PREFACE

Functional dyes are being increasingly used as key materials in a number of new technological applications, such as laser optical recording systems, thermal writing displays, laser printing, organic photovoltaics and photodynamic therapy. With the current availability of low cost semiconductor lasers emitting in the near infrared region (NIR), there is much interest in the development of new NIR absorbing dyes. The main objective of the present investigation was to synthesize some novel ruthenium and squaraine based dyes with improved absorption in the visible and near-infrared region capable of undergoing efficient photoinduced electron transfer. Another objective was to synthesize near-infrared absorbing dyes capable of generating singlet oxygen on photoexcitation.

Chapter 1 of the thesis presents a brief review covering some aspects of the current theoretical understanding of the structure-property relationships of dyes, with specific reference to cyanine and squaraine dyes.

Chapter 2 deals with the synthesis and photophysical characterization of the ligand, 4,4′-bis(p-dimethylamino)-α-styryl-2,2′-bipyridine (7) and some of its ruthenium complexes (8 and 9). The ligand (7) undergoes mono and di-protonation in the ground state with pKa values of 4.6 and 3.2 respectively. Excitation of the ligand results in the formation of its protonated species, due to substantial enhancement in its basicity (ΔpKa = 8.0). This may be attributed to a photoinduced intramolecular charge transfer process, which can result in enhanced charge density
on the pyridyl moiety. The strong ability of the ligand (7) to complex with transition metal ions, results in significant changes in its absorption spectrum which can be used as a method for detecting trace amounts of transition metal ions in solution. The triplet excited state properties of the ruthenium complexes as well as photosensitization of nanoporous TiO₂ films using these dyes were investigated.

The third Chapter of this thesis describes our efforts to synthesize water soluble squaraine dyes possessing high triplet quantum yields. A water soluble squaraine dye, bis(3-carboxymethylbenzselenanazol-2-ylidine)squaraine and its parent compound bis(3-methylbenzselenanazol-2-ylidine)squaraine were synthesized and characterized. The photophysical properties of these dyes in homogeneous and microheterogeneous media have been investigated. Compound 15 is only weakly fluorescent in aqueous media. In water, 15 forms dimer aggregates with an absorption band blue shifted to that of the monomer. The blue shift in the absorption band is indicative of formation of H-type aggregates which can be attributed to hydrophobic interaction between the chromophoric units of the dye. Heavy atom induced spin-orbit coupling due to the presence of selenium atoms within the molecular framework of the dyes, results in substantially high triplet quantum yields (\(\phi_T = 0.26-0.29\)), in contrast to the generally low intersystem crossing efficiencies normally observed for squaraines. Photoinduced electron transfer and singlet oxygen generation from the excited triplet states of these dyes have also been investigated.

An alternative strategy for enhancing the intersystem crossing efficiency in squaraines is to use substituents possessing low lying n-\(\pi^*\) states, since the oscillator
strengths for $S_0 \rightarrow T_1$ is much greater for $n-\pi^*$ than for $\pi-\pi^*$ transitions. The last
Chapter of the thesis (Chapter 4) describes photophysical studies on such squaraine
dyes possessing nitrogen heterocycles, which are expected to possess low-lying $n-\pi^*$
states. The effect of solvent polarity on the emission properties of bis($N$-
methylquinolin-2-ylidine)squaraine was investigated in protic and non-protic
solvents. The absorption and emission maxima show a hypsochromic shift with
increase in solvent polarity in both types of solvents. The fluorescence quantum
yields of the dye, on the other hand, increases with solvent polarity in aprotic
solvents, whereas it decreases with increase in solvent polarity in protic solvents. This
effect can be interpreted to the interchange of the lowest $n-\pi^*$ singlet state in
nonprotic solvents to a $\pi-\pi^*$ state in protic solvents, due to hydrogen bonding. The
substantial triplet yields observed for some of these dyes confirm $n-\pi^*$ character of
the lowest excited state. A novel NIR absorbing dye, bis($N$-methylacridin-9-
ylidine)squaraine belonging to this class of dyes has been synthesized and its
photophysical properties investigated. The absorption maximum of the dye ($\lambda_{\text{max}} =
900$ nm), is substantially red shifted compared to those of squaraine dyes reported
earlier in the literature. The triplet quantum yield of this dye was estimated to be $0.15$.

Note: The compound numbers listed in this preface refer to those given in different
Chapters of this thesis.