Abstract

Molecular design and synthesis of novel fluorescent chemosensors is an active area of supramolecular chemistry. The recognition and signalling moieties are the most important parts in the design of these chemosensors. Despite the numerous studies that were reported in the literature, finding new strategies and mechanisms in the design of fluorescent probes is still of continuing interest. In 2001, Tang and co-workers discovered a novel phenomenon –so called Aggregation Induced Emission (AIE), in which molecules show weak emission or no emission in dilute solution, however become active in the aggregated state as well as in the solid state. This phenomenon revolutionised the use of luminescent materials in organic light emitting diodes (OLEDs), and chemo and biosensors, as these applications involve the use of luminescent materials in a thin film form (solid state) or in aqueous surroundings.

However, for selective determination of targeting of biologically and environmentally relevant analytes, such as 2,4,6-Trinitrophenol (TNP), Al^{3+} and Zn^{2+} , in this thesis, Synthesis of low dimensional fluorescent organic materials and new AIEE active fluorescent chemosensors based on fluorophore containing Schiff bases have been successfully synthesized through rational designs. The probes and their adduct/molecular assembly were characterized by different spectroscopic techniques like ^{1}H NMR, ^{13}C NMR, UV-Vis spectroscopy, Fluorescence spectroscopy, FTIR, XRD, DLS and Time-resolved Fluorescence Measurements. Most of the cases, shape and size of particle were investigated by SEM, Optical Microscopy and Fluorescence Microscopy. In some cases, computational studies using DFT have been performed to have an insight on the photophysical properties of synthesized probes with their AIEE characteristics. The thesis consists of seven chapters which are outlined below.

Chapter I incorporates short introduction on low dimensional materials. This chapter describes various synthetic methods of low dimensional organic particles that have been over the few years. Different stabilization processes are also described in this chapter. Luminogenic materials with AIEE attributes have attracted much interest since the debut of the AIEE concept in 2001.In this chapter recent progress in the area of AIEE research is summarized. Mostly, the discovery and proposed mechanism of AIEE phenomenon of organic luminogens are well discussed. At last discuss a short

introduction on the fluorescent chemosensors and their signal transduction mechanisms and pathways for selective determination of some cations and explosive. As well, objective of the present work is highlighted.

Chapter II deals with Brief Literature Survey on AIE/AIEE Based Low Dimensional Material and Fluorescence Chemosensors for TNP, Al & Zn

Chapter III represents that efficient phosphorescence emission from aggregated hydrosol of Benz(a)anthracene (**P**^{1}) at room temperature. Aggregated hydrosol of **P**^{1} has been synthesized by re-precipitation method and SDS is used as morphology directing agent. Morphology of the particles is characterized using optical and scanning electronic microcopy (SEM). Photophysical properties of the aggregated hydrosol are carried out using UV–Vis, steady state and time resolved fluorescence study. The large stoke shifted structured emission from aggregated hydrosol of **P**^{1} has been explained due to phosphorescence emission of **P**^{1} at room temperature. In the crystalline state, the restricted intermolecular motions (RIM) such as rotations and vibrations are activated by crystal lattice. This rigidification effect makes the chromophore phosphorescent at room temperature. The possible stacking arrangement of the neighboring **P**^{1} within the aggregates has been substantiated by computing second order Fukui parameter as local reactivity descriptors. Computational study also reveals that the neighboring **P**^{1} molecules are present in parallel slipped conformation in its aggregated crystalline form.

Chapter IV describes solvatochromic effect of N,N′-bis(3-pentyl)perylene-3, 4, 9, 10-bis(dicarboximide) [**P**^{2}] in THF-DMF mixture. Fibroid like microstructure of EP-PDI has been synthesized by re-precipitation method using SDS as morphology directing soft template. Morphology of the particles is characterized using optical and scanning electronic microcopy (SEM). Photophysical properties of the aggregated hydrosol and also the solvatochromic effect of **P**^{2} are carried out using UV–Vis, steady state and time-resolved fluorescence study. The fluorescence spectra of **P**^{2} in THF show structured emission band and aggregated hydrosol exhibits E-type and Y-type excimer emission. The intense fluorescence emission property of **P**^{2} is used for sensing the presence of nitroaromatics in the medium. Among the different nitroaromatics, picric acid (PA) strongly quenches the fluorescence emission intensity of **P**^{2} and this quenching property of PA is being used to detect PA in THF having

concentration as low as 3.0 μM. The mechanism of this quenching has been explained due to ground state complexation between **P[2]** and PA.

Chapter V describes a heteroatom containing Schiff base, 4-[(2-Hydroxy-naphthalen-1-ylmethylene)-amino]-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-one (**P[3]**) has been synthesized using one step condensation method. Compound, **P[3]** is weakly emissive in solution state but a strong emission is observed in its aggregated state due to the restriction of intramolecular rotation (RIR) and large amplitude vibrational modes of **P[3]**. This phenomenon is known as aggregation induced emission enhancement (AIEE). Various morphologies of **P[3]** microstructures have been synthesized using reprecipitation method. SDS is also used as a morphology directing agent. Morphologies of the particles are characterized using optical and scanning electron microscopy (SEM). Photophysical properties of aggregated **P[3]** hydrosol are studied using UV–Vis absorption, steady state and time resolved fluorescence spectroscopy. The 'turn off' luminescent property of aggregated **P[3]** hydrosol is used for the selective detection of trace amounts of picric acid in aqueous medium and the fluorescence quenching is explained due to ground state complexation between **P[3]** and picric acid with quenching constant (Kq), $1.91 \times 10^5\ M^{-1}$.

Chapter VI represents 2-Phenylquinoline (**P[4]**) displayed novel aggregation induced emission enhancement (AIEE) characteristics in its aggregate/solid state. It also allows reversible fluorescence switching in acidic and basic media and changes the emission color from sky blue to intense blue in its aggregate state through protonation. Such behavior enables it to be utilized as a fluorescent pH sensor in acidic and basic media. **P[4]** microparticles with distinct morphologies are synthesized through a reprecipitation method and SDS is used as the morphology directing agent. The photophysical properties, size and growth process of the particles are characterized by UV-Vis absorption, steady state and time resolved spectroscopy, optical and scanning electron microscopy studies. The ''turn off'' luminescence property of the aggregated **P[4]** hydrosol in the presence of 2,4,6-trinitrophenol (TNP) is used for the selective detection of trace amounts of TNP in water and the super-amplified fluorescence quenching has been explained as due to ground state complexation between **P[4]** and TNP.

Chapter VII describes a antipyrine based fluorescent probe, 4-[(2-Hydroxy-3-methoxy-benzylidene)-amino]-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-one (**P^5**) has been successfully synthesized using one step condensation method. It exhibited dual sensing property toward Al^{3+} and Zn^{2+} over other relevant metal ions and also displayed novel aggregation induced emission enhancement (AIEE) characteristics in its aggregate/solid state. Various morphologies of **P^5** microstructures have been synthesized using reprecipitation method. SDS is also used as a morphology directing agent. Morphologies of the particles are characterized using optical microscopy. Photophysical properties of aggregated **P^5** hydrosol are studied using UV–Vis absorption, steady state and time resolved fluorescence spectroscopy. The 'turn on' luminescent property of **P^5** is used for the selective sensing ability of trace amounts of Al^{3+} and Zn^{2+} in organic medium and a significant fluorescence enhancement with a turn-on ratio of over ~200-fold was triggered via chelation-enhanced fluorescence through sensor complex (Al- **P^5**) formation.