

ABSTRACT

The thesis entitled “**Aggregation and Prototropic Behavior within Ionic Liquid based Media**” is concerned with understanding the behavior of important prototropic probes and cyanine dyes within neat and aqueous ionic liquid (IL) systems. Specifically, prototropism of common prototropic probes and aggregation properties of various cyanine dyes that reveal important properties of neat and aqueous IL media are explored with detailed optical spectroscopic investigations to understand the unique role of these unusual substances. The long term aim is to establish ILs as important and preferred media as far as prototropism and dye aggregation are concerned.

ILs have received increased attention from both academia and industrial research communities due to their unusual features. Many chemical processes demonstrate effects and outcomes that are very different within a milieu constituted of *only* ions as opposed to a molecular solvent. ILs also show increased applicability in a variety of analytical methodologies encompassing electroanalysis, separation, extraction, spectrometry, and sensing. The recent investigations on ILs are partly due to their *potential* environmentally-benign nature as well. Due to their important absorbance and luminescence properties, various probes are used routinely to determine the properties of solvent media. Solvent milieu, in turn, may affect the photophysical properties of such probes resulting in altered aggregation and prototropic behavior. The importance of prototropism is manifested through various applications, such as, in developing effective photoprotecting agents, in laser dyes, in photodynamic therapy, and in developing fluorescence probes for biological molecules, among other. Furthermore, molecular aggregates of dyes, specifically those of cyanines, are known to play important role in many technological applications, such as, in photography, as sensors, as photoconductors, in biology, in medicine, in

nanotechnology through the formation of self-assembled materials, in future light harvesting systems, to name a few. Recent studies by numerous researchers, have demonstrated the potential of ILs in altering the behavior of certain dyes and prototropic probes. The hypothesis that ILs and aqueous IL systems afford altered (and perhaps unusual) outcomes towards Prototropism and aggregation is thoroughly tested in this thesis.

The Chapter titled “Prototropic Behavior of Naphthols within Neat and Aqueous Mixture of Ionic Liquids” deals with the study of the prototropic behavior of 1- and 2-naphthols in IL based media. The study has been divided into two parts. The first part of the Chapter highlights IL-controlled excited-state behavior of naphthols. Unusual excited-state properties of 1- and 2-naphthols dissolved in various ILs that depend heavily on the molecular architecture of the IL cation are reported. Specifically, we found that the fluorescence from the anionic prototropic form of the photoacid is observed when the solubilizing IL contains pyrrolidinium and C2-substituted imidazolium cations, whereas no fluorescence characteristic of naphtholate is seen when solubilizing IL is composed of imidazolium cation having acidic C2 proton. This is attributed to the formation of a ‘dark’ complex between imidazolium cation (Im^+) and excited naphtholate involving C2-H of Im^+ . The second part describes the effect of addition of water-miscible ILs, [bmim][BF₄], [bmim][OTf], and [bmpyrr][OTf], on photophysical properties of 2-naphthol at various pH. Electronic absorbance behavior of 2-naphthol dissolved in aqueous mixtures of ILs is observed to be similar to that found in water at different pH. The excited state properties, however, are changed dramatically in presence of ILs. Presence of imidazolium ILs results in significant quenching of the fluorescence emission from 2-naphtholate anion. On the contrary, pyrrolidinium IL does not quench the fluorescence from the anionic species. Aromatic imidazolium cation acts as an electron/charge acceptor during the quenching process where

formation of a weakly fluorescent complex between imidazolium cation and excited 2-naphtholate anion possibly involving the acidic C2 proton of imidazolium is proposed. Due to the absence of such acidic proton, nonaromatic pyrrolidinium cation is not able to form a complex with excited 2-naphtholate and cannot act as an electron/charge acceptor.

The Chapter titled “Prototropism of Acridine within Neat and Aqueous Mixture of Ionic Liquids” deals with the study of prototropic behavior of acridine when dissolved in neat and aqueous mixture of ILs. The study has been divided into two parts. The first part of the Chapter describes the role of the acidity of IL cation on the prototropic behavior of acridine. We observed that acidity of IL cation can tune the prototropism of acridine in the excited-state. More specifically, fluorescence emission from the protonated form of acridine is observed when it is dissolved in imidazolium ILs having acidic protons at C2 position, whereas neutral acridine emission is observed in case of pyrrolidinium ILs due to the absence of such acidic proton. Interestingly, acidity of C2-methyl substituted imidazolium ILs is found to be temperature dependent and hence fluorescence from the protonated as well as neutral forms of acridine can be observed depending upon the temperature. In the second part, effect of addition of small amount of aqueous acid or base to acridine dissolved in ILs is studied. It is found that addition of small amount of such aqueous component can fine tune the properties of ILs and make them suitable medium so as to have desired prototropism of acridine. Protonation and deprotonation of acridine dissolved in ILs can be achieved irrespective of the identity of the IL, in ground as well as in excited state, by addition of small amount of 0.1 M aqueous HCl or 1 M aqueous NaOH, respectively.

The Chapter titled “Aggregation Behavior of Cyanine Dyes in Neat and Aqueous Mixture of Ionic Liquids” is divided into two parts. The first part describes the aggregation behavior of

cyanine dyes TDBC, DMTC in neat and 1 M aqueous NaOH added ILs. It was found that TDBC and DMTC are triggered to form fluorescent H-aggregates by addition of only 2 wt% 1 M aqueous NaOH to ILs 1-alkyl-3-methylimidazolium tetrafluoroborate $[C_n\text{mim}][\text{BF}_4]$, whereas addition of 2 wt% 1 M aqueous NaOH to cyanine dye solutions in ILs with other anions results in J-aggregation. H-aggregation is unambiguously demonstrated to be specific to the $[\text{BF}_4]^-$ -based ILs. We propose the different hydrolytic properties of BF_4^- as compared to other anions in ILs to be the reason for this dramatic difference in IL-dependent cyanine dye aggregation. In the second part, effect of addition of ILs on the aggregation behavior of a cyanine dye, TDBC, was investigated. In basic aqueous buffer solutions ($\text{pH} \geq 10$), TDBC preferably exists in its J-aggregated form. Addition of > 5 wt% hydrophilic ILs is observed to disrupt the TDBC J-aggregates converting them to monomeric form most likely because of the interaction between bulky IL cation and the J-aggregates in a time dependent manner. This is evidenced by the observed increase in monomer band absorbance at the expense of the absorbance band due to J-aggregates over time. Inorganic salts at similar molar concentrations do not cause this phenomenon but instead induce TDBC precipitation. At low concentrations (< 5 wt%), the added IL acts similar to the inorganic salts reducing the overall absorbance of TDBC in the solution most likely due to cation exchange causing TDBC precipitation. The unique and dual behavior of ILs as additives toward affecting cyanine dye aggregation is demonstrated.

Chapter titled “Conclusions and Future Perspectives” presents highlights and salient features of the work presented in the thesis. In brief, it is concluded that ILs are unique in affecting prototropism and aggregation due to their inherent architecture. Further, it is emphasized that the photophysical behavior of probes and dyes in IL based media can be different than that in conventional organic solvents. All-in-all, the findings of this work will help

in understanding the different types of molecular interactions within IL-based media and could be of potential use to both academia and industry.