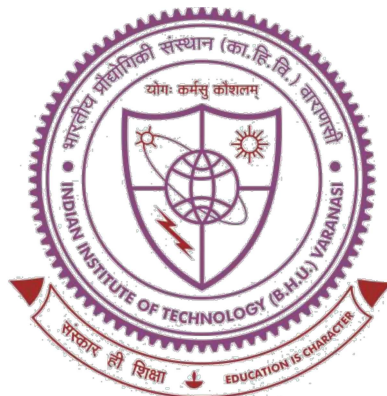


**Multifunctional Metal-Organic Gels Based on Low  
Molecular Weight N,O Donor Ligands**



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**By**

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nature easily through TEM analysis. Mechanism of metallogels formation was well established through FT IR, UV-vis, NMR, ESI-MS, TEM, SEM, and PXRD, whereas, true gel material was proved by rheology. Nyquist impedance plot suggested that the gelation process has significant a role in order to improve the conductance property of a material. The story of present metallogel might be helpful in setup new parameters for synthesis of metallogel and its application in the development of optoelectronic devices.

## **CHAPTER 6**

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### **CONCLUSION**

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In conclusion, through this thesis, we proposed the synthesis of various multi-functional metallogels involving fluorescence/coordination polymer/charge transfer *etc.* Chapter 1 summarizes the recent interest in the area of metallogel along with highlighting the lacks of literature towards cost effective low molecular weight gelator for fluorescent metallogel, nanofabrication and nanocatalysis using metallogels and intramolecular charge transfer metallogel. Taking the above findings of literature, in chapter 2, we described the synthesis and properties of a fluorescent metallogel obtained from non-fluorescent constituents *viz.* an ultra-low molecular weight symmetrical ligand **H<sub>2</sub>SA** and LiOH. Designing of **H<sub>2</sub>SA** was originally inspired from our previous work where they obtained fluorescent metallogel with nanoball morphology. The ligand **H<sub>2</sub>SA** obtained by replacing the middle tartaric acid derived core by hydrazine keeping the N,O binding site similar to that ligand. This provides rigidity to entire system which might be helpful in achieving planarity to the resulting adduct after addition of LiOH. The resulting metallogel showed multi-stimuli responsive behavior towards temperature, mechanical stimuli and ultrasound. Further, slight changes in functional groups and spacer lead to transformation from fiber to crystalline fiber to flower shaped crystals to normal crystals and the fluorescence properties of all the adducts, such as CHEF to ICT. LiOH not only deprotonated **H<sub>2</sub>SA**, but also originate the fluorescence through CHEF and inhibition of the ESIPT phenomenon. Further, CHEF and  $\pi$ - $\pi$  stacking played a crucial role in the appearance of fluorescence and metallogel formation. True gel phase material was attested by rheological studies. The gel described in chapter 2 may find application in designing of other lower molecular weight gels and can be used for metal ion sensing.

In the next chapter (Chapter 3), we modified the ligand **H<sub>2</sub>SA** by keeping the binding site similar (N,O donor) and increasing one benzene ring with introduction of chirality to the ligand **H<sub>4</sub>T<sup>-L-tyr</sup>**. Ligand **H<sub>4</sub>T<sup>-L-tyr</sup>** was able to produce a coordination polymeric fluorescent metallohydrogel using combination of LiOH and Zn(NO<sub>3</sub>)<sub>2</sub>. The mechanism of gelation has been investigated using FTIR, NMR, fluorescence, impedance, TEM, PXRD and rheological measurements. The selective combination of **H<sub>4</sub>T<sup>-L-tyr</sup>/Li<sup>+</sup>/Zn<sup>2+</sup>** was not only found to result in the fluorescence of the metallohydrogel, but it also proved responsible for the formation of conducting nanometric fiber-shaped assemblies. These nanofibers have been used as growth platforms to achieve the fabrication of uniform sized AuNPs (*ca.* 3-4 nm) in the absence of any external reducing agent. The AuNP-doped nanofibers (**AuCPH**) have proved useful as catalytic material in the reduction of *p*-nitrophenol with NaBH<sub>4</sub>. For the first time, in the case of metallohydrogel through this chapter, we provided detailed kinetics data for the abovementioned model reduction reaction. The conductance properties of these metallohydrogels (**CPH** and **AuCPH**) have also been explored and shown to be strongly dependent on the size of the alkali ions and on the temperature. Structurally close supporting ligand **H<sub>4</sub>T<sup>-L-Phe</sup>** was also monitored towards gelation under similar condition to **H<sub>4</sub>T<sup>-L-tyr</sup>** but it only led to gelatinous sol which signifies the role of tyrosine ring -OH towards gelation. We believe that this concept of metallohydrogel will open up new perspectives for the development and applications of soft materials in the field of electronics and catalysis.

In the fourth chapter, we synthesized three symmetrical chiral structural isomers (**1–3**) based on the A- $\pi$ -D-chiral-D- $\pi$ -A strategy with an objective to obtain the chiral metallohydrogel. The alkali metal ion triggered ICT and gelation of these isomers have been established by various experiments. Through this chapter, we described first ever intense red