Schiff base molecules are condensation products of primary amines and carbonyl compounds and they were first discovered by a German chemist, Nobel Prize winner, Hugo Schiff in 1864. Schiff bases played an important role as ligands even a century after their discovery in field of co-ordination chemistry, and form stable complexes with different transition metal ions. Schiff bases and their metal complexes have been shown to be promising lead for both synthetic and structural research due to their relatively simple synthesis, low cost and structural diversity.

Structurally, Schiff base (also known as imine or azomethine) is an analogue of a ketone or aldehyde (scheme 1) in which the carbonyl group (C=O) has been replaced by an imine or azomethine group. A Schiff base is a type of chemical compound containing a carbon-nitrogen double bond as functional group, where the nitrogen atom connected to aryl group or alkyl group but not hydrogen.

Schiff bases are chosen for our desired purpose after considering following facts. First, steric and electronic effects around the metal core can be finely tuned by an appropriate selection of bulky and/or electron withdrawing or donating substituents incorporated into the Schiff bases. Secondly, the two donor atoms, N and O, of the chelated Schiff base exert two opposite electronic effects: the phenolate oxygen is a hard donor and stabilizes the higher oxidation state of them at all atom; whereas the imine nitrogen is a border line donor and stabilizes the lower oxidation state of the metal ion. Schiff bases are primarily used in Medicines, Perfumery, chemodosimetry, covalent organic frameworks and Cell imaging as well as formation of organic-inorganic gels (depends on activity of metal ion used). Various Scientists like Jiang and coworkers observed excellent gelation behavior and multistimuli-

responsive properties in the gel state due to the introduction of the salicylidene Schiff base moiety which can facilitate stable metal complex formation.

The activity of Schiff base ligands are usually increased by complexation and the influence of certain metals on the intrinsic chemical-physical activities of these Schiff bases, has endorsed them towards study of their coordination behavior. Utilizing this metal-ligand binding activity as the motivating force for the self-assembly a series of mechanically-strong metallo-supramolecular gels, which exhibit vivid reversible responses to a diversity of stimuli, including thermal, mechanical and chemical were prepared.

These stimuli responsive materials have gained great interest in recent years and that too derived from organic-inorganic complex moieties. Since these materials are able to exhibit a dramatic change in their properties in response to the application of an environmental stimulus, such as light, temperature, mechanical stress, pH, ionic strength, solvent polarity, electric fields, biological and chemical analytes etc. According to the kind of stimulus to which they respond, such materials can thus be classified as either photo-, chemo-, electro-, or mechano-active materials. Application of a stimulus causes a change in a material property such as shape or other physicochemical characteristic, and outputs one or more responses like fluorescence, mechanical stress, color change, etc.

The results of our work provide an emphasis on the validity of ligand design making use of metal-binding components in realizing metallogel systems with versatile properties. We anticipate that this may help open the way for a range of responsive soft materials and that too from economically viable methods.

Thesis Organisation

Chapter 1 Chapter 1 discusses the introductory remark on the Schiff bases and its origin in very brief. The different types of Schiff bases and their different synthetic approaches including both top-down and bottom-up are mentioned briefly. Since the study is focused on the Schiff bases, various types of aldehydes and amines used were discussed briefly. The literature reports revealed that the Schiff base reactions are economic, efficient and most of the times environment friendly. This chapter provides the summary of the different Schiff base metal complexes used so far for the synthesis of MOF, metallogels and their application reported. The current thesis work is aimed at the development of completely efficient and economic route for synthesis and characterization of metallogels and aggregates which could facilitate the application in various field like fluorescence, conducting materials and cell imaging. In the present thesis work, where the literature reports towards mechanism of gel formation and aggregation induced emission is given, this thesis also highlighted the several physical and chemical properties of metallogels and aggregates and their broad applications. This chapter also contains the objective of the current work.

Chapter 2 provides the materials and chemicals required throughout thesis work. This chapter provides the detail procedures of the preparation of Schiff bases, confirmation and quantification of metallogels. Synthesis of metal complexes with Schiff base ligands, used in this study along with instrumental details required for characterization.

Chapter 3 We reported the synthesis of an ultrasound induced multi-responsive fluorescent metallogel based on a non-fluorescent citric acid derived ligand (1), LiOH and Cd(OAc)2 in DMF. Ultrasound was shown to promote the de-metallation and re-complexation of Cd(II)

ions proceeding through the disruption and reformation of dynamic metal–ligand coordination bonds ultimately leading to gelation.

Both TEM and AFM images recorded after sonication revealed the presence of three-dimensional (3-D) networks involving thin nanofibers of ~20 nm in diameter and of several micrometers in length. These well-defined structures stand in sharp contrast to the random non-directional aggregates observed under the same conditions before sonication, which clearly brings to light the key role of sonication in the structuring process associated with gelation.

The net quenching of ~55% of the fluorescence intensity observed in the complete sonication-induced gelation process can be attributed to aggregation caused quenching (ACQ). Thus, sonication played a key role in the establishment of a quite complicated phenomenon, 'demetallation–remetallation–AIE–ACQ', in gel formation.

A deviation from the aforesaid combination in terms of the regioisomer, alkali base, and transition metal ion including Zn (II), solvent and triggering effect like mechanical or heat could only produce a solution instead of a gel. The crystal structure obtained with Zn (II) analogous to metallogel constituents supports the structure involved in gelation with Cd(II). This "sonometallogel" was also found to be thermos-responsive and reversibly fluidized under suitable mechanical stress. The true gel phase material has been proved by detailed rheological studies.

The conductance properties of the gel have been investigated by impedance measurements. The experimental Nyquist impedance diagrams (-Im(Z) vs. Re(Z)) provide a striking graphic illustration of the major effect of sonication on the ohmic resistance of the

gelator samples (1/Li^{+}/Cd(II); 0.6%, w/v; 291 K) in DMF. It reveals indeed that sonication results in a tenfold decrease of the measured resistance value from 15 938 ohms down to 1724 ohms which equals to a tenfold increase of the conductivity value from 4.5 mS m^{-1} to 40.6 mS m^{-1}.

Chapter 4 We have reported the synthesis of a chain length selective metallogelation of bis acylhydrazone included schiff base ligands obtained from a series of homologous dicarboxlylate derivative in presence of LiOH and Zn2+. The results presented are quite significant and different from other reported coordination polymer gels in number of ways

A number of reports selective to functional groups, stereochemistry, relative position of donor/acceptor and active metal center with bisacylhydrazones with their d10 complexes are available. However, a metallogel involving change in core with strategy towards tuning of morphological behavior has not been reported. It has been categorically observed that change in flexibility of core could alter the mode of complexation followed by gelation.

Till to date the effect of chain length were only explored in organic gels and none of the research had been carried over in the field of metallogel. Reckoning this observation, strategically, we framed the effect of variation in flexible spacer length over structural and optical properties of metallogel. Non-emissive solution of gelator became emissive upon deprotonation followed by metal addition due to CHEF along with AIE-ACQ effect. Fluorescence emission and UV-vis studies indicate the presence of aggregation.

Rheological studies indicated that sharp phase transition via gel-semi sol-solid at Tgel while gel-sol phase transition at yield stress. Variable temperature fluorescence studies also

support the rheological data analysis. The mechanism of gelation was examined by IR, 1H NMR, UV-vis, Job's plot, PXRD.

Chapter 5 Simple mixing based strategy for formation of metalogel by schiff base gelator has been achieved by using cobalt acetate dihydrate and deprotonated (LiOH) Adipoyl derived hydrazone based gelator at room temperature under atmospheric pressure. Tetra basic hexa-dentate nature of ligand is necessary condition for coordination of a metal ion through deprotonation of both phenolic and -NH labile protons adjacent to azo-methine group. Mechanical properties were scrutinized by Rheological experiments over freshly prepared (1.0% w/v) coordination polymeric Co(II) fixed concentration metalogel. Implementation of frequency sweep measurements between 0.1 and 100 rad s^{-1} at 25°C within linear viscoelastic region indicated that G' and G'' values were linear and increases slightly within the applied frequency (f) range (-1.0-2.0 rad s^{-1}) principally supporting its elastic nature.

TEM study on diluted metalogel revealed the bunch of extended and interconnected Nano fibers with close knitted and intermingled appearance with network of nanofibers of about ~30 nm in average diameter. Observed quenching upon addition of requisite amount of Co^{2+} required for metalogel formation indicates the presence of ACQ phenomenon in gelation process.

The direct optical band gap of the film can be calculated by applying Tauc's plot. The value of E_g of the materials film has been calculated as 2.99 eV. The recorded J–V characteristics of the Au/semiconducting gel interface demonstrate an asymmetrical nonlinear nature curve, which is the validation of a rectifying Schottky barrier diode (SBD).

We have calculated the rectification ratio (I_{on}/I_{off}) of our device and found to be 266 ± 15 which is very good for semiconducting gel based newly fabricated device.

In order to examine the photovoltaic property of complex materials, sandwiched structure of ITO/semiconducting gel/Al schottky devices was employed under illumination of green wavelength of light, all devices were illuminated from ITO side and photo response was recorded in the range ± 2 V and illumination of device from back side demonstrates the enhancements in current. The significant enhancement in current observed in reverse bias condition upon illumination. However, in forward bias condition, it remains nearly same as compare to dark current. The large increase in the photocurrent of under the reverse bias condition upon illumination was observed due to the formation of the good quality junction, which leads to formation of a strong built-in depletion region for the separation of charge carriers.

Chapter 6 Absorption characteristics of PRU/PRT have been batho-chromatically tuned to the visible region by extending the π-conjugation. The extended π-conjugation is evidently confirmed and revealed that π→π* transition was the major factor responsible for electronic absorption.

The photo physical property of PRU/PRT was carefully examined in different organic solvents at different concentrations and intriguingly, the fluorescence intensity of PRU increases enormously by the gradual addition of water up to 90%. This clearly indicated that this molecule has aggregation-induced emission (AIE) property. The mechanism of AIE of this molecule was suppression of photo induced electron transfer (PET) due to hydrogen bonding interaction of -NH donor with water.

Cell Viability assay on MDAMB-231 cell line by MTT. $8x10^3$ cells were incubated with various concentrations of PRU and PRT complexes for 24h. Applicability of this system towards cell line is completely feasible due to its high life period i.e. even after 24 hour there is no detrimental effect on imaging.

In the last, the major outcomes of every chapter are summarized which is followed by the future recommendation of the current research work. Thereafter, the references which have been cited in the entire thesis are presented.