# **B. TECH. PROJECT REPORT**

# On

# Synthesis of Multi-Stimuli Responsive Metallogel

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# DISCIPLINE OF METALLURGY ENGINEERING AND MATERIALS SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE

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# Synthesis of Multi-Stimuli Responsive Metallogel

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Submitted in partial fulfillment of the requirements for the award of the degrees

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# INDIAN INSTITUTE OF TECHNOLOGY INDORE

# December 2019

# **CANDIDATE'S DECLARATION**

I hereby declare that the project entitled "**Synthesis of Multi-Stimuli Responsive Metallogel**" submitted in partial fulfillment for the award of the degree of Bachelor of Technology in Metallurgy Engineering and Materials Science completed under the supervision of **Dr. Mrigendra Dubey, Assistant Professor, Discipline of Metallurgy Engineering and Materials Science,** IIT Indore is an authentic work.

Further, I declare that I have not submitted this work for the award of any other degree elsewhere.

Signature and name of the student(s) with date

## **CERTIFICATE by BTP Guide**

It is certified that the above statement made by the student is correct to the best of my knowledge.

Signature of BTP Guide with dates and their designation

# **Preface**

This report on Synthesis of Multi-Stimuli Responsive Metallogel is prepared under the guidance of Dr. Mrigendra Dubey.

# Preface write-up may be decided by the students. An example of the same is given below:

Through this report we have tried to lay out a synthesis route for metallogels and through the same route we have synthesized a chiral and fluorescent lithium induced metallogel. The metallogel is responsive to external stimuli such as temperature, mechanical force, and UV irradiation. We have characterized the metallogel through a number of instrumental techniques and have tried our best to understand and explore the mechanism of gel formation through these characterizations.

We have tried to the best of our abilities and knowledge to explain the content in a lucid manner. We have also added models and figures to make it more illustrative.

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I would also like to thank SIC, IIT Indore for extending instrumental facilities for this work.

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#### **Abstract**

A Li<sup>+</sup>-induced fluorescent metallogel (3.6% w/v) has been synthesized from a non-fluorescent ligand H<sub>2</sub>PSL and LiOH in DMF at ambient room temperature. Each steps of products involved in ligand synthesis was well characterized by using FTIR, <sup>1</sup>H-NMR and ESI-Mass instrumental techniques. Another ligand, H2LMAL, was synthesized from (L)-malic acid for exploring the effect of solvophilic and solvophobic functional groups on fluorescence, conductance and gelation ability. The ligand H<sub>2</sub>LMAL was thoroughly characterized by <sup>1</sup>H-NMR and fluorescence experiments. The metallogel obtained was found to be responsive towards thermal and vigorous mechanical stimuli which was well demonstrated by using inverted vial tests. Interestingly, metallogel showed resistance towards ultrasound. Gelation was attempted with various solvents such as DMF, DMSO, methanol, chloroform, hexane, and water where only DMF was able to form the metallogel indicating the selectivity of Li<sup>+</sup> ions towards DMF in the particular environment. Also, gelation with alkali bases other than LiOH i.e. NaOH, KOH, CsOH, all of them either formed a clear solution or a suspension which clearly shows the selectivity of Li<sup>+</sup> towards gelation. The ligand H2PSL was derived from phenyl succinic acid by following the standard literature procedures. The lithium ions  $(Li^+)$  not only play vital role in metallogelation, but also in introduction of fluorescence property to the metallogel. First, it inhibits the mechanism of excited state intramolecular proton transfer (ESIPT); second, it gives rise to fluorescence in metallogel through the phenomena of chelation enhanced fluorescence (CHEF). Detailed fluorescence experiments have been performed to explore the phenomenon of ESIPT, CHEF, aggregation induced emission (AIE), and aggregation caused quenching (ACQ). Field emission scanning electron microscope (FE-SEM) revealed a fine fibrous morphology for xerogel. When the diluted metallogel was subjected to the TEM analysis, we observed the quite unusual phenomenon of creation of fibrous morphology begins with the aggregation of nano balls of about 31nm diameter. Furthermore, the images obtained from TEM also indicated the presence of nano nuclei, which we assume are the nucleation sites present at the centre of the nano balls, which on interacting with the electron beam started to disappear. A comprehensive rheological study of the obtained metallogel proves that it has a true gel phase. Instrumental techniques such as FTIR, <sup>1</sup>H NMR, ESI-mass, UV-visible spectrometry, fluorescence spectrometry, SEM, TEM and powder XRD have been used to establish the mechanism of metallogel formation.

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# **Chapter 1**

## **Introduction**

#### **1.1 Overview**

With an objective to understand and explore the effect and the response of external stimuli on metallogels and potential application of chiral metallogels in environment conservation we slightly modified the succinic acid derived ligand and synthesized a ligand derived from phenyl succinic acid which possesses a chiral centre with a phenyl ring which is expected to add to the  $\pi$ - $\pi$  stacking, one of the most utilized concept for metallogel synthesis.

Another ligand  $H_2LMAL$ , derived from (L)-malic acid was synthesized through the same route to understand the effect of solvophobic functional group (phenyl ring in  $H_2PSL$ ) and solvophilic functional group (hydroxy group in  $H_2LMAL$ ) on fluorescence, conductance, and gelation ability.

#### **1.2 Soft Materials**

Soft materials, especially supramolecular gels synthesized from low molecular weight gelators (LMWGs) gathered immense importance in the recent past as precursors for the synthesis of smart materials<sup>1–5</sup>. When subjected to external stimuli such as pH, temperature, light, sound and chemicals, they change their physical and chemical properties, sometimes reversibly<sup>6–11</sup>. As a result of their responsiveness towards a variety of external stimuli, supramolecular gels find important applications in the field of catalysis<sup>12</sup>, drug delivery<sup>13</sup>, tissue engineering<sup>14,15</sup>, sensing<sup>16</sup>, and light harvesting<sup>17–19</sup>.

One such class of these supramolecular gels is metallogels which utilize metal complexes in gel formation<sup>11,20–25</sup>. Usually, metallogel formation takes place through two strategies, either the individual metal complexes self-assemble with each other acting as gelators via H-bonding, weak Van der Waals interaction,  $\pi$ - $\pi$  stacking, metal-metal interactions etc. or metal and ligand interacting with each other to form an intermingled coordination network which act as gelators by trapping substantial amount of solvent into the network. The usage of metals in this process of self-assembly not only provides the stability to the gel but it also imparts properties that are solely dependent on the metallic centre such as magnetic<sup>26</sup> and catalytic properties<sup>27,28</sup>.

Supramolecular materials with pores of adequate surface area displayed important application in environment conservation<sup>29</sup>. Although studies on conservation of environment through the use of hydrogels for dye adsorption<sup>30</sup> or application of metal-organic gels for selective gas adsorption<sup>31</sup> or in the field of catalysis<sup>27</sup> have been reported, only a few reports on the application of chiral materials in such area has rarely been taken in account. Chirality has important applications in medicines and biological processes<sup>32–36</sup>. Supramolecular chirality arises from the induction of chirality in supramolecular assemblies formed by non-covalent interactions. By tuning the proportion of a particular enantiomer, the overall chirality can be tuned.

#### 1.3 Fluorescence and its associated phenomena

Fluorescence is a unique form of emission spectroscopy that can be a powerful tool in quantitative and qualitative analysis, and it can provide useful information. In any molecule, when an electron in the singlet state is excited by absorption of a photon, an excited singlet state is formed. Although the spin of the electron in the excited singlet state is paired with the electron in the ground singlet state. Fluorescence can be produced when the emitted photons come from the excited singlet states (Figure 1). Fluorescence emission can deactivate an excited singlet electron. Also, the excited singlet electron can be deactivated by internal conversion or by external conversion.

The reason behind few compounds exhibiting fluorescence is the ordinary return of an electronically excited molecule to the ground state by internal or external conversion<sup>53</sup>. Usually, the compounds aromatic functional groups exhibit the most intense and useful fluorescence, because these compounds have large  $\pi$  systems that provide enough  $\pi$  orbitals to fluoresce.

A compound with fluorescent groups may not show fluorescent properties if it contains elements with lone pairs of electrons, especially nitrogen. This quenching of fluorescence can be prevented by some metal ions by forming a coordinate bond with the lone pair electron donors. This effect is referred to as the Chelation Enhanced Fluorescence (CHEF) effect.



Figure 1: Partial energy diagram for a fluorescence system

Some organic luminophores have freely rotating functional groups (rotational degree of freedom), upon excitation these molecules relax down through rotations instead of releasing the given energy in the form of light. In solution form, these luminophores aggregate or crystallize, and as a result of aggregation or crystallization these rotations are restricted, and they become very fluorescent. This phenomenon is known as aggregation induced emission (AIE). Contrary to AIE, some luminophores show exact opposite phenomena i.e. they lose their fluorescence in solution phase whereas they show very high fluorescence prior to aggregation in solid phase. This phenomenon is known as aggregation caused quenching (ACQ).



Figure 2: Illustration of the two contrasting phenomena: AIE and ACQ.

# **Chapter 2**

# **Literature Survey**

Metallogels, have recently gained huge attention of the material scientists, chemists, and physicists all over the world, due to their unique properties. One of these properties is their stimuli responsive properties which enable the metallogel to be used in various applications. Due to the complexity in synthesizing metallogels and that too stimuli-responsive metallogels, there are very few reports available on metallogels and their applicability, though there are numerous reports on other types of gels such as hydrogels, organogels, but when it comes to incorporating a metal in those gels only a few people have managed to do it. Of all the stimuli responses, chirality produces the most interesting stimuli response, if a metallogel is a chiral one.

Yu, Pu and co-workers have reported a case of chiral sensing<sup>37</sup>. They synthesized a stable gel from a chiral gelator by mixing it with (R)-phenylglycinol (0.10 equiv.) in CHCl<sub>3</sub> (0.1 mL), followed by sonication for 1 minute. When the gelator was mixed with (S)-phenylglycinol (0.10 equiv.) in CHCl<sub>3</sub> (0.1 mL), the system could not form a stable gel and the gel collapsed, which shows the enantiomeric selectivity of the gelator towards (R)-phenylglycinol. The inability of the gelator to form a stable gel may be accredited to the amino acid displacing the Cu(II) ion from the ligand.





*Figure 3:* Molecular structure of the gelator. Visual enantioselective responses of the gel of 31 toward (*R*)-phenylglycinol (left) and (*S*)-phenylglycinol (right). Adapted with permission from ref. 37.



Figure 4: Fluorescence spectra of (R)-2 ( $5.0 \times 10^{-7} M$ ) in CH<sub>2</sub>C<sub>12</sub>/nhexane (2:3) in the presence of (R)- and (S)-phenylglycinol ( $5.0 \times 10^{-4} M$ ) ( $\lambda_{exc}$ ) 289 nm, slits: 2 nm/5 nm). Adapted with permission from ref. 37.

PL study confirms that the interactions of the gelator with (S)-phenylglycinol and (R)phenylglycinol are completely different with each other. The chiral complex of Cu(II) shows enantioselective fluorescence enhancement in the presence of various amino alcohols. The interaction of the gelator with (S)-phenylglycinol might be greatly amplified in the supramolecular assembly of the gel network. This work is an example of the most convenient visual detection method for chiral recognition.

Ihara and co-workers also reported a highly ordered assembly of achiral polyphyrins on a chiral molecular gel which also realized enantioselective recognition of amino acid methyl esters<sup>38</sup>.



*Figure 5:* Enantioselective recognition through chirally ordered porphyrin assembly. Adapted with permission from ref. 38.

They carried out circular dichroism (CD) to evaluate the enantiomeric selectivity for various  $\alpha$ amino acid methyl esters: Ala-OMe, Leu-OMe, Phe-OMe, His-OMe, and Lys-OMe. The CD pattern and intensity of g-TPP/Zn were not influenced by the addition of L- and D-enantiomers of Ala-OMe, Leu-OMe, and Phe-OMe. On the other hand, there was a dramatic change in the CD pattern upon addition of His-OMe, and Lys-OMe. This difference could be explained by the fact that the side-chain base groups of histidine and lysine have higher binding constants than does an a-amino group.



**Figure 6:** CD spectra of g-TPP/Zn (50 μM) with and without an equimolar of (a) Ala-OMe, (b) Leu-OMe, (c) Phe-OMe (d) Lys-OMe, and (e) Pro-OMe in cyclohexane at 20 °C. Adapted with permission from ref. 38.

Other types of stimuli responsiveness have also proved to be quite useful. Aida and co-workers for the first time reported a metallogelator based on trinuclear gold(I) pyrazolate complexes with long alkyl chains<sup>39</sup>. Metallogel was formed in hexane through van der Waals force exerted by long alkyl chains as well as through aurophilic interactions. Red-Green-Blue (RGB) color switching was

observed on the introduction of external stimuli. When the metallogel was doped with a small amput of silver(I) ions its red phosphorescence was converted into blue. Red phosphorescence was restored when chloride ions were added to extract Ag(I) ions. The blue phosphorescence of the Ag(I)-doped metallogel was turned into green phosphorescence in solution upon a gel-to-sol phase transition at high temperature.



**Figure 7:** Luminescence profiles of Au(I) pyrazolate complex in hexane. Pictures and schematic self-assembling structures; (a) sol, (b) gel, (c) sol containing AgOTf (0.01 equiv), and (d) gel containing AgOTf (0.01 equiv). Adapted with permission from ref. 39.

# **Chapter 3**

# **Methodology**

#### 3.1 Microscopy Techniques

#### 3.1.1 Transmission Electron Microscopy (TEM)

The transmission electron microscope (TEM) is a very powerful tool for material science. Features like crystal structure and structural features like dislocations and grain boundaries can be observed with the help of interactions between the electrons (of the electron beam, shone through a very thin sample) and atoms. TEM can be used to study the growth of layers, their composition and defects in semiconductors. High resolution analysis can also be done to analyze the quality, shape, size, and density of quantum wells, wires and dots. TEM operates on the same basic principles as the light microscope but instead of light electron beam is used. Because the wavelength of electrons is much smaller than that of light, the optimal resolution attainable for TEM images is many orders of magnitude better than that from a light microscope. Thus, TEMs can reveal the finest details of internal structure - in some cases as small as individual atoms. For this study, a JEOL JEM 2100 electron microscope was used.

#### **3.1.2 Scanning Electron Microscopy (SEM)**

This microscopic technique works at very small wavelengths (3.7pm at 100KeV) and electrons are deflected by a magnetic field. Electrons interact with particles of the material, and several characteristic signals such as background electrons, secondary electrons, x-rays, etc. are obtained. These signals can be used to get a further understanding of the material structure by coupling with appropriate detectors. The backscatter electrons are high energy electrons reflected from the sample surface via elastic scattering. This is useful for phase contrast analysis due to atomic size contrasts of different elements. The secondary electrons are low energy electrons obtained from few nanometers interaction with the sample surface via inelastic scattering. Imaging with this technique ensures a better surface topography. Consequently, very small surface features can be identified, such as grain boundaries, pores, voids, inclusions, precipitates, etc. SEM can be used to study surface morphology and topography of materials at a resolution of 10 nm. It is therefore an essential tool for texture analysis. In this study, JEOL JSM 7610F plus Field Emission Scanning Electron Microscope was used.

#### **3.2 Compositional Analysis**

#### **3.2.1 Powder X-Ray Diffraction (PXRD)**

Powder x-ray diffraction (PXRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The interaction of the incident rays with the sample produces constructive interference when Bragg's Law is satisfied ( $n\lambda = 2dsin(\theta)$ ). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted x-rays are detected, processed, and counted. In this study, a Bruker D2 phaser X-ray diffractometer with Cu-K<sub>\alpha</sub>=1.54056 Å) radiation, operating at 45kV and 30mA.

#### **3.2.2 Fourier Transform Infrared Spectroscopy (FTIR)**

Fourier Transform Infrared Spectroscopy (FTIR) is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid, or gas. Infrared spectroscopy involves the interaction of infrared radiation with matter. It covers a range of techniques, mostly based on absorption spectroscopy. As with all spectroscopic techniques, it can be used to identify and study elements with various composition. IR spectroscopy is often used to identify structure because functional groups give rise to characteristic bands, both in terms of intensity and position (frequency). To study the functional groups, mid infrared band of 4000-400 cm<sup>-1</sup> is used. The mid infrared region is used to study the fundamental vibrations and associated rotational vibrations of the functional groups associated with the sample. In this study, a Perkin Elmer FTIR spectrometer is used with mid infrared band with wavelength 2.5-25 µm.

#### **3.3 Photoluminescence Spectroscopy**

To explore the electronic structure of any material, photoluminescence spectroscopy is the most widely used, contactless, and nondestructive technique. Light is directed onto a sample, where it is absorbed and imparts excess energy into the material in a process called photoexcitation. This excess energy is usually dissipated through emission of light, known as luminescence. In case of photoexcitation, this luminescence is called as photoluminescence. The energy of the emitted light (photoluminescence) relates to the difference in energy levels between the two electron states involved in the transition between the excited state and the equilibrium state. The quantity of the emitted light is related to the relative contribution of the radiative process. This technique is

primarily used for detection of AIE and ACQ mechanisms, along with that, photoluminescence spectroscopy finds its applications in band gap determination, detection of defects and impurity levels, and determination of recombination mechanisms.



Figure 8: Essentials of a luminescence experiment apparatus.

# **Chapter 4**

# **Syntheses**

#### 4.1 Synthesis of the gelator derived from phenyl succinic acid – H<sub>2</sub>PSL

#### 4.1.1 Synthesis of phenylsuccinate ester (Esterification of phenylsuccinic acid)

To a methanolic solution of phenylsuccinic acid (1.00g, 5.1mmol) concentrated sulphuric acid was added as a catalyst and the reaction was mixture refluxed for 18hrs at 60°C. In vacuo reduction in volume with mild heating was done to obtain dimethyl phenylsuccinate ester as an oily and sweet-smelling substance.



Figure 9: Preparation of phenylsuccinate ester.

#### 4.1.2 Synthesis of phenylsuccinic di-hydrazide

To the obtained dimethyl phenylsuccinate (1.00g, 4.5mmol) 2 equivalents of hydrazine hydrate (0.45g, 9mmol) were added in methanol under refluxed conditions for 6 hours at room temperature. A white crystalline powder of phenylsuccinic hydrazide (PSAH) was obtained from above solution which was filtered, washed with methanol and diethyl ether and dried in desiccator.



Figure 10: Phenyl Hydrazide synthesis.

#### 4.1.3 Addition of salicylaldehyde to PSAH – obtaining H<sub>2</sub>PSL

The compound PSAH (0.300g, 0.32mmol) was dissolved in 2mL of water and then mixed in 20mL methanol to obtain a clear solution. To this solution, 2 equivalents of 2-hydroxybenzaldehyde (0.329g, 0.64mmol) in methanol was added dropwise and the solution was left and refluxed for 3 hours at 60°C. The white precipitate afforded from the solution was stirred for additional 2 hours at room temperature and then filtered, washed thoroughly with chloroform, methanol, hexane and diethyl ether to afford a white solid (H<sub>2</sub>PSL).



*Figure 11*: *Synthesis of H*<sub>2</sub>*PSL*.

#### 4.2 Synthesis of the ligand derived from (L)-malic acid – H<sub>2</sub>LMAL

#### 4.2.1 Synthesis of (L)-malic ester

Similar to the prior synthesis route, to a methanolic solution of (L)-malic acid (1.00g, 7.4mmol) concentrated sulphuric acid was added as a catalyst and the reaction was mixture refluxed for 18hrs at 60°C. In vacuo reduction in volume with mild heating was done to obtain dimethyl (L)-malic ester as an oily and sweet-smelling substance.



*Figure 12*: *Preparation of (L)-malic ester.* 

#### 4.2.2 Synthesis of (L)-malic dihydrazide

To the obtained malic diester (1.00g, 6.1mmol) 2 equivalents of hydrazine hydrate (0.61g, 12.2mmol) were added in methanol under refluxed conditions for 6 hours at room temperature. A white crystalline powder of malic hydrazide (LMAH) was obtained from above solution which was filtered, washed with methanol and diethyl ether and dried in desiccator.

$$H_{3}CO \xrightarrow{O} OCH_{3} + H_{2}N-NH_{2} \xrightarrow{40^{\circ}C, 6h} H_{2}N_{N} \xrightarrow{O} H_{2}N_{2} \xrightarrow{O} H_{2}N_{2} \xrightarrow{O} H_{2}N_{2} \xrightarrow{O} H_{2}N_{2} \xrightarrow{O} H_{2}N_{$$

Figure 13: Malic Hydrazide synthesis.

#### 4.2.3 Synthesis of H<sub>2</sub>LMAL

The compound LMAH (0.300g, 0.18mmol) was dissolved in 2mL of water and then mixed in 20mL methanol to obtain a clear solution. To this solution, 2 equivalents of 2-hydroxybenzaldehyde (0.451g, 0.36mmol) in methanol was added dropwise and the solution was left and refluxed for 3 hours at 60°C. The white precipitate afforded from the solution was stirred for additional 2 hours at room temperature and then filtered, washed thoroughly with chloroform, methanol, hexane and diethyl ether to afford a white solid (**H**<sub>2</sub>LMAL).



Figure 14: Synthesis of H<sub>2</sub>LMAL.

# **Chapter 5**

# **Results and Discussion**

With an objective to understand the effect of addition of chirality to succinic acid derived ligand earlier reported by us, herein, we synthesized **H<sub>2</sub>PSL** derived from phenylsuccinic acid having two chelating donor sites (N, O) separated by a  $-CH_2$  unit and a -CH unit substituted by a phenyl group (Figure 15)<sup>22,24</sup>. The phenyl group present in **H<sub>2</sub>PSL** is expected to provide a platform for aggregation via additional  $\pi$ - $\pi$  stacking which is followed by the formation of a CHEF assisted metallogel. Upon close inspection of the characterization results of <sup>1</sup>H NMR of **H<sub>2</sub>PSL** in d<sub>6</sub>-DMSO there is a possibility of the presence of four conformers (anti/syn, anti/anti, syn/anti, and syn/syn)<sup>22,40</sup> which upon deprotonation with LiOH converted into a single conformer (syn/syn) (Figure 16).



*Figure 15*: *Representation of the steps involved in metallogel formation along with the changes in fluorescence.* 



Figure 16: Conversion of four enantiomers into one.

The deprotonation of  $H_2PSL$  with 2 equivalents of alkali base i.e. LiOH in DMF followed by sonication for about 10 minutes led to the formation of fluorescent metallogel. The gelation was confirmed by the conventional inverted vial test. The metallogel obtained was found to be responsive to heating, mechanical shaking whereas resistant to ultrasound (Figure 17).



*Figure 17:* Stimuli-responsive behaviour towards temperature and mechanical force as well as resistance for ultrasound of metallogel.

Alkali bases other than LiOH i.e. NaOH, KOH, CsOH also failed to form metallogel with  $H_2PSL$  in DMF under aforementioned conditions, which implies the selectivity of ionic Li<sup>+</sup> radius towards gelation (Figure 18, 19 and Table 1). Further, optimizing the gelation parameters for gelation of  $H_2PSL$  with LiOH in various solvents such as CH3OH, DMSO, CHCl3 (Table 2) either led to the formation of gelatinous precipitate or solution.



Figure 18: Gelator H<sub>2</sub>PSL with (A) NaOH, (B) KOH, and (C) CsOH under white light.



Figure 19: Gelator  $H_2PSL$  with (A) NaOH, (B) KOH, and (C) CsOH under UV lamp  $(\lambda_{em}=365nm).$ 

Solvent	$H_2PSL + LiOH$	$H_2PSL + NaOH$	$H_2PSL + KOH$	$H_2PSL + CsOH$
DMF	G	S	S	SP

**Table 1:** The solubility and gelation ability of  $H_2PSL$  in DMF with alkali metalsS = Soluble, G = Gel, SP = Suspension

Solvent	H <sub>2</sub> PSL+LiOH
Water	I
Methanol	I
Ethanol	I
DMSO	S
DMF	G
Chloroform	SP

Table 2: Gelation ability of H<sub>2</sub>PSL with all solvents in the presence of LiOH

#### I = Insoluble, S = Soluble, G = Gel, SP = Suspension

#### **5.1 Complexation Analysis**

FTIR spectroscopy of the gelator i.e. ligand **H**<sub>2</sub>**PSL** revealed the presence of characteristic peaks of v(-OH), v(-NH) at 3250 cm<sup>-1</sup> and 3052 cm<sup>-1</sup> respectively, while, a strong peak at 1653 cm<sup>-1</sup> attributed to v(-C=O) group (Figure 20). Along with the aforementioned peaks, the v(-C=N) is found to be at 1532 cm<sup>-1</sup> which indicates towards the presence of the ligand in the phenolic form. On comparing the FT-IR spectra of the ligand with that of the xerogel, no significant change was observed. The characteristic peaks corresponding to v(-OH), v(-NH) shifted to 3256 cm<sup>-1</sup> ( $\Delta v = 6$ cm<sup>-1</sup>) and 3056 cm<sup>-1</sup> ( $\Delta v = 4$  cm<sup>-1</sup>) respectively, with their intensities diminished. Following the same trend almost no change was observed in the characteristic peaks of v(-C=O), v(-C=N) observed at 1652 cm<sup>-1</sup> ( $\Delta v = 1$  cm<sup>-1</sup>) and 1532 cm<sup>-1</sup> ( $\Delta v = 0$  cm<sup>-1</sup>) respectively. These infinitesimally small changes in the FT-IR spectra of the gelator and the metallogel hints towards the formation of long intermolecular network as a result of weak interaction forces between Li+ and the functional groups present in H<sub>2</sub>PSL i.e. -C=O, -OH and -C=N.



Figure 20: A comparative FT-IR spectrum for H<sub>2</sub>PSL and xerogel obtained from H<sub>2</sub>PSL/Li<sup>+</sup>.

#### **5.2 Mass Spectral Analysis**

For the purpose of ensuring the formation of metallogel which was unclear from the FTIR spectral analysis, we performed a thorough ESI-MS spectral analysis of the diluted metallogel (Figure 21). The ESI-MS spectra observed for the gelator calcd for  $[(C_{24}H_{22}N_4O_4)_2-Na]$  883.3; found 883.4 and the isotopic abundance pattern for ligand peak at m/z= 883.3 matches fairly well with the simulated peak pattern. Another major peak observed for the diluted metallogel calcd for  $[C_{24}H_{22}N_4O_4-Li]$  437.18; found 437.2 again matches nicely with the simulated peak pattern at m/z=437.2 which indicates towards the proposition of formation of 1:2 coordination complex between H<sub>2</sub>PSL and LiOH.



*Figure 21:* ESI-MS (DMF/CH<sub>3</sub>OH) spectra of diluted metallogel of H<sub>2</sub>PSL/Li<sup>+</sup>.

#### 5.3 UV-vis Study

With an objective to explore the complexation of ligand with  $Li^+$  and interaction of  $Li^+$  with different functional groups attached in ligand we carried out electronic absorption study (Figure 22). The absorbance spectra exhibiting two vividly coupled bands for **H<sub>2</sub>PSL** (10<sup>-5</sup> M, DMF,

298K) at  $\lambda_{max}$ = 282 nm and 290 nm endorse for  $\pi$ - $\pi$ \* transition, this splitting of peaks reinforce the fact that the ligand exhibits dissimilar planarity<sup>22</sup>. However, a less intense band at  $\lambda_{max}$ = 322 nm endorse for n- $\pi$ \* transition. Deprotonation of ligand through stepwise addition of 2 equivalents of LiOH (10<sup>-3</sup> M, DMF) revealed some unusual phenomena, for the first four additions out of total 16 additions the absorbance remained constant and then increased for the next addition. Then upon subsequent additions it remained constant and then increased at the tenth addition and further it decreased until the last addition. A negligible blue shift ( $\Delta\lambda$ = 1 nm) was observed for the band at 322 nm. A stoichiometric ratio of 2:1 is expected to be present between Li<sup>+</sup> to the gelator **H2PSL**.



*Figure 22:* UV-vis titrations in DMF of the gelator  $H_2PSL$  with LiOH showing no change in the electronic spectra.

#### 5.4 Aggregation Study

With an objective to further explore the presence of various fluorescence phenomena in the metallogel i.e. CHEF and AIE, we performed fluorescence experiment over H<sub>2</sub>PSL and the metallogel (Figure 23). The transformation of a non-fluorescent solution of H<sub>2</sub>PSL ( $\lambda_{ex}$ =320nm,  $\lambda_{em}$ =481nm, stokes shift=62111.80 cm<sup>-1</sup>, 1x10<sup>-2</sup> M, DMF, blue line) into a blue-green fluorescent

solution when deprotonated with LiOH  $(1x10^{-1} \text{ M}, \text{DMF}, \text{red line})$  with a significant rise in the fluorescence intensity can be recognized as the chelation of Li<sup>+</sup> and PSL<sup>2</sup>- and can be attributed to the phenomenon of chelation enhanced fluorescence (CHEF) as reported in our previous works as well<sup>22,25,41-45</sup>. It is noteworthy to observe that the irregular shape of the fluorescence spectra of **H2PSL** transformed into a well-shaped spectrum upon subsequent additions of LiOH solution.

Thermal responsiveness and the reversibility of the metallogel was further investigated by the fluorescence experiment which showed the metallogel losing its intensity upon heating and it regained 79% of its intensity when it came back to room temperature (Figure 18). The exact imitation of the fluorescence curves strongly supports the thermal reversibility of the metallogel up to  $70^{\circ}$ C.

In order to confirm the presence of AIE and ACQ phenomena we performed fluorescence dilution experiment on freshly prepared metallogel, with its dilution ranging from  $10^{-2}$  M to  $10^{-4}$  M and observed enhancement and quenching phenomena in two steps. In the first step, the peak corresponding to the metallogel at 482 nm undergoes quenching with blue shift of about  $\Delta \lambda = 17.2$  nm (Figure 18), suggesting the removal of AIE with the dilution from  $10^{-2}$  M to  $10^{-3}$  M. Afterwards, when the metallogel was diluted from  $10^{-3}$  M to  $10^{-4}$  M the peak corresponding to 490nm undergoes blue shift of about  $\Delta \lambda = 11.2$  nm with continuous enhancement in the intensity, suggesting the removal of ACQ from the metallogel. The occurrence of quenching and enhancement behavior during the course of dilution of the metallogel indicates the presence of AIE and ACQ respectively along with CHEF phenomena in the metallogel.





**Figure 23:** Fluorescence experiment (A) non fluorescent  $H_2PSL$  (10<sup>-3</sup> M, DMF, blue line) turned fluorescent upon deprotonation and titration with LiOH (10<sup>-1</sup> M, DMF, red lines) as observed by enhancement in the intensity. (B) fluorescent  $H_2LMAL$  (10<sup>-3</sup> M, DMF, black) turned non fluorescent upon deprotonation and titration with LiOH (10<sup>-1</sup> M, DMF, red lines) as observed by quenching in the intensity. (C) Metallogel temperature up ramp fluorescence experiment from 30°C to 70°C. (D) Metallogel temperature down ramp fluorescence experiment from 30°C to 70°C. (E, F) Gel dilution fluorescent experiment performed over metallogel in the range of 10<sup>-2</sup> M to 10<sup>-3</sup> M dilution.</sup>

Based on the observations drawn from above, we summarised the plausible mechanism of gel formation in figure 24.



*Figure 24:* A model representation for plausible mechanism of the gelation along with structural changes.

#### 5.5 Morphological Characterization

When examined under field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM), definite morphological features were obtained.

FESEM study of xerogel obtained from  $H_2PSL/Li^+$  revealed a fibrous morphology and TEM study of diluted metallogel showed the formation of nano-balls of about ~31nm in average diameter (Figure 25), suggesting that the formation of fibres begins with the formation of nano-balls. These nano-clusters further aggregate and give rise to the fibres which are clearly evident in the SEM images (Figure 26). Similar unique observations were reported in our previous publications as well in which a metallogel derived from L-tartaric acid ligand exhibited nano-cluster morphology<sup>24</sup> and another instance where a metallogel derived from citric acid ligand showed a nano-fibrous morphology<sup>22</sup>.

PXRD patterns of **H<sub>2</sub>PSL** in the range  $2\Theta = 5^{\circ} - 80^{\circ}$  indicates its crystalline nature while that of the xerogel indicates its amorphous nature. **H<sub>2</sub>PSL** shows peak at  $2\Theta = 5.18^{\circ}$ , 7.72°, 12.36°, 15.22°, 16.64°, 17.44°, 18.82°, 20.9°, 22.2°, 27.08°, 28.58°, 30.56°, 31.3°, 37.88° and 42.66° whereas xerogel showed major peaks at  $2\Theta = 7.84^{\circ}$ , 14.24°, 17.04°, 22.48° and 30.32° (Figure 27).



*Figure 25:* TEM images of the diluted metallogel at four different magnifications. The entities encircled in yellow perimeter shows the presence of nano balls which eventually lead to the formation of nano fibres.



Figure 26: SEM images of the xerogel at four different magnifications.



Figure 27: PXRD pattern of the xerogel (black lines) and H<sub>2</sub>PSL (red lines).

Three periodic diffraction peaks were obtained in the PXRD pattern of the xerogel at  $2\Theta$  = 7.82°, 14.24° and 22.48° corresponding to *d*-values 11.29Å, 6.21Å and 3.95Å respectively with the sequential ratio of about d : d/2 : d/3. The characteristic ratio of *d*-values advocates the presence of layered arrangement between molecule aggregates with the distance between layers equalling to 11.29Å. Also, the presence of the diffraction peaks at  $2\Theta$  =

17.04° and 22.48° corresponding to the *d*-values 5.19Å and 3.95Å respectively bolsters the presence of  $\pi$ - $\pi$  stacking enhanced by the presence of phenyl group present in the derived ligand<sup>46–50</sup>. However, the crystallization of Li<sup>+</sup> in salt form cannot be ruled out<sup>22,24,51</sup>.

#### 5.5 Rheological Study

Rheological experiments were performed over freshly prepared metallogel (3.6% w/v) to examine its true gel phase and its viscoelastic properties.



**Figure 28:** (*A*) Dynamic oscillation strain sweep of *G* and *G* and *G* trequency of 1 rad s<sup>-1</sup> at 25°C. (B) Dynamic shear stress of *G* and *G*. (C) Dynamic temperature ramp of complexation viscosity measurement at 5°C min<sup>-1</sup>. (D) Dynamic shear stress of *G* and *G*. (E) Dynamic temperature ramp vs *G* and *G* and *G*. (D) Dynamic stress of 1°C min<sup>-1</sup>, strain 0.5%

and frequency 1 rad s<sup>-1</sup>. (F) Dynamic temperature ramp of loss tangent (tan $\delta = G''/G'$ ) plot at 5°C min<sup>-1</sup>, which indicates the critical temperature ( $T_{gel}$ ) 90°C for metallogel.

The predominantly linear nature of the storage modulus (G') and the loss modulus (G'') with a slight increase within the applied frequency range (f) (-1.0 to 2.0 rad s<sup>-1</sup> on the logarithmic scale) advocates the elastic nature of the metallogel when subjected to frequency sweep experiment between 0.1 to 100 rad s<sup>-1</sup> at 25°C within linear viscoelastic region (Figure 28)<sup>52</sup>. Furthermore, the superiority of G' over G'' and the crossing of G' over G'' suggest that there is no phase separation or transition which is predicted for a true gel phase. The fact that G' and G'' are very insensitive to any change in the angular frequency provide further evidence of elasticity. Effect of temperature on G' and G'' was recorded within the temperature range 25°C-130°C (Figure 28). Storage modulus and loss modulus remained unaffected to any change in temperature up to 85°C and with subsequent increase in temperature their values started to decrease which indicates towards the liquification of the metallogel.

Storage modulus (G') and loss modulus (G'') were obtained at 25°C and 1 rad s<sup>-1</sup> as a function of shear stress and shear strain (Figure 28). The value of storage modulus (G'), when the metallogel was subjected to oscillatory shear, was found to be higher than the value of loss modulus (G'') by an order of ~0.75 magnitudes of shear stress. This agrees with the true gel phase of the metallogel where no variation in the values of G' and G'' was observed with substantially long range of increasing applied stress. At a yield stress of about 2.6 Pa the curves of G' and G'' intersect which establishes the mechanical breakup of the gel and beyond this point deviation in linearity results in gel-sol phase transition.

However, the in-phase storage modulus G' and out-of-phase loss modulus G'' remained constant up to a strain of magnitude of 2.5% beyond which the deformation of the internal network occurred. A curve between loss tangent ( $\tan \delta = G''/G'$ ) and temperature is plotted to observe the thermal stability and the thermal responsiveness of the metallogel. A significant change in the curve at around 90°C indicate the phase transition temperature "T<sub>gel</sub>" (critical temperature) of the metallogel. These results of the dynamic temperature ramp conclude that the phase transition of the metallogel occurs at 90°C which is

understandable for a metallogel formed in DMF. Thus, the rheological experiments show that the present metallogel has similar rheological properties as the hydrazine derived metallogel<sup>25</sup> whereas it possesses a much higher yield stress than all of our previously reported metallogels<sup>22,23,25</sup>.

#### 5.6 Thermogravimetric Analysis

TGA experiments were performed over dried xerogel which was obtained by vacuum desiccating the metallogel and washing with methanol and water to remove any unwanted substance (Figure 29). The temperature varied from room temperature to 800°C at the rate of 5°C/min. The xerogel was found to be stable up to approximately 250°C. At around 300°C, the xerogel completely lost its stability and decomposed to 30 percentage of its original weight.



*Figure 29:* Thermo Gravimetric Analysis (TGA) of isolated compound from xerogel (washed with H<sub>2</sub>O/CH<sub>3</sub>OH to remove any extra salt and vacuum dried).

# **Chapter 6**

# **Conclusions and Scope for Future Work**

#### **6.1 Conclusions**

To conclude our work, we explored two flexible system H<sub>2</sub>PSL and H<sub>2</sub>LMAL, out of which H<sub>2</sub>PSL exhibited a dramatic increase in the fluorescence through the mechanisms of CHEF and AIE which were followed by ACQ mechanism which led to the gel formation. Furthermore, we demonstrated the selectivity of gelation towards lithium ions by using other bases, NaOH, KOH, and CsOH. The selectivity of gelation towards the solvent is also demonstrated, which confirmed DMF to be the most suitable solvent for gelation. SEM analysis revealed nice nanofibrous morphology in the metallogel. Further, TEM analysis revealed that these nanofibers actually originate with the formation of nanoballs. Gelation mechanism is well established by UV-vis, FTIR, PXRD, fluorescence, and TEM experiments. The true gel phase of the metallogel was proved by rheological experiments done over freshly prepared metallogel.

#### **6.2 Scope for Future Work**

In future, further experiments over  $H_2PSL$  and  $H_2LMAL$  such as <sup>1</sup>H-NMR titration, can be performed to further explore the role of solvophobic and solvophilic functional group on fluorescence and gelation ability. Circular Dichroism experiment can be performed over  $H_2PSL$ and  $H_2LMAL$  to understand the effect of functional group on chirality. The desired chirality can be obtained by synthesizing carbon dots of  $H_2PSL$  and  $H_2LMAL$  and tuning the proportion of  $H_2PSL$  and  $H_2LMAL$  in their carbon dots solution and the resultant solution can be explored for its applicability in bio-imaging and live cell imaging.

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