PREFACE

Design and synthesis of \( \pi \)-conjugated oligomers and polymers with novel optical and electronic properties is of central importance in the area of advanced material research. One of the major goals of these studies is the fundamental understanding of the structure-property relationship that might form the basis for the design of novel materials with tailored properties. In this context, polymers with low optical band gap (\( E_g \)) have great significance due to their application as intrinsic electronic conductors, NLO and NIR active materials. Several strategies have been developed for the synthesis of low \( E_g \) polymers such as increasing the quinoid character of the aromatic moieties, rigidification of the polymer backbone and the use of monomers with strong donor-acceptor interactions. An alternative approach is the use of organic dye molecules, which possess inherently low HOMO-LUMO separation. In this context, squaraine dyes have generated considerable interest because of their unique optical and electronic properties. The main objective of the present study is the designing of low optical band gap squaraine polymers, their model systems and investigation of their optical, electronic and aggregation properties.

Each chapter of the thesis is presented as an independent unit and therefore the structural formulae, schemes, figures and references are numbered chapter wise. The main findings of each chapter are given in the abstract.

In the first chapter of the thesis, a brief introduction to the low band gap polymers is given followed by a review of various strategies developed for the band gap reduction with special emphasis on minimization of bond length alternation and enhanced donor-acceptor interaction of the backbone. An overview of the literature of squaraine dye derived oligomers and polymers are presented and their properties are described. Attention has been paid to discuss the aggregation induced changes in the optical properties of conjugated
polymers and their model systems, which is relevant to the studies of low $E_g$ polymers.

The second chapter describes a novel approach for the designing of extremely low band gap polysquaraines with intense near-IR absorption and high intrinsic conductivity. This approach illustrates the synthesis of several electron rich 1,4-dialkoxydivinylbenzene-bridged bispyrroles, and their copolymerization with squaric acid. The solution UV-vis-NIR spectra of the new polymers showed several maxima between 772-1040 nm with onset of absorption ranging from 1120-1300 nm. The remarkable shift in the absorption spectra of the new polysquaraines towards the near-IR region indicates high degree of conjugation and planarity of the polymer backbone. The band gaps of these polymers are around 1 eV with the lowest value of 0.79 eV for polysquaraine with shortest alkyl chains. The conductivities of these polymers could be modulated between $10^{-7}$ to $10^{-4}$ S/cm by varying the length of the alkyl side chains. This was in agreement with the molecular packing data obtained from the X-ray diffraction analysis, which revealed an interdigitated arrangement. The present study demonstrates that the donor-acceptor strategy can be successfully employed for lowering of the band gaps in polysquaraines and their optical and electronic properties can be effectively controlled by tailoring the length of the alkyl side chains.

The third chapter of the thesis deals with the aggregation behaviour of polysquaraines in solution. The UV-vis-NIR spectra of the new polymers showed more than one absorption maximum, the intensities of which vary with solvent and temperature, indicating the existence of interchain aggregates of the rigid planar structures. Temperature dependent changes in the absorption spectra of polysquaraines provided insight into the existence of $\pi$-stacked assembly in solutions. At higher temperatures, the disruption of the aggregates occurs and consequently a marginal change can be seen in the absorption spectra. The existence of stable aggregates was further supported by the concentration
dependent studies at higher temperatures. Interesting spectral changes were observed in mixed binary solvent systems such as THF-water and toluene-DMSO with varying compositions. In order to have a better understanding of the aggregation behaviour, two model squaraine dyes with extended conjugation were synthesized and their aggregation behaviour was compared with that of the polysquaraines. The model squaraine dyes form blue shifted H-type aggregates in toluene-DMSO whereas the polysquaraines undergo dis ordering of the π-stacked assembly to a "frustrated" assembly, which can be considered as "pseudo" H-aggregates.

In the last chapter, synthesis of some model squaraine dyes and the study of their aggregation behaviour particularly in mixed water-DMSO solvents are described. The synthesis and studies of these molecules are relevant because they serve as model compounds for the low band gap polysquaraines. Even though, the aggregation behaviour of several squaraine dyes has been studied, a group of dyes, which received least attention, is squaraine dyes derived from conjugated pyrrole derivatives. The nature and stability of the aggregates are remarkably influenced by the composition of the solvent mixtures as well as the length of alkyl chain substituents of the dyes. Depending upon the nature of the alkyl side chains, these squaraine dyes form different kinds of H-type and J-type aggregates in solution and solid-state.

The optical band gap of the reported polymers are one of the lowest ever reported. The intense NIR absorption of the reported polysquaraines is a rare property of π-conjugated polymers in general. The aggregation behaviour of polysquaraines is unique when compared to that of other π-conjugated polymers. The alkyl side chains of the polysquaraines and their model systems play significant role in controlling the optical, electronic and aggregation properties. The results presented here are expected to lead the designing of new organic materials with novel optoelectronic properties.