4.1. ABSTRACT

With an objective to develop infrared absorbing dyes as probes for metal ions and sensitizers in solar cells, we synthesized a few quinaldine based croconaine dyes. These dyes exhibited absorption maximum in the infrared region (840-870 nm) with high molar extinction coefficients (1-5 x 10^5 M^-1 cm^-1). Upon interaction with divalent metal ions these dyes were
found to form complexes with a 2:1 stoichiometry having high association constants in the order \(10^5-10^7\ \text{M}^{-1}\), while the monovalent metal ions caused negligible changes in their spectral properties. As characterized through FTIR and NMR, the complex formation with divalent metal ions involves the participation of the croconyl moiety and results in strong chelation enhanced fluorescence emission.

Another interesting aspect of these dye molecules is their ability to undergo intermolecular interactions and form H-type and J-type aggregates. By making use of this property, we have demonstrated the possibility of tuning the absorptive range of a photoelectrochemical cell. These dyes when deposited as thin film on optically transparent electrodes or on nanostructured TiO\(_2\) film resulted in H-aggregates with a blue-shifted absorption maximum at 660 nm. The excitons formed upon excitation of the dye aggregates undergo charge separation at the TiO\(_2\) and SnO\(_2\) interfaces. The H-aggregates in the thin film are photoactive and produce anodic current when employed in a photoelectrochemical cell. Our results reveal that the suitably substituted croconaine dyes can have potential applications as probes for divalent metal ions and also in dye sensitized solar cells.
4.2. INTRODUCTION

Dyes that absorb or emit in the long wavelength (> 650 nm) region of the optical spectrum have gained increasing attention in the last few years, especially because of their potential optoelectronic and biomedical applications. Several attempts have been made towards developing compounds that absorb in the near-infrared (NIR) region. One commonly employed approach is to increase the extent of \( \pi \) conjugation, however, this would eventually lead to its convergence limit. Further, most of the near-infrared absorbing dyes require tedious synthetic methodologies. Of these, cyanine dyes have received considerable attention as NIR dyes due to their remarkable absorption and emission properties. However, photobleaching and low chemical stability of these dyes has necessitated the development of alternate dyes with absorption in the infrared (IR) region including squaraines and croconaines.

The interest in IR dyes as indicators and labels grew strongly in the last decade, triggered by significant advances in optical detection and imaging technologies. Two of the main advantages of operating in the IR region are the virtually negligible background absorption and the absence of autofluorescence. In this context, there is an intense search for potent IR fluorophores. On the other hand, most IR dyes show intense
absorption bands because their chromophores are characterized by a
highly conjugated and often largely extended π-electron system.\textsuperscript{14}

\begin{center}
\begin{tikzpicture}
\draw[thick, black] (0,0) -- (1,0) -- (1,1) -- (0,1) -- cycle;
\draw[thick, black] (1,0) -- (2,0) -- (2,1) -- (1,1) -- cycle;
\draw[thick, black] (0,0) -- (1,1);
\draw[thick, black] (1,0) -- (2,1);
\node at (0.5,0.5) {\textODO{O}};
\node at (1.5,0.5) {\textODO{O}};
\node at (0.5,0) {\textODO{OH}};
\node at (1.5,0) {\textODO{Y}};
\node at (2.5,0.5) {\textODO{Y}};
\end{tikzpicture}
\end{center}

Croconaines are a class of dyes possessing sharp and intense
absorption bands in the near-infrared to infrared region (Chart 4.1) and
can, in general, be considered as an acceptor in conjugation with two
donors, D-A-D.\textsuperscript{15} Although, croconaine dyes are the higher homologues of
squaraine dyes, the photophysical and photochemical properties of these
dyes have not been studied extensively.\textsuperscript{16} These dyes are usually prepared
by the condensation between croconic acid and an electron rich aromatic,
heteroaromatic or olefinic compounds in a one-step reaction. In this
context, we synthesized quinoline based croconaine dyes \textbf{1a-d}, absorbing
in the infrared region (Chart 4.2) and examined the potential use of these
dyes as probes for metal ions and also in solar cell applications. Our results
indicate that the croconaine dyes undergoes efficient interactions with
various metal ions leading to chelation enhanced fluorescence intensity.\textsuperscript{17a}
In addition to this, the thin films of the croconaine dyes can generate photocurrent when employed in an electrochemical cell.\textsuperscript{17b}

![Chemical structure of croconaines]

\textbf{Chart 4.2}

4.3. RESULTS

4.3.1. Synthesis of Croconaine Dyes

The synthesis of the dyes 1a-c has been achieved by the condensation reaction between 2:1 equivalents of the quinaldinium salts 3a-c and croconic acid in ethanol at 80 °C using quinoline as catalyst. The quinaldinium salts 3a-d, in turn, was isolated by the reaction of the substituted quinaldines 2a-d with methyl iodide at 100 °C in a sealed tube.\textsuperscript{18} With a view to improving the solubility and cellular permeability of the dyes, cholesterol anchored croconaine dye 1d was synthesized from the corresponding quinaldinium salt 3d, following the same synthetic strategy.
as in the previous cases. The reaction mixture following work up and column chromatography gave the cholesterol linked croconaine dye 1d in 75% yield. All the croconaine dyes were characterized on the basis of analytical and spectral techniques. For example, in the $^1$H NMR spectrum of the unsubstituted croconaine dye 1a in DMF-$d_6$, showed the aromatic protons in the range from δ 7.5-7.3 ppm, while the 3-H proton appeared as a doublet at 8.9 ppm with $J = 9.4$ Hz. In addition, the olefinic proton can be seen as a sharp peak at δ 6.4 ppm, while the N-methyl protons appear as a singlet at δ 3.9 ppm. In the FTIR spectrum, the characteristic carbonyl stretching frequency of the croconyl ring appeared at 1604 and 1558 cm$^{-1}$. The FAB mass analysis showed a molecular mass of 420.14, which corresponds to the molecular formula $C_{27}H_{20}N_2O_3$ of the croconaine dye 1a.

Scheme 4.1
4.3.2. Photophysical Properties of Croconaine Dyes

The croconaine dyes \(1a-d\) showed sharp and intense absorption in the infrared window with absorption maximum ranging from 840-875 nm and high molar extinction coefficients in the range \(\varepsilon = 1-5 \times 10^5\) \(\text{M}^{-1}\) \(\text{cm}^{-1}\). Figure 4.1 shows the absorption spectra of the various croconaine dyes. The unsubstituted croconaine dye \(1a\) showed absorption maximum at 840 nm in DMF, while the halogenated dyes \(1b\) and \(1c\) exhibited absorption maximum, which is \(ca.\) 20 nm red-shifted from the parent unsubstituted derivative, 860 and 865 nm, respectively (Table 4.1). The dyes \(1a-c\) have low solubility in common organic solvents. However, the substitution of quinaldine ring with the cholesterol moiety resulted in increased solubility of the dye \(1d\) in THF and CHCl\(_3\). The dye \(1d\) showed an absorption maximum at 871 nm in THF.

![Normalized Absorbance vs Wavelength](image)

**Figure 4.1.** Normalized absorption spectra of the croconaine dyes \(1a-d\).
All these dyes were found to have negligible fluorescence quantum yields and hence their singlet excited state characterization using emission spectroscopy was difficult and femtosecond transient absorption spectroscopy was employed to probe the excited state behaviour of the croconaine dyes. The time-resolved spectra of the transients recorded following 775 nm laser pulse excitation of the croconaine dye 1d in CH$_2$Cl$_2$ are shown in Figure 4.2. The formation of singlet excited state can be seen from the transient absorption spectrum recorded immediately after 130 fs laser pulse excitation. The difference in the absorption spectra shows a broad absorption peak in the visible region with split maxima at 630 and 720 nm. The decay of this absorption band in the visible region parallels

**Table 4.1. Excited-State Properties of Croconaine Dyes**

<table>
<thead>
<tr>
<th>Dye</th>
<th>$\lambda_{\text{max}}$, nm</th>
<th>$\varepsilon$, M$^{-1}$cm$^{-1}$</th>
<th>$S_1$-$S_n$ abs max, nm</th>
<th>Excited singlet lifetime (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a$^b$</td>
<td>842</td>
<td>1.3 x 10$^5$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1b$^b$</td>
<td>861</td>
<td>1.9 x 10$^5$</td>
<td>630, 720</td>
<td>7.3</td>
</tr>
<tr>
<td>1c$^b$</td>
<td>865</td>
<td>1.4 x 10$^5$</td>
<td>635, 685</td>
<td>4.4</td>
</tr>
<tr>
<td>1d$^c$</td>
<td>865</td>
<td>4.2 x 10$^5$</td>
<td>630, 720</td>
<td>4.1</td>
</tr>
</tbody>
</table>

$^a$Average of more than 2 experiments and the error is ca. ± 5 %. $^b$DMF. $^c$CHCl$_3$. 

130
the bleaching recovery at 860 nm. The excited state lifetime, as monitored from the decay at 630 nm, is 7.3 ps. The excited singlets of 1b and 1c also show similar broad absorption in the 600-720 nm region and exhibit lifetimes of 4.4 and 4.1 ps in DMF, respectively. The decreased lifetime of these dye singlets as compared to 1d is expected to arise from the difference in the solvent medium.

![Graph](image)

**Figure 4.2.** Transient absorption spectra recorded following the 775 nm laser pulse excitation of 1d in CH₂Cl₂. (A) Time resolved absorption spectra recorded at 0, 1, 3, 6, 13, 23 and 83 ps and (B) absorption-time profiles recorded at 630 and 860 nm.

The bleaching recovery for all three dyes was completed within ~40 ps. This complete recovery of the ground state in turn indicates the absence of long-lived transients and confirms that the singlet excited state is the only transient formed when monomer croconaine dye is excited with 775 nm laser pulse. Absence of long-lived transient rules out the possibility of intersystem crossing in the formation of triplet excited state. The side chain
modification with Br, I or cholesterol group had little effect on the formation or deactivation of the croconaine dye singlet excited states.

Since the intersystem crossing efficiency was found to be negligible under direct excitation of the croconaine dyes, triplet-triplet (T-T) energy transfer method was adopted to characterize the triplet excited state of these dyes. Pyrenecarboxaldehyde, **PyC** \((E_T = 186\ \text{kcal/mole}; \lambda_{\text{max}} = 440 \text{ nm and } \varepsilon_{\text{max}} = 20000 \ M^{-1}\text{cm}^{-1})\) in \(\text{CH}_2\text{Cl}_2\) was used as a sensitizer to transfer triplet energy to **1d** in a nanosecond laser flash photolysis set up (equations 4.1 and 4.2).

\[
\begin{align*}
\text{PyC} \xrightarrow{\text{hv}} & \ 1\text{PyC}^* \xrightarrow{\text{ISC}} \ 3\text{PyC}^* \\
3\text{PyC}^* + \text{1d} \rightarrow & \ \text{PyC} + 3\text{1d}^* 
\end{align*}
\]

The transient absorption spectrum recorded immediately after 355 nm laser pulse excitation of **PyC** shows absorption maximum at 440 nm, corresponds to the triplet excited state (spectrum *a* in Figure 4.3). In presence of **1d**, the deactivation of the pyrene triplet proceeds via T-T energy transfer as illustrated in equation 4.2. This is evident from the growth of a new absorption band in the visible region (spectra *b* and *c* in Figure 4.3). The broad absorption band seen around 500 and 680 nm corresponds to the triplet of excited state of **1d**. The bimolecular rate as determined from the dependence of pseudo-first order decay rate constant
Figure 4.3. T-T energy transfer between excited 0.1 mM PyC and 0.02 mM 1d in dichloromethane. Time-resolved spectra were recorded following 355 nm laser pulse excitation: (a) 50 ns (b) 500 ns (c) 5 µs and (d) 20 µs.

of PyC triplet on the concentration of 1d is $1.8 \times 10^{10}$ M$^{-1}$s$^{-1}$. If we assume energy transfer to be 100%, we can determine the extinction coefficient of triplet excited state of 1d. By comparing the maximum absorbance values and the extinction coefficient of PyC triplet, we obtained a value of 15500 M$^{-1}$cm$^{-1}$ for 1d triplet at 680 nm. The triplet excited state of 1d is relatively long lived (lifetime of 7.2 µs) compared to its singlet excited state (7.3 ps). Spectrum d in Figure 4.3 shows the residual absorption following the decay of triplet excited state. The formation of the photoproduct is an indication of the photochemical reactivity of triplet excited state. Since the triplet excited state has a longlife, if formed under direct excitation, we could have seen a long-lived transient in Figure 4.2. These results further confirm that
the intersystem crossing is a minor pathway in the deactivation of the singlet excited state of the croconaine dyes.

4.3.3. Study of Interactions with Mono- and Divalent Metal Ions

With a view to investigate the ability of the croconaine dyes 1a-d as bidentate ligands and thereby their potential use as probes, we have carried out their interactions with various mono- and divalent metal ions such as Li⁺, Na⁺, K⁺, Ag⁺, Ca²⁺, Mg²⁺, Zn²⁺, Pb²⁺ and Cd²⁺ ions. The derivative 1d was selected as a representative example, because of its higher solubility and stability. Figure 4.4A shows the changes in the absorption spectrum of the dye 1d on addition of Zn²⁺ ions. With increasing concentration of Zn²⁺ ions, we observed a decrease in the absorption band at 871 nm, with the concomitant formation of the band at 788 nm. The corresponding changes in the fluorescence spectra of the dye 1d with increasing addition of the metal ions are shown in Figure 4.4B. The dye 1d alone is weakly fluorescent. With the addition of Zn²⁺ ions, a significant increase in the fluorescence intensity was observed with an emission maximum at 814 nm.

The progressive increase in the fluorescence intensity reached saturation with the addition of 0.5 equivalents of the metal ions and ca. 28-fold fluorescence enhancement could be observed with Zn²⁺ ions (Φ = 2.5 x
The stoichiometry of the complex formed between the croconaine dye 1d and the representative metal ion Zn$^{2+}$ ions was found to be 2:1 as evident from the Job’s plot (Figure 4.5). Benesi-Hildebrand analysis of the complex formation between the dye 1d and Zn$^{2+}$ ions was studied by following the changes in the fluorescence spectra. These analysis gave a binding constant of $1.1 \pm 0.3 \times 10^7$ M$^{-1}$, which is in good agreement with the value obtained from the absorption changes.

The interaction of the dye 1d with different alkali, alkaline earth, transition and heavy metal ions was also examined. The complexation of 1d with other metal ions led to the formation of a new absorption band characteristic of the complexation with the corresponding metal ions. For example, with the addition of Pb$^{2+}$ ions to the dye solution in THF, a decrease in the band corresponding to the dye at 871 nm was observed.
with the concomitant formation of a new band at 735 nm (Figure 4.6A). With increasing concentration of Pb$^{2+}$ ions, the initially weakly fluorescent dye showed ca. 26-fold enhancement in fluorescence intensity ($\Phi = 2.2 \times 10^{-3}$) with the emission maxima at 816 nm (Figure 4.6B). Similar observations have been made with Cd$^{2+}$ ions; however, the new band corresponding to the [1d-Cd$^{2+}$] complex was observed at 804 nm and ca. 14-fold fluorescence enhancement ($\Phi = 1.4 \times 10^{-3}$) was observed with emission maxima at 818 nm. Based on the fluorescence data, the binding constants for Pb$^{2+}$ and Cd$^{2+}$ ions were calculated and these values are found to be $6.5 \pm 0.5 \times 10^6 \text{ M}^{-1}$ and $2.6 \pm 0.3 \times 10^6 \text{ M}^{-1}$, respectively. The relative changes in the fluorescence intensity of the croconaine dye 1d upon the addition of different metal ions are shown in Figure 4.7.

**Figure 4.5.** (A) Job’s plot for the complexation of the croconaine dye 1d with Zn$^{2+}$ ions in THF. Figure B shows the Benesi-Hildebrand analysis of the emission changes for the complexation between the dye 1d and Zn$^{2+}$ ions.
The monovalent metal ions such as Li⁺, Na⁺ and K⁺ ions caused negligible changes in the absorption and fluorescence spectra. In contrast, the addition of other divalent metal ions like Pb²⁺, Cd²⁺, Mg²⁺, Hg²⁺, Ca²⁺ and Ba²⁺ ions showed significant affinity for the dye resulting in the chelation

![Graph A](image1.png)

**Figure 4.6.** Changes in the (A) absorption and (B) emission spectra of the dye 1d (7.75 µM) in THF with the addition of Pb²⁺ ions. [Pb²⁺] a) 0, and e) 3.87 µM. Excitation wavelength, 700 nm.

![Graph B](image2.png)

**Figure 4.7.** Relative fluorescence enhancement of the croconaine dye 1d (7.75 µM) upon interaction with different metal ions.
enhanced fluorescence intensity. However, the relative changes were found to vary with different metal ions. Similar, but less significant effects were observed in the absorption and emission spectra of the dye 1d upon adding other divalent metal ions like Mg$^{2+}$, Hg$^{2+}$, Ba$^{2+}$ and Ca$^{2+}$ ions. The absorption and emission maxima as well as the association constants calculated for the various metal complexes of 1d are summarized in Table 4.2. As shown in

**TABLE 4.2.** Absorption and fluorescence maxima, association constants and quantum yields of the various metal ion complexes of 1d in THF.$^a$

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_{\text{max}}$, nm</th>
<th>$\Phi_F$$^b$</th>
<th>Association constant $(K)$$^c$ M$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1d-Zn$^{2+}$]</td>
<td>788 814</td>
<td>2.5 x 10$^{-3}$</td>
<td>1.1 ± 0.3 x 10$^7$</td>
</tr>
<tr>
<td>[1d-Pb$^{2+}$]</td>
<td>735 816</td>
<td>2.2 x 10$^{-3}$</td>
<td>6.5 ± 0.5 x 10$^6$</td>
</tr>
<tr>
<td>[1d-Cd$^{2+}$]</td>
<td>804 818</td>
<td>1.4 x 10$^{-3}$</td>
<td>2.6 ± 0.3 x 10$^6$</td>
</tr>
<tr>
<td>[1d-Mg$^{2+}$]</td>
<td>805 815</td>
<td>5.5 x 10$^{-4}$</td>
<td>3.2 ± 0.4 x 10$^6$</td>
</tr>
<tr>
<td>[1d-Ba$^{2+}$]</td>
<td>750 818</td>
<td>4.7 x 10$^{-4}$</td>
<td>8.0 ± 0.2 x 10$^5$</td>
</tr>
<tr>
<td>[1d-Hg$^{2+}$]</td>
<td>735 812</td>
<td>4.2 x 10$^{-4}$</td>
<td>2.6 ± 0.3 x 10$^5$</td>
</tr>
<tr>
<td>[1d-Ca$^{2+}$]</td>
<td>755 820</td>
<td>3.2 x 10$^{-4}$</td>
<td>1.3 ± 0.4 x 10$^5$</td>
</tr>
</tbody>
</table>

$^a$Average of more than 2 experiments and the error is ca. ± 5 %.

$^b$Fluorescence quantum yields were calculated using indocyanine-green (IR-125) as the standard ($\Phi = 0.13$, in DMSO).

$^c$Association constants were calculated based on fluorescence changes.
the table, the [1d-M\textsuperscript{n+}] complexes have absorption maxima in the range 735-805 nm, while the emission maxima is in the range 812-820 nm. For example, the absorption and emission maxima for the complex [1d-Zn\textsuperscript{2+}] was observed at 788 and 814 nm with association constant 1.1 ± 0.3 ×10\textsuperscript{7} M\textsuperscript{-1}, while for the [1d-Ba\textsuperscript{2+}] complex, we observed a lower value of 8.0 ± 0.2 × 10\textsuperscript{5} M\textsuperscript{-1}.

4.3.4. Characterization of Metal Ion Complexation

The complexation between various metal ions and the dye 1d was confirmed through \textsuperscript{1}H NMR and infrared (FTIR) spectral analysis of the complex. The \textsuperscript{1}H NMR spectrum of the croconaine dye 1d in CDCl\textsubscript{3} showed five aromatic protons as multiplets in the region between δ 7-9.1 ppm,

![NMR spectra](image)

**Figure 4.8.** \textsuperscript{1}H NMR spectra of the dye 1d in CDCl\textsubscript{3} with increasing concentration of Zn\textsuperscript{2+} ions in CD\textsubscript{3}CN. The mole ratio of [Zn\textsuperscript{2+}] to [1d] is a) 0, b) 0.25 and c) 0.5.
while the olefinic and \(N\)-methyl protons appeared as singlets at \(\delta 6.4\) and \(3.9\) ppm, respectively (Figure 4.8). With the addition of \(\text{Zn}^{2+}\) ions, a broadening of the aromatic signals as well as the olefinic and \(N\)-methyl protons could be observed.

The infrared (FTIR) spectrum of the dye 1d is shown in Figure 4.9. The bands at 1660, 1598 and 1560 cm\(^{-1}\), are characteristic of the carbonyl groups of the croconyl moiety, while the band at 1755 cm\(^{-1}\) is assigned to the carbonyl group attached to the cholesterol moiety. The FTIR spectrum of the \([1d-\text{Zn}^{2+}]\) complex showed the carbonyl band at 1610 cm\(^{-1}\), while the bands at 1598 and 1560 cm\(^{-1}\) were merged to give a new band at 1564 cm\(^{-1}\). This clearly indicates the involvement of two carbonyl groups of the croconyl moiety of 1d in the complexation with \(\text{Zn}^{2+}\) ions. As expected, the

![Figure 4.9. IR spectra of the croonaine dye 1d and the [1d-\text{Zn}^{2+}] complex.](image-url)
band at 1755 cm\(^{-1}\) corresponding to the carbonyl group attached to the cholesterol moiety showed negligible changes. Moreover, no significant changes were observed in the protons of the aliphatic region in the \(^1\)H NMR spectrum of the [\textbf{1d}-Zn\(^{2+}\)] complex, indicating that the cholesterol moiety has no significant interactions with the metal ions.

### 4.3.5. Light Harvesting Properties of Croconaine Dyes

Dye sensitization of nanocrystalline semiconductors have attracted considerable attention since Grätzel first reported on the highly efficient ruthenium complex sensitized nanocrystalline TiO\(_2\)-based dye sensitized solar cell (DSSC).\(^{21}\) Polypyridyl complexes of ruthenium, such as N3 dye,\(^{21a}\) and the ‘black dye’\(^{21e}\) have been reported to have solar energy to electricity conversion of up to 10.4%. Various sensitizers based on coumarin,\(^{22}\) indoline,\(^{23}\) cyanine,\(^{24}\) hemicyanine,\(^{25}\) merocyanine,\(^{26}\) perylene,\(^{27}\) xanthene,\(^{28}\) triarylamine,\(^{29}\) squaraine\(^{30}\) and thiophene\(^{31}\) have been explored. Since the croconaine dyes under investigation exhibit intense absorption in the infrared region, it was our interest to investigate the potential of these dyes as sensitizers in solar cells.

One of the possible ways to utilize the croconaine dyes for harvesting infrared photons (in a photoelectrochemical cell) is to cast thin films on the electrode surface. Two different approaches were adopted for casting the
films of the croconaine dye 1d in the electrode surface. A drop cast method was employed to cast thin film of 1d on glass slide by applying the chloroform solution and air drying, while the other method involved the assembling of the dye molecules as thin films on nanostructured TiO$_2$ and SnO$_2$. The absorption spectra of the dye film cast on conducting glass and the dye molecules deposited on TiO$_2$ and SnO$_2$ films are shown in the Figure 4.10. The dye film cast on the conducting glass exhibits blue-shifted absorption band with a maximum at 660 nm, indicating thereby, the formation of H-aggregates under these conditions.$^{32}$ The presence of both monomer and aggregate forms are evident from the absorption spectra as shown in Figure 4.10 (traces b and c).

![Absorption spectra of the croconaine dye 1d cast or deposited on (a) glass slide using drop cast method, (b) nanostructured TiO$_2$ film, (c) nanostructured SnO$_2$ film using dip-adsorption method and (d) monomer solution spectrum.](image)

**Figure 4.10.** Absorption spectra of the croconaine dye 1d cast or deposited on (a) glass slide using drop cast method, (b) nanostructured TiO$_2$ film, (c) nanostructured SnO$_2$ film using dip-adsorption method and (d) monomer solution spectrum.
The observation of smaller peaks in the higher energy region (e.g., 560 nm) is indicative of higher ordered aggregates such as trimer and tetramer of 1d. The broadness of the aggregation peak indicates the degree of randomness of the aggregates formed in these films. As compared to the solution spectrum, the absorption peak of the monomer dye on TiO$_2$ and SnO$_2$ surface is slightly blue shifted with maximum around 840 nm. The presence of monomer form in these films indicates that the surface of the oxide particles promotes dispersion of dye molecules without aggregation.

The excited state behaviour of the croconaine dye films were further investigated using pump-probe spectroscopy. Figure 4.11 shows the time-resolved absorption spectra recorded following 775 nm excitation of 1d film cast on conducting glass electrode. A difference absorption peak at 610

![Figure 4.11](image)

**Figure 4.11.** Transient absorption spectra recorded following the 775 nm laser pulse excitation of 1d film on glass. (A) Time resolved absorption spectra recorded at 0, 1, 3, 25, 100 and 1340 ps and (B) the absorption-time profiles recorded at 615 and 660 nm.
nm and bleaching at 670 nm can be seen as the excitonic state of the dye aggregate is generated using infrared laser excitation. The transient decay when fitted to biexponential decay analysis, gave lifetime values of 1.1 and 7.6 ps. The inhomogeneity of the aggregates in the film is expected to influence the decay kinetics and contribute to the deviation from the monoexponential decay behaviour.

The excited singlet of H-aggregate is nonfluorescent because of the forbidden transition between the lower excited singlet level and ground state.\textsuperscript{33} Thus, the excited H-aggregates undergo intersystem crossing to produce relatively long-lived triplet species. More than 98% of the bleached dye is recovered in \(~30\) ps. Based on this observation, we can conclude that the intersystem crossing is not a dominant deactivation pathway for the excited dimer of 1d. Further, the excited state or excitonic state formed with direct excitation of the dye aggregate on a glass surface undergoes rapid annihilation without producing charge separated state or triplet excited state. In order to see whether the semiconducting property of TiO\textsubscript{2} and SnO\textsubscript{2} can influence the charge separation process, we evaluated the transient spectra following laser pulse excitation of 1d films.

Figure 4.12 compares the transient spectra recorded following the 387 nm laser pulse excitation of the 1d film on glass and TiO\textsubscript{2} surface. The higher energy of the laser pulse chosen for this experiment ensured the excitation of all aggregated forms of the dye in the film. Neither the SnO\textsubscript{2} or
Figure 4.12. Transient absorption spectra recorded following the 387 nm laser pulse excitation of 1d film on (A) glass and (B) nanostructured TiO$_2$ film. The absorption-time profiles recorded for (C) 1d film on glass at 580 and 690 nm and (D) nanostructured TiO$_2$ film at 500 and 670 nm.

TiO$_2$ ($E_g >3.5$ eV) substrate can be directly excited with 387 nm laser pulse. The transient absorption and decay behavior of the 1d films on the glass surface was similar to the one observed with 775 nm laser pulse excitation. Any higher energy states formed during 387 nm laser pulse excitation are quickly relaxed to form the excitonic state similar to the 775 nm laser pulse excitation. The transient decay deviates from the monoexponential behavior. The biexponential kinetic analysis of the transient decay yielded lifetimes of 1 and 11 ps.
Interestingly, a different type of transient absorption behaviour was observed on the TiO\textsubscript{2} surface with a broad maximum around 500 nm. The bleaching in the 670 nm confirms that the origin of the transient is still centered on the dimer of \textit{1d}. Upon fitting the transient decay at 500 nm to biexponential kinetic analysis, we obtain lifetimes of 0.5 and 3.4 ps. Two notable differences emerge from these experiments. (i) The transient observed on the TiO\textsubscript{2} and SnO\textsubscript{2} surface exhibits blue shifted absorption compared to the excitonic absorption on the glass surface. (ii) The initial decay times of the transient on the TiO\textsubscript{2} and SnO\textsubscript{2} surface are shorter than the one observed on the glass surface and formation of long-lived transient is also visualized from the residual bleaching at 690 nm. These results suggest that a significant fraction of the excitonic state of the aggregate dye dissociates at the TiO\textsubscript{2} surface to generate the charge separated pair.

The transient absorption around 500 nm is attributed to the charge separated state. Most of these separated charges undergo recombination, however, a small fraction (<10%) of the charge separated state is stabilized as the electrons are trapped within the TiO\textsubscript{2} particles. The possible reaction pathways with which the excited dye aggregates in the film undergo deactivations are summarized in equations 4.3-4.6. If indeed TiO\textsubscript{2} is capable of accepting electrons from the charge separated dye aggregate, we should be able to collect these charges at the electrode surface in a photoelectrochemical cell.
(dye)$_2$ + hv $\rightarrow$ (dye)$_2^*$  eq (4.3)

(dye)$_2^*$ $\rightarrow$ (dye)$_2$  eq (4.4)

(dye)$_2^*$ $\rightarrow$ (dye$^+$ + dye$^-$) $\rightarrow$ (dye)$_2$  eq (4.5)

(dye$^+$ + dye$^-$) + TiO$_2$ $\rightarrow$ (dye$^+$ + dye) + TiO$_2$ (e)  eq (4.6)

4.3.6. Photocurrent Generation at Dye Modified TiO$_2$ Electrode

The nanostructured TiO$_2$ film was first cast on a conducting glass electrode (OTE/TiO$_2$) using TiO$_2$ colloids. The dye 1d deposited on the TiO$_2$ surface (referred as OTE/TiO$_2$/1d) was found to be photoactive and generates photocurrent in a photoelectrochemical cell when irradiated with light. Figure 4.13 shows the photocurrent response to On-Off cycles of illumination and the power characteristics of the cell. The photocurrent response is prompt and reproducible at several cycles of illumination. As the electrons are transported towards the collecting electrode surface, the dye is regenerated by the redox couple (I$_3^-$/I$^-$) at the electrolyte interface. A maximum current of 0.23 mA/cm$^2$ and a photovoltage of 190 mV was observed for visible-IR illumination (100 mW/cm$^2$) of the electrode. Although overall power conversion efficiency is small (<0.1%), the generation of anodic photocurrent confirms the light initiated electron flow towards TiO$_2$ film and the collecting OTE surface.
The incident photon to charge carrier generation efficiency (IPCE) of OTE/TiO$_2$/1d electrode and OTE/SnO$_2$/1d electrode is shown in Figure 4.14. These experiments were carried out in a two arm flat cell and the illumination area was limited to 0.28 cm$^2$. The dye 1d modified OTE/TiO$_2$ electrode shows photocurrent response in the 500-800 nm region, thus matching the absorption of the H-aggregates. The maximum IPCE was $\approx$1.2 % (curve a) at 650 nm. The performance of OTE/SnO$_2$/1d electrode was relatively poor with maximum IPCE of 0.6%. It is interesting to note that the IPCE at longer wavelengths (> 800 nm) is relatively low and there was no contribution from the monomer dye to the photocurrent generation. The blue-shift in the IPCE peak compared to the absorption maximum indicate that higher aggregates of dye 1d contribute to the photocurrent
generation with greater efficiency. The varying photocurrent generation efficiency of monomers aggregates has been elucidated in earlier studies.\textsuperscript{34} Compared to the dye 1d, the other croconaine dyes, 1b and 1c, performed poorly and no attempt was made to further evaluate the photoelectrochemical performance of these two dyes.

4.4. DISCUSSION

The ground ($S_0$) and excited states ($S_1$) of the croconaine dyes are intramolecular D-A-D charge transfer (ICT) states.\textsuperscript{35} The $S_0$-$S_1$ electronic excitation in these systems involves a CT process that is primarily confined to the central C$_5$O$_3$ cyclopentane ring. The intramolecular charge transfer
character (ICT) of this transition, combined with an extended $\pi$ conjugation is responsible for the sharp and intense absorption bands of these dyes.

The interaction of the metal ions at the carbonyl group lowers the $\pi$ conjugation as well as the CT character, resulting in the formation of a hypsochromically shifted absorption band for the dye-metal complex. The formation of the $[1d\text{-}M^{2+}]$ complex reduced the bond energy of the conjugated C=O bond, leading to the reduction of the carbonyl stretching frequency as seen in the FTIR analysis. In addition, in the $^1$H NMR spectra, the peaks corresponding to the aromatic, olefinic and $N$-methyl protons get broadened upon metal ion binding. The presence of electron rich carbonyl oxygen allow only the interaction with divalent metal ions, in a 2:1 binding mode as evidenced through Jobs and Benesi-Hildebrand analysis and the sensitivity of the binding follows the order, Zn$^{2+}$ > Pb$^{2+}$ >> Cd$^{2+}$ >> Mg$^{2+}$ ≈ Hg$^{2+}$ ≈ Ca$^{2+}$ ≈ Ba$^{2+}$ ions (Figure 4.15).

Figure 4.15. Schematic representation of the complexation between divalent metal ion, $M^{2+}$ and the croconaine dye $1d$. 

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Depending on the nature of substituents and the medium, squaraine and croconaine dyes can form H-aggregates or J-aggregates, (Figure 4.16); the formation of which have been explained by the molecular exciton theory. According to this theory, the dye molecule is regarded as a point dipole and the excitonic state of the dye aggregate splits into two levels through the interaction of transition dipoles. The dye molecules can aggregate in a parallel way (plane-to plane stacking) to form a H-aggregate (sandwich-type arrangement) or in a head-to-tail arrangement (end-to end stacking) to form a J-aggregate. A transition to the upper state having parallel transition moments (in parallel aggregates) and to a lower state with perpendicular transition moments (in a head-to-tail arrangement) leads to hypsochromic (blue) and bathochromic (red) shifts, respectively.\textsuperscript{37}

![Exciton band energy diagram for molecular excitons for H- and J-aggregates.](image-url)

\textbf{Figure 4.16.} Exciton band energy diagram for molecular excitons for H- and J-aggregates.
In the case of the croconaine dye 1d, it is the H-aggregate of the dye that undergo charge separation over TiO$_2$ electrode, rather than the monomer dye. In a dye-sensitized photocurrent generation mechanism, the excited singlet of the sensitizing dye directly injects electrons into the TiO$_2$ particles. The oxidation potential of the ground state dye (1d) as determined from the cyclic voltammetry experiment is 1.22 V vs. NHE. This value corresponds to ~ 0.23 V for the oxidation potential of the excited monomer (assuming the singlet energy as 1.45 eV). Since the conduction band energy of TiO$_2$ (0.5 V vs. NHE) is more negative than the oxidation potential, the excited monomer form of the dye cannot directly participate in the charge injection process. As a result of this energy mismatch, we are not able to observe sensitized photocurrent generation from the monomer. However, the dye aggregates are capable of generating photocurrent as the excitons undergo charge separation and thus contribute to the photocurrent generation.$^{38}$

4.5. CONCLUSIONS

In conclusion, a new class of substituted quinoline based croconaine dyes was synthesized and their interactions with metal ions and light harvesting properties have been investigated. Due to the presence of a stronger acceptor moiety, these croconaine dyes exhibited around 100 nm
red-shifted absorption compared to the corresponding squaraine dyes. The presence of the two carbonyl groups facilitates complex formation of the croconaine dyes with divalent metal ions. The lowered ICT character and decreased conjugation in the ring resulted in the formation of a new absorption band at lower wavelength region for the dye-metal ion complex and the metal binding is signaled through ‘turn on’ fluorescence intensity.

The photophysical properties of the croconaine dyes in the monomeric and aggregated forms have been characterized using femtosecond spectroscopy. The excitation of the H-aggregate of the thin films produces excitons, which are capable of undergoing charge separation on the TiO$_2$ and SnO$_2$ surface. When the dye molecules adsorbed on TiO$_2$ films were excited with visible-IR light anodic current generation was observed, wherein only the aggregates contribute to the photocurrent generation. The low $IPCE$ of the croconaine dye film shows that the net charge separation is poor. Improvement in the dye aggregate/semiconductor heterojunction is necessary to further improve the efficiency of charge separation. Results of the investigations demonstrate that croconaine dyes act as potential probes for metal ions in the infrared region and also in light harvesting applications.


4.6. EXPERIMENTAL SECTION

4.6.1. General Techniques

The equipment and procedure for spectral recordings are described elsewhere.\textsuperscript{39} All melting points were determined on a Mel-Temp II melting point apparatus. The IR spectra were recorded on a Perkin Elmer Model 882 infrared spectrometer. The electronic absorption spectra were recorded on a Shimadzu UV-3101 or 2401 PC UV-VIS-NIR scanning spectrophotometer. The fluorescence spectra were recorded on a SPEX-Fluorolog F112X spectrofluorimeter. \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were measured on a 300 MHz Bruker advanced DPX spectrometer. Ultrafast (femtosecond) transient absorption experiments were conducted using a Clark-MXR 2010 laser system and an optical detection system provided by Ultrafast Systems (Helios). The source for the pump and probe pulses is the fundamental of the Clark laser system (775 nm, 1 mJ/pulse, fwhm 130 fs, 1 kHz repetition rate). Nanosecond laser flash photolysis experiments were performed with a 355 nm laser pulse (5 mJ, pulse width 6 ns) from a Quanta Ray Nd:YAG laser system. All the solvents used were purified and distilled before use. Fluorescence quantum yields were calculated using IR-125 as the standard (\(\Phi_{\text{DMSO}} = 0.13\)).\textsuperscript{40} Metal ion binding studies were carried out by the addition of equal aliquots of metal ion stock solution in
water to 3 mL of dye in THF.

4.6.2. Materials

Cholester-3-yl-2-methylquinoline-6yl carbonate (2d), mp 101-102 °C (lit. mp 101-102 °C),¹⁸b 6-iodo-2-methylquinoline (2c), mp 108-109 °C (lit. mp 108-109 °C),⁴¹ 6-bromo-2-methylquinoline (2b), mp 95-96 °C (lit. mp 95-96 °C),⁴¹ cholester-3-yl-N-methyl-2-quinaldinium-6yl carbonate iodide (3d), mp 216-217 °C (lit. mp 216-217 °C),¹⁸b 6-iodo-N-methyl-2-quinaldinium iodide (3c), mp 222-223 °C (lit. mp 222-223 °C),⁴¹ and 6-bromo-N-methyl-2-quinaldinium iodide (3b), mp 237-239 °C (lit. mp 237-239 °C)⁴¹ were prepared by modifying the reported procedures. Croconic acid, Hg(ClO₄)₂, Pb(ClO₄)₂, Cu(ClO₄)₂, Zn(ClO₄)₂, Ca(ClO₄)₂, NaClO₄, KClO₄, LiClO₄, Mg(ClO₄)₂ were purchased from Aldrich and used as such.

4.6.3. General Procedure for Synthesis of Croconaine Dyes 1a-d

A mixture of the corresponding quinaldinium salt (0.06 mmol), croconic acid (0.03 mmol) and quinoline (0.5 mL) was refluxed in ethanol (6 mL) for 24 h. The solvent was distilled off under reduced pressure to obtain a residue, which was washed with methanol and DMSO to give the corresponding croconaine dyes 1a-c.

1a (80%, based on conversion): mp >300 °C, IR (KBr) νₘₐₓ cm⁻¹ 3035, 1604, 1558, 1454; ¹H NMR (DMF-d₆, 300 MHz) δ 9.14 (1H, d, J = 9.4 Hz), 7.9
(2H, d, J = 9 Hz), 7.82 (2H, m), 7.53 (1H, m), 6.46 (1H, s), 4.14 (3H, s); FAB-MS: m/z Calcd for $\text{C}_{27}\text{H}_{20}\text{N}_{2}\text{O}_{3}$: 420.14. Found: 420.06. Anal. Calcd for $\text{C}_{27}\text{H}_{20}\text{N}_{2}\text{O}_{3}$: C, 77.13; H, 4.79; N, 6.66. Found: C, 76.92; H, 4.65; N, 6.54.

**1b (85%):** mp >300 °C, IR (KBr) $\nu_{\max}$ cm$^{-1}$ 3055, 1654, 1608, 1543; FAB-MS: m/z Calcd for $\text{C}_{27}\text{H}_{18}\text{Br}_{2}\text{N}_{2}\text{O}_{3}$: 578.25. Found: 579.35. Anal. Calcd for $\text{C}_{27}\text{H}_{18}\text{Br}_{2}\text{N}_{2}\text{O}_{3}$: C, 56.08; H, 3.14; N, 4.84. Found: C, 55.74; H, 2.97; N, 5.10.

**1c (85%):** mp >300 °C, IR (KBr) $\nu_{\max}$ cm$^{-1}$ 3055, 1653, 1606, 1546; FAB-MS: m/z Calcd for $\text{C}_{27}\text{H}_{18}\text{I}_{2}\text{N}_{2}\text{O}_{3}$: 672.25. Found: 672.31. Anal. Calcd for $\text{C}_{27}\text{H}_{18}\text{I}_{2}\text{N}_{2}\text{O}_{3}$: C, 48.04; H, 2.70; N, 4.17. Found: C, 48.21; H, 2.90; N, 4.16.

**Procedure for the synthesis of dye 1d:** A mixture of the cholesterol linked quinaldinium salt 3d (0.06 mmol), croconic acid (0.03 mmol) and quinoline (0.5 mL) was refluxed in ethanol (6 mL) for 24 h. The solvent was distilled off under reduced pressure to obtain a residue, which was then subjected to column chromatography over silica gel. Elution of the column with a mixture (1:9) of methanol and chloroform gave 75% of the croconaine dye 1d, mp 290-292 °C, IR (KBr) $\nu_{\max}$ cm$^{-1}$ 2947, 1755, 1660, 1598, 1560; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 8.99 (2H, d, J= 9.4 Hz), 7.55-7.39 (8H, m), 6.39 (2H, s), 5.37 (2H, s), 4.55 (2H, s), 3.95 (6H, s), 2.44 (4H, s), 1.96-0.75 (82H, m); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 196.6, 188.3, 186.8, 183.2, 154.1, 153.1, 140.4, 130.3, 128.2, 124.9, 123.2, 121.4, 118.2, 117.5, 114.3, 111.1, 108.4, 103.3, 81, 73.3, 72.1, 58.2, 57.7, 51.5, 43.8, 41, 37.7, 37.3, 33.4,
31.2, 30.9, 29.7, 29.5, 25.8, 25.4, 24.4, 24.2, 24.1, 22.6, 20.8, 20.3, 13; FAB-MS: m/z Calcd for \( \text{C}_{83}\text{H}_{108}\text{N}_{2}\text{O}_{7} \): 1277.75. Found: 1277.69. Anal. Calcd for \( \text{C}_{83}\text{H}_{108}\text{N}_{2}\text{O}_{7} \): C, 78.02; H, 8.52; N, 2.19. Found: C, 77.85; H, 8.3; N, 2.13.

4.6.4. Determination of Stoichiometry of Complexation

In the Jobs plot method, the total molar concentration of the two binding partners (e.g. dye and metal ions) is held constant, but their mole fractions are varied. The fluorescence intensity (or peak area) that is proportional to complex formation is plotted against the mole fractions of these two components. The maximum on the plot corresponds to the stoichiometry of the two species if sufficiently high concentrations are used.

4.6.5. Determination of Association Constants

The binding affinities of the semisquaraine dyes were calculated using Benesi-Hildebrand equation 4.7 for 2:1 stoichiometry, where \( K \) is the equilibrium constant, \( I_0 \) is the fluorescence intensity of the free dye, \( I \) is the observed fluorescence intensity in the presence of metal ions and \( I_s \) is the fluorescence intensity at saturation. The linear dependence of on the reciprocal of square root of the metal ion concentration indicates the formation of a 2:1 complex between the dye and the metal ion.
\begin{equation}
\frac{1}{I-I_0} = \frac{1}{I-I_s} + \frac{1}{K(I-I_0)[M^{n+}]^{1/2}} \quad \text{eq (4.7)}
\end{equation}

4.6.6. Preparation of Electrodes

To prepare the SnO\textsubscript{2} Electrodes (OTE/SnO\textsubscript{2}), the SnO\textsubscript{2} (15\%) suspension obtained from Alfa chemicals was first diluted (1 mL of SnO\textsubscript{2} solution with 47 mL of water and 2 mL of ammonium hydroxide) to obtain 0.3\% solution. 500 \textmu L of this diluted suspension was spread over 2 cm\textsuperscript{2} area of an optically transparent electrode (OTE). These electrodes were then air-dried on a warm plate and annealed in an oven at 673 K for 1 h. Details on the preparation of electrodes can be found elsewhere.\textsuperscript{42}

To prepare the TiO\textsubscript{2} Electrodes (OTE/TiO\textsubscript{2}), TiO\textsubscript{2} colloids were first prepared by hydrolyzing titanium isopropoxide in glacial acetic acid solution followed by autoclaving the suspension at 507 K for 12 h. The details of the procedure can be found elsewhere.\textsuperscript{43} 500 \textmu L of the suspension was spread over the OTE plate using a syringe. After air drying the electrodes were annealed in an oven at 673 K for 1 h.

4.6.7. Photoelectrochemical Measurements

Photoelectrochemical measurements were performed using a standard two-compartment cell consisting of a working electrode and Pt wire gauze counter electrode. All photoelectrochemical measurements
were carried out in acetonitrile containing 0.5 M LiI and 0.05 M I₂. Photocurrents were measured using a Keithley model 2601 source meter. A collimated light beam from a 150 W Xenon lamp with a 400 nm cut-off filter was used for excitation of the electrodes. A Bausch and Lomb high intensity grating monochromator was introduced into the path of the excitation beam for selecting appropriate wavelength. The incident photon-to-photocurrent efficiency (IPCE) at various excitation wavelengths was determined from the equation 4.8, where \( i_{sc} \) is the short-circuit photocurrent (A/cm\(^2\)), \( I_{inc} \) is the incident light intensity (W/cm\(^2\)) and \( \lambda \) is the excitation wavelength.

\[
IPCE(\%) = \frac{i_{sc} \times 1240}{I_{inc} \lambda} \times 100
\]  
\text{ eq (4.8)}

### 4.7.  REFERENCES


Croconaines as Probes and Sensitizers


Chapter 4


Croconaines as Probes and Sensitizers


