PREFACE

This thesis primarily focuses on the synthesis and applications of novel metallogels. Since the discovery of metal-organic gel (metallogel) in late 1990s, these smart materials have been grabbing an increasing interest due to the wide variety of applications in multidisciplinary areas like biomedical, pharmaceutical, catalysis and batteries. Metallogels were discovered nearly 20 years back but their formation from low molecular weight gelators and library of gelators is still quite inadequate which is discussed in **chapter 1**.

Gels are being synthesized since the nineteenth century, but a pin point definition of gel is still a matter of argument. Gels are generally identified by their physical appearance and behavior like soft solid like character with no flow of trapped liquid. Generally very less amount is sufficient to immobilize the large amount of solvent. A gelator can be utilized to characterize its macromolecular structure *i.e.* gel which could be helpful in correlating the characteristic properties of material in micro and its macro level organization. The fact may be useful in unveiling the direct relation between small changes in gelator and outcome in macroscopic state. the most striking aspects of LMWGs is that they usually possess better multi-stimuli responsive behaviors towards external stimuli and simple synthetic modifications in the gelator structure may lead to drastic change in synthesized gel. These factors are well elaborated in the present thesis.

In chapter 2, a fluorescent metallogel (1% w/v) has been synthesized from non-fluorescent ingredients *viz.* the smallest possible low molecular weight aromatic symmetrical ligand H_2SA and LiOH in a chloroform and methanol mixture. The chelation of Li^+ is not only responsible for the inhibition of excited state intramolecular proton transfer (ESIPT) or the origin of fluorescence through chelation enhanced fluorescence (CHEF) in H_2SA, but also for aggregation leading to gelation. The metallogel obtained from H_2SA/Li^+ reveals a fibrous morphology while H_2SA with other, bigger size, alkali metal ions like $Na^+/K^+/Cs^+$ demonstrates the growth of crystals with different shapes. The effect of the size of the alkali metal ion over gel formation is well explored by FTIR, UV-vis, fluorescence, average lifetime measurements, SEM and PXRD. The metallogel shows multi-stimuli responsive behavior towards thermal and mechanical stress as well as reswelling properties. The regioisomer H_2PBA (**2**) also shows emission upon treatment with LiOH due to the presence of intramolecular charge transfer (ICT), this is well established by various experiments. The mechanism of gel formation is well established by FTIR, ^1H NMR, UV-vis, fluorescence, lifetime measurements, SEM and single crystal and powder XRD instrumental techniques. The involvement of various phenomena in gel formation has been further supported by other synthesized model compounds *viz.* H_2MBA, PMO, H_2SEA and H_2SPA. True gel phase material is proved by detailed rheological experiments.

In chapter 3, a multi-stimuli responsive conductive co-ordination polymeric fluorescent metallohydrogel (1% w/v, **CPH**) has been synthesized employing non-fluorescent components *viz,* L-tyrosine derived low molecular weight (LMW) $\mathbf{H_4T^{-L-tyr}}$, LiOH and $Zn(NO_3)_2$ in 1:3:1 proportions at pH 11-12. **CPH** shows multi-stimuli response reversible gel-sol transition towards thermal, mechanical and ultrasound stimuli. **CPH** also possesses shape persistent property and partial reswelling property. Mechanism of nanofiber formation followed by gelation was well explained using suitable models and supported by fluorescence, TEM, PXRD, NMR, TGA and Mass spectrometry. Fluorescence is originated in **CPH** due to Zn^{2+} coordination which reduces the non-radiative decay. True gel phase material was proved by detailed rheological experiments. Excellent high ionic conductivity of 5.05×10^{-3} S cm^{-1} and 4.18×10^{-3} S cm^{-1} at 295 K are observed for metallohydrogel with and without Au Nps. Further, uniform sized ultra-fine Gold nanoparticles (~3 nm) (Au Nps) were deposited only over nanofiber template without using any external reducing agent. Freshly prepared Au Nps were utilized as catalyst in reduction of Nitrophenol using $NaBH_4$. Respective rate constants and Activation energies of the reaction with and without Au Nps are 0.221 min^{-1}, 58.94 KJmol^{-1} and 0.014 min^{-1}, 595.14 KJmol^{-1}, respectively.

In chapter 4, three L-tartaric acid based symmetrical A–π–D-chiral-D–π–A type structural isomeric nitrobenzylidenes (**1**–**3**) and carboxybenzylidenes (**4**) have been synthesized with intent to achieve isomer specific metallogels with intramolecular charge transfer properties. Alkali metal ions in **1-3** systems not only trigger charge transfer but also play a vital role in gelation while this phenomenon was completely absent in **4**. The presence of intramolecular rather than intermolecular charge transfer as well as aggregation has been well established by various kinds of experiments using UV-vis, CD, ^{1}H NMR, DFT and crystallography techniques. The role of alkali metal ions in triggering ICT was proved by titration with their respective crown ethers. Notably, Na^+ afforded twisted fiber morphology whilst Li^+ gave merely long range fibers. The true gel phase material was proved by detailed rheological studies.

In chapter 5, synthesis of chain length selective gelation (1% w/v) from succinic (n=2, **H_2SL**) and adipic acid (n=4, **H_4AL**) derived ligands out of seven different bis acylhydrazones based saturated homologous dicarboxlylate derived bolaamphiphiles have been demonstrated. The LiOH deprotonated **H_2SL** and **H_4AL** both led to the formation of a fluorescent metalloorganogel upon addition of $Cd(OAc)_2$. The coordination complexes responsible for