_{HE} = 38 nm; Δλ_{LE} = 67 nm for 2→5], the lowering of the energy gap between the H and L gap [3 > 2 > 5 (ΔE = 3.184 eV for 3, ΔE = 2.938 eV for 2 and ΔE = 2.823 eV for 5)] and the anodic shift [5 > 2 > 3 (ΔE_{1/2} = 33 mV for 5→2 and ΔE_{1/2} = 4 mV for 2→3)] upon moving from 3→2→5 suggested the order of the strength of the acceptors in these chromophores to follow the trend -CN < -CHO < =C(CN)$_2$ (Table 5). Further, the crystal structures depicted a higher value of the average bond length (ABL) for unsubstituted cyclopentadienyl ring of chromophore 5 (1.3708 Å) as compared to 3 (1.4120 Å) which also portrayed higher acceptor strength of =C(CN)$_2$ as compared -CN.

Table 5. Linear/nonlinear optical and electrochemical properties of 2-3 and 5 (in DCM).

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>λ$_{max}^a$ (nm)</th>
<th>ΔE$_b^c$ (eV)</th>
<th>E$_{1/2}^d$ (V)</th>
<th>β$_{HRS}^d$ (10$^{-30}$ esu)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HE (ICT)</td>
<td>LE (MLCT)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>371</td>
<td>501</td>
<td>2.938</td>
<td>0.576</td>
</tr>
<tr>
<td>3</td>
<td>347</td>
<td>485</td>
<td>3.184</td>
<td>0.572</td>
</tr>
<tr>
<td>5</td>
<td>409</td>
<td>568</td>
<td>2.823</td>
<td>0.609</td>
</tr>
</tbody>
</table>

*aObserved at a concentration of 2.8 x 10$^{-5}$ M; *bΔE is the difference between E$_{HOMO}$ and E$_{LUMO}$ values calculated theoretically; *cE$_{1/2}$=(E$_{ox.}$+E$_{red.}$)/2; *dFirst hyperpolarizability values.

In accordance with the trend of the increasing acceptor strength as confirmed from the absorption, electrochemical, crystal data and theoretical calculations, the β values were supposed to follow the order 5 > 2 > 3, but surprisingly the order was 2 > 3 > 5 (Table 5). Although the chromophore 5 has a more powerful electron withdrawing group yet 3 exhibited higher β (54±2 x 10$^{-30}$ esu) than 5 (24±1 x 10$^{-30}$ esu). This could be understood by visualising their single crystal X-ray crystal packing diagrams (Figure 13). The crystal structures of 3 and 5 showed antiparallel dimeric alignment with the neighbouring chromophores in crystalline state. The cyanothienyl moiety of 3 in the dimer showed fairly better overlap, while in 5, the 5,5-dimethyl-2-enyldene malononitrile acceptor did not show any overlap with the donor ferrocene group (Figure 13). This greater overlap of 3 renders a more efficient D–A assembly for greater nonlinearities which is absent in case of 5.
Further, we have compared the performance of this suite of ferrocene chromophores with similar ferrocene-derived chromophores containing 2-dicyanomethylene-3-cyano-4-methyl-2,5-dihydrofuran (TCF) acceptor from literature, which although possess larger $\beta$ values than the values obtained in this study yet the $\beta_0^{\text{int}}$ of the shorter 2 and 3 are very much comparable with the conjugated TCF chromophores. Further, the chromophores 5 and 6 of Group B are the monosubstituted analogues of 8 and 9 of Group C. The structure-property relationships of the monosubstituted chromophores 5 and 6 undergo characteristic variation upon disubstitution (8 and 9) of the ferrocene moiety. The presence of three, instead of two, HE bands (as in case of monosubstituted chromophores) in disubstituted chromophores 8 and 9 (Figure 14), is a result of the observed splitting in one of the HE bands of the monosubstituted analogues into two of equivalent extinction coefficients. This behaviour suggested the two substituents on each of the cyclopentadiene ring to behave as two independent dipolar moieties. The appearance of these twin bands in case of disubstituted chromophores could be attributed to the small energy gaps between the H/L and H-1/L+1 of the disubstituted chromophores 8 and 9 which were otherwise very large for the monosubstituted chromophores 5 and 6.

![Figure 13. Crystal-packing diagrams along the crystallographic b axis of chromophore (a) 3 and (b) 5.](image)

![Figure 14. UV-visible absorption spectra of the 5/8 and 6/9 in DCM (2.8 x 10^{-5} M).](image)
Thus, in brief, in this chapter:

1. The ferrocene–π–A chromophores were characterized by a weak LE band and an intense HE band attributable to the MLCT and π→π* transitions, respectively.
2. The increase in the strength of the acceptor appended in the ferrocene–π–A system and the increase in the π-bridge conjugation led to a bathochromic shift in the absorption bands of the chromophores as a consequence of the lowering of the H-L energy gaps of the chromophores.
3. The disubstituted chromophores showed absorption bands at almost the similar wavelengths as their monosubstituted counterparts with a band splitting in one their HE bands, resulting from the lower energy gaps between the H/L and H-1/L+1 energy levels.
4. All the “push-pull” ferrocene–π–acceptor systems depicted positive solvatochromism in their absorption bands. This behaviour is further enhanced upon increasing the acceptor strength and/or increasing the conjugation length of the system.
5. All these chromophores exhibited one-electron electrochemically reversible redox wave characteristic of the constituent ferrocene-ferrocenium redox couple of the chromophores. Increasing the acceptor strength led to an anodic shift in the redox wave of the chromophores depicting an increased electron deficiency at the metal center. While the increase in the π-bridge conjugation length led to a cathodic shift due to the stabilization of the charge over a longer conjugated path. The disubstitution of the ferrocene donor also resulted in an anodic shift in the redox waves due to the presence of two acceptor moieties in these systems.
6. The increase in the acceptor strength, the π-bridge conjugation length and the disubstitution of the donor moiety led to an increase in the nonlinearities ($\beta_{HRS}$, $\beta_{HRS,0}$) of the chromophores.
7. The $\beta$ values of the corresponding oxidized ($\beta_{ox,HRS}$) chromophores were lower as compared to their unoxidized versions (as observed from the quadratic curves), which indicated the conversion of ferrocene donor into the corresponding ferrocenium acceptor. This was further corroborated from the spectroelectrochemical studies which showed the disappearance of the MLCT band upon oxidation of the chromophores which reappeared upon reduction. The tunability of the electron
density at the ferrocene metal center led these chromophores to be described as molecular “on/off” switches.

8. The absorption, theoretical and electrochemical data evidenced the order of the increasing acceptor strength to follow the trend -CN < -CHO < -CN-W(CO)₆ < =C(CN)₂.

9. The crystal packing arrangements of the chromophores had an equal significance as that of electrostatic interactions between the dimers of a chromophore.

10. The off-resonant intrinsic hyperpolarizabilities $\beta_0^{\text{int}}$ is a better figure of merit for device applications, where the bulk susceptibility per volume is more important than the molecular hyperpolarizability per chromophore.

**Chapter 5**

Cation recognition behaviour of ferrocene based “push-pull” chromophores

The extensive $\pi$-delocalization over these molecules imparts distinctive colours to these chromophores and has been used as a tool to observed “naked-eye” colour changes upon recognition of the analytes. In this chapter, we have presented application of some ferrocene based chromophores in the quantitative cation detection.

The section 4.4 discerns the sensing applications of the ferrocene–$\pi$–acceptor chromophore 5. It neither has an efficient heteroatom based complexing unit, nor a fluorescent unit. We envisaged that owing to the tendency of ferrocene to undergo efficient oxidation to ferrocenium moiety, it might just be able to capture a cation with some assistance from the $\pi$-bridge resulting in some noticeable absorption and redox changes. Indeed, when solutions of a number of metal ions were added to a solution of 5, significant changes in the absorption spectrum as well as redox potential were noticed in case of Cu²⁺.

The chromophore 5 in CH₃CN exhibited two CT bands, the HE band at 406 nm attributed to $\pi\rightarrow\pi^*$ electronic transitions, while a LE band at 557 nm attributed to d-d transition of Fe²⁺ or MLCT. The assignments of the bands were confirmed by TD-DFT calculations carried out using Gaussian 09 suite of programmes. The absorption bands were found to be stable over the pH range 2.0–12.0, which constitute an advantage for performing the sensing experiments with various analytes in environmental and biological settings without resorting to buffered media.

The incremental addition of an aqueous solution of Cu²⁺ (5.7 x 10⁻⁷ to 8.57 x 10⁻⁵ M) ions to a solution of 5 (2.8 x 10⁻⁵ M, in CH₃CN) resulted in hypsochromic shift of the HE band from 406 to 379 nm (Figure 15a) with a concomitant appearance of a new band at 871
Summary

nm accompanied by a colour change from dark brown to yellow (Figure 15b). However, in the presence of other metal ions no significant spectral as well as visual changes were observed under identical conditions.

Figure 15. (a) Changes in the absorption spectrum of 5 (2.8 x 10\(^{-5}\) M, in CH\(_3\)CN) upon titration with aqueous solution of Cu\(^{2+}\) (5.7 x 10\(^{-7}\) to 8.57 x 10\(^{-5}\) M) (inset: changes at 871 nm); (b) Observed “naked-eye” colour change. Yellow circles at 386 and 735 nm indicate isosbestic points.

Fitting of the titration data of 5 and Cu\(^{2+}\) in HypSpec—a non-linear least squares fitting programme suggested 1:1 stoichiometry (5:Cu\(^{2+}\)) of the most stable species present in the solution with a binding constant of \(\log \beta_{1,1} = 4.99\). The 1:1 stoichiometry was further confirmed by using the method of continuous variations (Job’s plot) where the absorbance at 871 nm got to a maximum when molar fraction of Cu\(^{2+}\) was 0.5 (Figure 16), thereby establishing 1:1 stoichiometry for the complex.

Figure 16. Job’s plot indicating 1:1 stoichiometry of the complex formed in the titration of 5 with Cu\(^{2+}\).
Insignificant spectral and/or visual changes were observed upon carrying out titrations of 5 with Cu$^{2+}$ in the presence of Hg$^{2+}$, Zn$^{2+}$ and Pb$^{2+}$, rendering 5 as highly selective chemosensor for Cu$^{2+}$ over the commonly interfering metal ions. Further, the sensing process was found to be fully reversible as the spectroscopic and/or visual changes reversed upon addition of a solution of EDTA to a solution of the complex 5:Cu$^{2+}$ formed during the titration.

Upon monitoring the sensing event through redox changes (cyclic voltammetry), it was observed that the stepwise addition of Cu$^{2+}$ ions resulted in diminished current intensity of the original band of 5 at $E_{1/2} = 0.538$ V, accompanied by the formation of a new redox wave at a more positive potential $E_{1/2} = 0.816$ V, attributed to the formation of a complex of 5 with Cu$^{2+}$ ion (Figure 17). Overall the binding process depicted a two wave electrochemical behaviour. The preference of 5 to bind Cu$^{2+}$, exclusively has been attributed to the presence of partially filled d-orbital in Cu$^{2+}$ which could accept electrons, from the oxidation of Fe$^{2+}$ to Fe$^{3+}$.

![Cyclic voltamogram](image)

**Figure 17.** Changes in the cyclic voltamogram of 5 ($1.0 \times 10^{-3}$ M, in CH$_3$CN) upon addition of 1.0 equiv. of aqueous solution of Cu$^{2+}$ ($1.5 \times 10^{-5}$ to $1.0 \times 10^{-3}$ M, in water).

Thus, the proposed mechanism of binding of Cu$^{2+}$ with 5 involves the $\pi$-system of the ferrocene and/or the conjugated bridge which may act as a donor group for the cation, forming a $\pi$-complex (Scheme 1). This mechanism is fully evidenced by the disappearance of LE band of 5 at 557 nm accompanied by the appearance of a new band at 871 nm owing to the formation of ferrocenium species and a high energy shift of $\pi \rightarrow \pi^*$ transition (406 $\rightarrow$ 379 nm) due to the interaction of metal ion with the $\pi$-bridge electrons, in the presence of Cu$^{2+}$ ions.
In order to enhance the practical utility of 5 as a Cu$^{2+}$-selective probe, it was immobilized on silica gel of 60-120 mesh to develop a solid-state sensor for rapid “on-field” detection. This receptor-doped silica produced, an instant colour change from dark olive to greenish yellow, pale yellow and light olive upon addition of aqueous solution of 0.1 M, 0.01 M and 0.001 M Cu$^{2+}$ ions, respectively (Figure 18).

In section 4.5, synthesis, characterization, absorption/emission properties and chemosensing behaviour of a new Schiff-base (E)-(ferrocen-1-yl-methylene)pyren-1-yl-amine 10 (Scheme 2), consisting of ferrocene and pyrene as the constituent fragments, has been described.

The chromophore 10 (5.0 x 10$^{-6}$ M, in THF:H$_2$O, 1:99 v/v) exhibited a broad split band centred at 387 nm (17800 M$^{-1}$ cm$^{-1}$) which upon addition of Cr$^{3+}$ decreased in intensity as well as showed a high energy shift leading to the appearance of a new band at
336 nm (Figure 19). The two bands at 283 and 238 nm (24800 and 32600 M \(^{-1}\) cm\(^{-1}\), respectively) along with a low intensity broad band at 474 nm (4000 M \(^{-1}\) cm\(^{-1}\)) showed no significant changes in the presence of Cr\(^{3+}\). The absorption changes at 387 nm led to change in colour of 10 from yellow to almost colourless (Figure 19 inset).

**Figure 19.** Changes in the absorption spectrum of 10 (5.0 x 10\(^{-6}\) M, in THF) upon addition of solution of Cr\(^{3+}\) (2.8 x 10\(^{-5}\) M to 5.0 x 10\(^{-4}\) M, in H\(_2\)O) in THF: H\(_2\)O/1:99 v/v. Inset: visual colour change of solution of 10 upon addition of 5.0 x 10\(^{-4}\) M Cr\(^{3+}\).

Further, excitation of 10 at 350 nm, (5 x 10\(^{-6}\) M, in THF) resulted in a weak emission band at 445 nm, attributed to the monomer emission of pyrene with a very low quantum yield (\(\Phi = 0.016\)). The low value is attributable to the photo-induced electron transfer (PET) operating in 10. No change in emission was observed upon treatment of 10 with a wide range of metal ions (Li\(^+\), Na\(^+\), K\(^+\), Ca\(^{2+}\), Ba\(^{2+}\), Mg\(^{2+}\), La\(^{3+}\), Ce\(^{3+}\), Pr\(^{3+}\), Nd\(^{3+}\), Sm\(^{3+}\), Eu\(^{3+}\), Gd\(^{3+}\), Tb\(^{3+}\), Yb\(^{3+}\), Lu\(^{3+}\), Al\(^{3+}\), Fe\(^{3+}\), Hg\(^{2+}\), Mn\(^{2+}\), Pb\(^{2+}\), Ni\(^{2+}\), Co\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\), Ag\(^+\), Cu\(^{2+}\)) (5 x 10\(^{-4}\) M, in distilled H\(_2\)O), except Cr\(^{3+}\) which enhanced both, the intensity (by nearly 38 fold) as well as the quantum yield (\(\Phi = 0.528\)), as compared to the free chromophore 10. Thus, the response of Cr\(^{3+}\) towards 10 was quantified by sequential addition of Cr\(^{3+}\) ions (2.8 x 10\(^{-6}\) M to 5.0 x 10\(^{-4}\) M, in H\(_2\)O) to a solution of 10 (5.0 x 10\(^{-6}\) M, in THF). A gradual increase in the intensity of the emission band centred at 442 nm (slightly blue shifted as compared to the emission band of the dyad 10 which emitted at 445 nm) was observed (Figure 20), consequently leading to a “turn-on” behaviour of 10 which was also clearly visible under the influence of UV light (Figure 20 inset). The increase in fluorescence intensity continued until the addition of 5.0 x 10\(^{-4}\) M of Cr\(^{3+}\) ions and corresponded to the detection limit of 1 x 10\(^{-6}\) M.
Figure 20. (a) Changes in the emission spectra of 10 (5.0 x 10^{-6} M, in THF) recorded after five min. of addition of solution of Cr^{3+} (2.8 x 10^{-6} M to 5.0 x 10^{-4} M, in H_{2}O) (overall THF:H_{2}O ratio, 1:99 v/v); (b) Visual change in fluorescence of 10 upon addition of 5.0 x 10^{-4} M Cr^{3+}; (c) Depiction of blue shifted emission of 10 in the presence of Cr^{3+}.

Further, it was observed that the addition of EDTA, to the solutions of 10+Cr^{3+} did not cause any reversal of the spectroscopic and colour changes. These observations indicated the operating mechanism for detection of Cr^{3+} to be some non-reversible process other than complexation mechanism operative in 5. Had it been a simple case of complexation and decomplexation (upon addition of EDTA), it would let the fluorescence turn “off” as the PET operating in 10 would be turned “on” upon removal of Cr^{3+}.

The observed “turn-on” behaviour of the dyad 10 was attributed to the formation of 1-aminopyrene (highly fluorescent) in the solution as a result of Cr^{3+} mediated hydrolytic cleavage of 10 (Scheme 3).

Scheme 3. Cr^{3+} induced hydrolysis of chemodosimeter 10.
Further, 10 was found to be perfectly non-cytotoxic, thus the “turn-on” behaviour of 10 upon recognition of Cr\(^{3+}\) was exploited for the development of in vitro detection of Cr\(^{3+}\) ions in breast cancer cell lines. The cells treated with Cr\(^{3+}\) ions and 10 alone showed (confocal imaging) negligible intracellular fluorescence, whereas, when treated with different concentrations of Cr\(^{3+}\) followed by 10, blue emission was observed, thus qualifying 10 as an imaging agent in live cells.

Thus, in brief, in this chapter:

1. The ferrocene based “push-pull” chromophore 5 was explored for selective and sensitive detection of Cu\(^{2+}\). The interaction of 5 and Cu\(^{2+}\) is manifested in terms of absorption as well as electrochemical changes suggesting 5 to be a dual signalling chemosensor for Cu\(^{2+}\). Further, the sensing process is accompanied by “naked-eye” colour changes and is reproducible in solid state as demonstrated by the colour changes when 5 was adsorbed on silica gel.

2. A “turn-on” fluorescence based ferrocene-imine-pyrene dyad 10 was developed for selective colorimetric as well as fluorimetric determination of Cr\(^{3+}\). The dyad 10 constitutes a simple and inexpensive chemodosimeter which demonstrates a highly viable and useful application for the detection of Cr\(^{3+}\) in human breast cancer (MCF7) cell lines.