PREFACE

Semisquaraine, squaraine and croconaine dyes have been the subject of many recent investigations owing to their excellent optical and electronic properties. The intramolecular charge-transfer (CT) character of the $S_0$-$S_1$ electronic excitation combined with an extended conjugated $\pi$-electron network gives rise to the intense bands observed in the visible to near-infrared (NIR) region for these dyes. These peculiar spectral features along with remarkable stability and wide molecular structure diversity promoted their exploitation in a number of applications including photoconductivity, data storage, light emitting field-effect transistors, solar cells, non-linear optics, fluorescent probes, fluorescent NIR dyes, sensors, fluorescence patterning, photodynamic therapy (PDT) and in two-photon absorption (TPA) applications. Photochemistry of these systems has been extensively studied and many derivatives of the parent squaraine and croconaine moieties have been synthesized mostly for improvements in various applications. In this context, the present thesis entitled “Synthesis and Study of Photophysical and Metal Ion Binding Properties of a Few Novel Semisquaraine and Croconaine
"Dyes" describes our efforts towards the design of a few novel semisquaraine and croconaine dyes and study of their metal ion binding and light harvesting properties under different conditions.

The thesis has been divided into four chapters, of which the first chapter describes a brief account on semisquaraine and croconaine dyes. Focus was placed on the various methods reported for these derivatives. Further, emphasis has been given to the various applications reported in the literature for the semisquaraine and croconaine dyes.

The second chapter of the thesis describes the synthesis and characterization of a few novel quinaldine based semisquaraine dyes 1a-k and 2a-k derived from dibutyl squarate and squaric acid, respectively. Reaction of the quinaldinium salts containing electron withdrawing groups with squaric acid gave the corresponding squaraine dyes in quantitative yields, whereas the semisquaraine dye intermediates were isolated in quantitative yields from the quinaldinium salts containing electron donating groups. Surprisingly, when the quinaldinium salts substituted with electron donating groups were reacted with dibutyl squarate, we isolated semisquaraine derivatives, which were found to be structurally
different from those obtained with squaric acid. Characterization of these dyes on the basis of spectroscopic and analytical evidence including the single crystal X-ray structure analysis indicated that the semisquaraine dyes obtained through squaric acid and dibutyl squarate were found to be Z- and E-isomers, respectively.

Theoretical calculations showed that the geometrical semisquaraine dye E-isomer showed a dihedral angle of 9.5° between the quinoline and squaryl rings, whereas a dihedral angle of 32° was observed for the Z-isomer. Both the semisquaraine derivatives showed intense absorption maxima in the region of 450-550 nm with negligible fluorescence quantum yields. Notably, the structural differences of the semisquaraine isomers were manifested in the different reactivity exhibited by these two dyes. The Z-isomer of the semisquaraine dye reacted readily with a second nucleophilic enamine to form the unsymmetrical squaraine dye, while the E-isomer required the hydrolysis of the butyl adduct before the dye reaction. The uniqueness of this study is that, although semisquaraine dyes have been understood to be the intermediates formed during the squaraine dye reaction, this is for
the first time the existence of semisquaraine isomers have been proposed and observed.

The squaryl ring of the semisquaraine dyes have electron rich oxygen atoms, which enable them to act as stable bidentate ligands for various metal ions. In this regard, a comparative study of the metal ion binding properties of the semisquaraine dye Z-isomers 1a-e and E-isomers 2a-e is presented in the third chapter of the thesis. Among the various mono and divalent metal ions, it was observed that these semisquaraine dyes showed significant interactions with mercuric ions. The addition of one equivalent of mercuric ions to semisquaraine Z-isomer in acetone, resulted in the formation of a new blue shifted band in the absorption spectrum, together with a concomitant increase in the fluorescence intensity of ca. 18-fold. This resulted in a color change of the solution from deep red to orange and visual ‘turn on’ fluorescence intensity in the presence of Hg$^{2+}$ ions.

Similarly, the addition of mercuric ions to a solution of the E-isomer, caused a decrease in the absorption maximum of the dye at 475 nm with a concomitant ca. 42-fold enhancement in the fluorescence intensity. In the presence of Hg$^{2+}$ ions, we observed
change in color from deep orange to colorless solution and visual ‘turn on’ emission intensity at 467 nm. The association constants for the binding of mercuric ions with the semisquaraine Z- and E-isomers for 1:1 stoichiometry have been estimated and are found to be 2.4 ± 0.1 x 10^5 M^{-1} and 2.2 ± 0.1 x 10^4 M^{-1}, respectively. The Z-isomer-Hg^{2+} complex was found to be one order more stable than the E-isomer-Hg^{2+} complex, indicating the importance of the orientation of groups in the complexation. The binding site of the two semisquaraine dyes was characterized through various experimental techniques such as FT-IR, $^1$H NMR and $^{13}$C NMR spectral analysis, which showed that these dyes bind to Hg^{2+} ions through the electron rich carbonyl groups.

To understand whether the semisquaraine dyes can act as selective probes for mercuric ions under aqueous medium, the interaction of the semisquaraine dyes with various mono and divalent metal ions were studied under different micellar conditions. Of all the conditions examined, it has been observed that a solvent system consisting of a mixture (9:1) of water and acetone containing sodium dodecyl sulfate (SDS) has been found to be very effective with respect to the stability of the semisquaraine dye as
well as to the selectivity and sensitivity of the metal ion binding event. Our results indicated that the Z-isomer, which showed high binding affinity towards the mercuric ions in acetone, showed selective binding interactions under the aqueous medium as well with an association constant ($K$) of $4.0 \pm 0.1 \times 10^4$ M$^{-1}$. In contrast, the E-isomer, which showed one order lower binding affinity, exhibited negligible interactions with Hg$^{2+}$ ions under identical conditions. The selectivity of semisquaraines towards Hg$^{2+}$ ions can be attributed to the soft acid nature as well as the size of the metal cation. Results of these investigations reveal that the semisquaraine dyes selectively interact with Hg$^{2+}$ ions as compared to other biologically and environmentally relevant metal ions like Li$^+$, Na$^+$, K$^+$, Ag$^+$, Ca$^{2+}$, Mg$^{2+}$, Zn$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, Cu$^{2+}$ and Fe$^{3+}$ ions, thereby indicating their potential use as efficient dual chromogenic and fluorogenic probes for Hg$^{2+}$ ions.

The synthesis and study of metal ion binding and light harvesting properties of a few quinaldine-based croconaine dyes 1a-d form the subject matter of chapter four of the thesis. These dyes were synthesized in quantitative yields by the condensation reaction between the quinaldinium salts and croconic acid and have
been characterized based on spectroscopic and analytical evidence. These dyes showed absorption maximum in the infrared region (IR, 840-870 nm) with high molar extinction coefficients ($\varepsilon = 1.5 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$). As observed in the case of the semisquaraine dyes, the croconaine dyes could also act as bidentate ligands for various metal ions. The addition of divalent metal ions resulted in decrease in the absorption maximum of the dye at around 870 nm with the formation of a new blue shifted band at 735-805 nm. These dyes exhibited negligible fluorescence emission, but upon binding with metal ions showed an enhancement in fluorescence intensity in the infrared region at around 810-820 nm. These dyes showed high affinity for divalent metal ions with high association constants in the order of $10^5$-$10^7 \text{ M}^{-1}$, while the monovalent metal ions showed negligible affinity. The stoichiometry of the complexes with divalent metal ions was found to be 2:1 and exhibited selectivity in the order $\text{Zn}^{2+} > \text{Pb}^{2+} >> \text{Cd}^{2+} >> \text{Mg}^{2+} \approx \text{Hg}^{2+} \approx \text{Ca}^{2+} \approx \text{Ba}^{2+}$.

As the croconaine dyes have strong absorption in the infrared region, we have investigated their potential applications in light harvesting systems. These dye molecules found to undergo intermolecular interactions and form H-type aggregates. By making
use of this property, we have demonstrated the possibility of tuning the absorptive range of a photoelectrochemical cell using the croconaine dyes. The excited singlet of the monomeric dye quickly deactivated (4-7 ps) without undergoing intersystem crossing to generate triplet excited state. The triplet excited-state of the croconaine dye produced via triplet–triplet energy transfer method showed relatively a long lifetime of 7.2 μs.

The dye molecules when deposited as thin film on optically transparent electrodes or on nanostructured TiO$_2$ film, they formed H-aggregates with a blue-shifted absorption maximum around 660 nm. The excitons formed upon excitation of the dye aggregates resulted in charge separation at the TiO$_2$ and SnO$_2$ interface. The H-aggregates in the thin film were photoactive and produced anodic current when employed in a photoelectrochemical cell. These studies reveal that the suitably substituted croconaine dyes with electron rich carbonyl groups at the croconyl moiety can have potential applications as molecular probes for divalent metal ions and as sensitizers in light harvesting devices.

**Note:** The numbers of various compounds given here correspond to those given under the respective Chapters.
1.1. INTRODUCTION

Squaraines and croconaines belong to a class of dyes having resonance stabilized zwitterionic structure, while semisquaraine dyes are the intermediate structure in the squaraine dye formation reaction (Chart 1.1).\textsuperscript{1,2} These dyes have attracted increasing attention in recent years due to their favourable spectroscopic properties such as narrow absorption bands with high molar absorption coefficients ($\epsilon > 10^5$ M\textsuperscript{-1}cm\textsuperscript{-1}) and moderate fluorescence quantum yields in polar and aqueous media.\textsuperscript{3} Attracted by these features, the squaraine and croconaine dyes have been utilized as
deeply coloured and fluorescent materials for various applications such as optical recording\textsuperscript{4} solar energy conversion\textsuperscript{5,6} electrophotography\textsuperscript{7} nonlinear optics\textsuperscript{8} photodynamic therapy\textsuperscript{9} multiphoton absorption\textsuperscript{10} biochemical labelling\textsuperscript{11} and chromo- and/or fluorogenic probes\textsuperscript{12} for sensing of pH\textsuperscript{13} cations\textsuperscript{14,15} anions\textsuperscript{16} and neutral molecules\textsuperscript{17,18} as well as for the study of self-assembled dye aggregates\textsuperscript{19}.

The ground (\(S_0\)) and the excited (\(S_1\)) electronic states of these systems are intramolecular charge transfer (CT) in nature\textsuperscript{20}. The aromatic/heterocyclic moiety and the oxygen atoms are electron donors and the central four membered ring is an acceptor. The \(S_0\)-\(S_1\) electronic excitation involves a charge transfer character (CT) process that is primarily confined to the central \(C_4O_2\) or \(C_5O_3\) rings in squaraines and croconaines, respectively. In these cases, the intramolecular charge transfer takes place from the oxygen atoms of the squaryl ring and the aromatic/heterocyclic moiety to the central acceptor \(C_4O_2\) or \(C_5O_3\) unit. Thus the squaraine and croconaine dyes can be generally described as
Semisquaraines and Croconaines

Compounds containing two donor moieties (D) connected to a central \( C_4O_2 \) or \( C_5O_3 \) electron withdrawing group (A) forming a donor-acceptor-donor (D-A-D) system, whereas the semisquaraines may be considered to be a donor (D) in conjugation with an acceptor \( C_4O_2 \) (A) unit.\(^{21}\) The intramolecular charge transfer character of the \( S_0-S_1 \) transition combined with an extended \( \pi \)-electron network, gives rise to the observed sharp and intense bands in the visible to infrared region for these dyes.

Due to the favourable photophysical properties, the squaraine chemistry has been at the centre stage of research from both fundamental and technological viewpoints. In contrast, the potential of the semisquaraine dyes has been limited only to the synthesis of unsymmetrical squaraine dyes and their applicability has remained unexplored. Similarly, the croconaine dyes, which are the higher homologues of squaraine dyes, have received less attention due to the difficulties associated with their synthesis. Due to these reasons, the design and development of novel semisquaraine and croconaine dyes are of paramount importance for potential optoelectronic applications. This Chapter presents a brief overview on the various synthetic strategies adopted for the synthesis of semisquaraine derivatives and their applications. In addition, the importance of the croconaine dyes is discussed with particular emphasis on the applications of this class of dyes.
Further, the objectives of the present investigations are also briefly described in this Chapter.

1.2. SYNTHESIS OF SEMISQUARAIN DYES

The reaction between squaric acid and an electron rich aromatic or heterocyclic species yields squaraine dyes through the intermediacy of the semisquaraine dyes. The typical squaraine synthesis is carried out by condensation of 1 equivalent of squaric acid (1) with 2 equivalents of aromatic or heterocyclic compounds. For example, the synthesis of aniline based dye 4 has been achieved by the reaction of two equivalents of the corresponding aniline derivative 2 with 1 equivalent of squaric acid in an azeotropic solvent mixture of butanol-benzene (Scheme 1.1). The reaction
Semisquaraines and Croconaines mechanism for the squaraine dye reaction proposed by Sprenger and Ziegenbein, shows that this reaction takes place through the formation of an intermediate system formed by the nucleophilic attack of the aromatic compound (Ar-H) at the carbonyl carbon in the half-ester of squaric acid (Scheme 1.2).\textsuperscript{22} This intermediate system is popularly known as the semisquaraine dye. The subsequent attack of another Ar-H followed by dehydration gives the squaraine dye. However, the separation of the semisquaraine, thus formed, from the squaraine dye was difficult and performed only by means of special procedures and under different conditions.\textsuperscript{23}

Later, alternate reaction strategies have been reported for the synthesis of semisquaraine derivatives in quantitative yields by employing

\begin{align*}
\text{Scheme 1.2}
\end{align*}
derivatives of squaric acid.\textsuperscript{24} Among them, the most widely employed method is the use of dialkyl squarates reported by Terpetschnig and Lakowicz.\textsuperscript{25} In this strategy, the equimolar amounts of heterocyclic compounds such as 1,2,3,3-tetramethylindolium salt \textbf{10} is reacted with diethyl or dibutyl squarates, followed by hydrolysis to afford indolinyldenemethyl-substituted semisquaraine dye \textbf{12}. (Scheme 1.3).\textsuperscript{11a} This procedure was applicable to benzothiazolium and benzoselenazolium salts with an active methyl group at the 2-position.

![Chemical structure](image)

\textbf{Scheme 1.3}

Green and Neuse\textsuperscript{26} reported a Friedel-Crafts type reaction of aromatic systems with 3,4-dichloro-3-cyclobutene-1,2-dione in the presence of AlCl\textsubscript{3} to obtain semisquaraine derivatives in quantitative yields (Scheme 1.4). Squaryl chloride or 3,4-dichloro-3-cyclobutene-1,2-dione (\textbf{13}) employed in the reaction was prepared from squaric acid through chlorination with thionyl chloride.\textsuperscript{27} The monosubstituted squaryl chlorides obtained were converted to semisquaric acids \textbf{15} by hydrolysis under acidic conditions.
Law and Bailey\textsuperscript{28} have employed \([2+2]\) cycloaddition reaction of tetraethoxyethane with arylacetylchloride \(16\) to obtain semisquaraine dye \(18\) (Scheme 1.5). The semisquaraine dyes prepared through the various reaction pathways are converted to the unsymmetrical squaraine dyes by condensation with a second different aromatic or heterocyclic derivative. The synthesis and isolation of the semisquaraine derivatives through the various reaction pathways indicated above enabled the easy synthesis of different unsymmetrical squaraine dyes with varying donor strengths. Such effective procedures provide immense possibilities to design a variety of
squaraine dyes with tunable optical properties in the visible to the near-infrared (NIR) range.

Even though the reaction of aromatic or heterocyclic systems with squaric acid takes place through the intermediacy of semisquaraine, the isolation of the semisquaraine dye as the exclusive product was not observed in this reaction pathway. In this context, we observed that the isolation of the intermediate products in the squaraine dye reaction depends mostly on the nucleophilicity of the heterocyclic system used. For example, when we carried out the condensation reaction between the quinaldinium salt $19a$ and squaric acid in 2:1 equivalents, (Scheme 1.6), we did not get the expected squaraine dye; instead a different product having much shorter wavelength absorption was obtained quantitatively.

Since squaraine dyes, in general, are brightly coloured compounds with absorption in the near-infrared region, the progress of the reaction was monitored by absorption spectroscopy in addition to the thin layer chromatography. No absorption band in the near-infrared region was observed during the initial stages of the reaction. However, an absorption band around 485 nm was observed within 4 h of the reaction and this band increased in intensity with reaction time. The reaction mixture following work up and column chromatography after 30 h, gave the semisquaraine dye $20a$ as the major product.
Further investigation of the effect of various substituents revealed that substituents with electron donating groups such as the hydroxyl or the ethoxy (19a,b) gave only the corresponding semisquaraine dyes 20a-b in quantitative yields. In contrast, the salts with electron withdrawing substituents (19c-g) like the halogen substituted, nitro or the cyano gave the corresponding squaraine dyes 21c-g, through the intermediacy of the semisquaraine dyes 20c-g under analogous conditions. The variation in the reactivity of the substituted quinaldinium salts 19a-g in the dye reaction can be explained on the basis of the electronic effects of the different substituents.
Squaraine dye forming reaction involves the reaction between an electron rich aromatic derivative and squaric acid. The success of the reaction depends mainly on the nucleophilicity of the aryl species. In the present study, the nucleophile is an enamine formed from the quinaldinium salt, which reacts with squaric acid resulting in the formation of the semisquaraine dye. Subsequently, the semisquaraine undergoes further reaction with another moiety of the enamine to give the squaraine dye. The presence of electron-donating groups on the benzene ring of the quinaldinium salts 19a-b reduces the acidity of the hydrogen atoms of the 2-methyl group, thereby, decreasing the formation of the enamine nucleophile. Nevertheless, the enamine formed reacts with squaric acid resulting in the corresponding semisquaraine dyes 20a-b. Furthermore, the electrophilic terminus of these semisquaraines is rendered less reactive by the electron-donating substituents and hence further reaction with the less acidic salts becomes extremely difficult. As a result, the reaction stops with the formation of the semisquaraine only in the case of the salts 19a-b.

In contrast, in the presence of neutral (19c), electronegative (19d,e) and electron-withdrawing substituents (19f,g), the hydrogen atoms of the 2-methyl group of the quinaldine moiety are relatively more acidic and thereby favours the formation of the enamine nucleophile very efficiently. These salts yield higher concentrations of the nucleophile and hence results in the formation of the corresponding squaraine dyes 21c-g in quantitative
yields through the intermediacy of the semisquaraine intermediates \textbf{20c-g}. Thus, by proper tuning of the nucleophilicity of the quinaldinium salt employed in the squaraine dye reaction, one can obtain semisquaraine or squaraine dye in quantitative yields.

\section*{1.3. \textbf{PHOTOPHYSICAL PROPERTIES OF SEMISQUARAINE DYSES}}

Semisquaraine dyes have an absorption in the region 350-500 nm region depending on the aromatic donor group present. For example, the semisquaraine based on \textit{N,N}-dialkylated aniline derivatives have absorption maxima in the region 400-450 nm and emission maxima at 450-500 nm,\textsuperscript{30} whereas semisquaraine dyes based on heterocycles such as benzothiazoles or indoles have absorption in the range 450-500 nm.\textsuperscript{31} Recently, Hecht and co-workers\textsuperscript{32} reported semisquarine dye \textit{22} having \textit{ortho}-dialkylamino substituents (Chart 1.2). This semisquaraine dye exhibited absorption maxima at 355 nm in nonpolar (methylene chloride) and polar nonprotic solvents (acetonitrile), while polar protic solvents (methanol) induced a dramatic hypsochromic shift to 269 nm. Furthermore, they observed that strong emission occurs only in methanol ($\lambda_{\text{ex}} = 269$ nm, $\lambda_{\text{em}} = 354$ nm). These results suggest the presence of an intramolecular N-H-O hydrogen bonding in nonprotic media, while in protic solvents such a bonding is inhibited, resulting in the formation of a