METALLOGELS IN CATALYSIS

M.Sc. Thesis

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METALLOGELS IN CATALYSIS

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of Master of Science

> by PRIYANSHU NAUTIYAL



DEPARTMENT OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE MAY, 2022



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "Metallogels in Catalysis" in the partial fulfillment of the requirements for the award of the degree of MASTER OF SCIENCE and submitted in the DEPARTMENT OF CHEMISTRY, INDIAN INSTITUTE OF TECHNOLOGY INDORE, is an authentic record of my own work carried out during the time period from July 2021 to June 2022 under the supervision of **Prof. Suman Mukhopadhyay**, Professor, IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree at this or any other institute.



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This is to confirm that the candidate's above statement is true to the best of my/ our knowledge.



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DEDICATED TO

MY PARENTS

And elder brothers

And all the well-wishers

ABSTRACT

A gelator molecule N², N⁴, N⁶-tri(pyridin-2-yl)-1,3,5-triazine-2,4,6triamine (PN2) has been synthesized and characterized well by ESI-MS and ¹H NMR spectroscopy techniques. **PN2** shows stable gel formation in of 5-(3,5-bis((1H-tetrazol-5the presence triethylammonium yl)carbamoyl)benzamido)tetrazol-1-ide (G7) which acts as a trigger molecule for the gel formation of PN2. The combination of G7 and PN2 tends to show stable organogelation and metallogelation in the DMSO-H₂O solvent mixture. The thermal study of PN2, G7 and xerogels of G7PN2 has been done by TGA analysis. Three metallogels namely M¹G7PN2, $M^{2}G7PN2$, and $M^{3}G7PN2$ [M¹=Fe (III), M²=Cu (II), and M³=Ag(I)] were obtained from the combined gelator system. The morphology transformation from organogels to metallogels have been investigated by FE-SEM analysis. Among these, the synthesis and stabilization of silver nanoparticles has been done using M¹G7PN2. These M¹G7PN2AgNPs nanocomposite have been used as catalysts to reduce nitro-substituent into their amine product. UV-vis spectroscopy was used to check the progress of the reaction. ¹H NMR was also used to confirm the reduction process. In addition, the nanocomposite M¹G7PN2AgNP powder is also transformed into a metallogel in the presence of the G7 and PN2. This metallogel also shows thixotropic behavior which was confirmed by time oscillation sweep experiments.

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NOMENCLATURE

θ	Angle
Å	Angstrom
cm	Centimeter
δ	Chemical shift (N.M.R.)
°C	Degree Centigrade
υ	Frequency
G	Gram
μL	Micro Litre
mg	Milligram
mM	Milli Molar
mmol	Milli Mole
mL	Milli Litre
Μ	Molar
mol	Moles
nm	Nanometer
%	Percentage
S	Seconds
Λ	Wavelength

ACRONYMS

AIEE	Aggregation induced emission enhancement
С	Carbon
DMF	Dimethylformamide
DMSO	Dimethyl sulphoxide
ESI-MS	Electrospray Ionization-Mass Spectrometry
FE-SEM	Field Emission Scanning Electron Microscope
FT-IR	Fourier Transform-Infrared
Н	Hydrogen
Fe	Iron
MeOH	Methanol
Ν	Nitrogen
NMR	Nuclear Magnetic Resonance
0	Oxygen
PXRD	Powder X-Ray Diffraction
Ag	Silver
UV	Ultraviolet
H ₂ O	Water

CHAPTER 1

Introduction

1.1 General Introduction

Metal-organic compounds are found with wide range of structural and physical diversities, from metal-coordination complexes to soft materials, and have applications in areas such as dye adsorbent¹, biomaterials², catalysis³, drug delivery⁴, material science and sensing⁵, and many others. Researchers can create metal-coordination complexes as well as soft materials with a variety of structural features because of the unlimited combinations of inorganic and organic building blocks. Soft materials have been discovered to be an intriguing new class of materials. The use of metalorganic compounds to construct the soft material with desirable properties is proving to be a successful strategy. Though there are several literature papers that look into the design and application of metal-based soft materials, there is still a lot of room to come up with new low molecular weight gelators and metal-based soft materials, as well as investigate their fascinating properties. Although the organic gelator molecule have capability to formed organogel but the incorporation of metal ions inside it can impart some additional properties to make it suitable for various applications and might also trigger the gel formation due to metal ligand interactions.⁶

Soft materials are those materials that are easily affected by pressures or temperature changes. Some of the examples of soft materials include liquids, polymers, foams, gels, colloids, granular solids, and others. Gels are type of soft material that have wide range of uses in variety of scientific domains. Entrapment of solvent molecules in the available spaces of the solid system by various forces leads to formation of these viscoelastic soft materials⁷. Gels are a type of soft material that we come across in our everyday lives, but we are often unaware of it (Figure 1.1) and they are materials that appear to be in a phase between solid and liquid and have a jelly-like texture. Various non-covalent interactions such as van der Waals interaction, hydrophobic interactions, dipole-dipole interactions, H-bonding interactions play defining roles in tuning the structure of the soft materials.^{8–10}These non-covalent interactions endow gels with ability to respond towards heat, sound, pH, light etc., attributing different interesting properties and functionalities.⁶ Inversion test is a common way to identify gel since it is stable against gravitational force when turned upside down.



Figure 1.1 Uses of gel in daily life

Gels are basically made up of two parts: the gelator and the solvent. In general, the gelator entraps the solvent molecules as a primary component to form three-dimensional structure, resulting in a favorable balance of crystallization and solution. There are primarily three outcomes noticed throughout the process of gelator solubility in the solvent.¹¹ First, crystal formation occurs when molecules self-assemble in a highly organized manner. Second, random self-assembly could result in an amorphous

precipitate. Third, the production of gel is caused by self-assembly in an orderly manner by entrapping the solvent.¹¹(Figure 1.2)



Figure 1.2 Modes of aggregation

1.2 Classification of gels

Gels can be categorized in many different ways. Firstly, the presence or absence of metal nodes can be used to classify gels. Metallogels are those gels that contain a metal complex or ion, whereas organogels does not contain any metal ion inside its network. Water is immobilised in a solid network of hydrogels, whereas organic solvents or a mixture of organic solvents are immobilised in a solid network in organogels. The solid networks in gels are made up of a tiny quantity of polymeric gelators or LMWGs (typically less than 5% by weight).^{12–14} Non-covalent interactions such as hydrogen bonding, hydrophobic contacts, dipolar interactions, electrostatic interactions, and π - π stacking play an important role in the self-assembly of the gelator molecules in various solvents, allowing them to expand one-dimensionally to form fibrils. These fibrils are then formed into fibres via van der Waals interactions. A typical fibrous network of gel is

formed by three-dimensional entanglements of these fibres^{15–18}. Xerogels or aerogels are gels in which the solvent has been removed. Dried hydroor organogels are referred to by this terminology.

The origin of the gels may also be recognized for their classification. It can be natural gels (obtained from natural sources gelatin, chitosan, alginate, etc.) or artificial gels (made in laboratories).

Furthermore, we may categorise gels based on the molecular aggregation driving factors. Chemical gels are crosslinked polymers formed by covalent bonds that are unable to dissolve again, whereas physical gels are made of low molecular weight (LMW) molecules or polymers formed by non-covalent interactions that result in reversible gel-to-sol phase transitions.¹¹

Metallogels are further divided into two groups. A discrete metal complex gel is formed when a synthesized metal complex act as a gelator molecule and self-assembles through non-covalent interactions to produce a fibrous network that entraps the solvent molecules.^{19,20} There is no direct engagement of metal ions in the formation of these types of metallogels. The other one is the coordination polymer gel (CPG) in which nodes are metal ions, while linkers are LMWGs. Here metal–ligand interaction causes gelation, and metal ions play an active role in the development of the gel network.¹⁶ (Figure 1.3)



Figure 1.3 Classification of gels on the basis of (a) gel component (b) occurrence

1.3 Characterizations and properties of gels

The characteristics and characterizations of gels are studied using a variety of experimental approaches. Nowadays, wide experimental

approaches are available to help researchers understand the structure, bulk nature, and process of gelation.²¹ Gels are created by a self-assembly mechanism, which is investigated largely through their thermodynamic and rheological features. Visual evaluations such as the inverted test tube method and falling ball technique can also be used to determine the viscosity point (Figure 1.4). The heating-cooling approach, on the other hand, implies that gel is thermo-reversible.²²

To comprehend gelation, a variety of skills and strategies are employed²³ (Figure 1.5). The mechanical strength of the gel can be determined using rheological studies.²⁴ Rheology testing involves analyzing the internal reaction of materials to forces and measuring the deformation of matter under the impact of induced stress. The rheological experiment is carried out by subjecting the gel to oscillatory stress, and the resultant values of G' (elastic storage modulus) and G'' (elastic loss modulus) are used to assess the gel's strength. However, in the case of gels, the rheological experiment should indicate that G' is higher by at least an order of magnitude than G''.²⁵

Furthermore, numerous microscopic methods may be used to identify the structure of gel at the molecular level, from nano to microscale. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are two techniques that may be used to show the morphologies of gels. Fourier transforms infrared (FTIR), powder Xray diffraction (PXRD), nuclear magnetic resonance (NMR) spectroscopy is used to study the non-covalent interaction.

After aggregation, the gel formation might cause aggregation-caused quenching (ACQ), which implies a decrease in molecular emission intensity. Some gelator molecules, have an aggregation-induced enhanced emission (AIEE) feature, which implies an increase in emission intensity following aggregation.^{26–28} Self- healing is also one of the most outstanding characteristics of the gel. It is the capacity of

gels to self-heal and regenerate after being disrupted by external stimuli.^{29–31}



Figure 1.4 Inversion test for gels



Figure 1.5 Techniques to understand gelation

1.4 Metallogels in Catalysis

Metal complexes are widely recognized as significant agents in a variety of organic reactions, and a number of metal catalysts with high activity have been devised and produced.^{32–35} Metallogels are a special kind of supramolecular gels where metal ligand interaction remains play an important role in their formation, along with the other non-covalent interaction.⁷ These metallogels might possibly be used as a new sort of supramolecular catalyst in organic processes, thanks to the incorporation of

metal centres into gelator molecules, which has gained a lot of interest recently.

Catalytic transformation refers to the use of catalysts to efficiently lower the activation energy of breaking chemical bonds while also providing high yields and selectivity.^{36,37} Supramolecular gels will be candidates for novel type of catalysts with distinct advantages, such as well-defined structures and morphologies, recycle utilisation, and easy separation, if catalytic sites including metal centres and active organic functional groups are introduced into the gelator molecules.^{38,39} Supramolecular gels with rational designs can also be employed as potential templates for the production of metal nanoparticles (MNPs) as active catalysts.⁴⁰

1.5 Organization of the thesis

The aim of this project is to synthesize gelator molecules with prospective suitable properties for fabrication of metallogels with the incorporation of suitable metal ions s. Based on the properties of the metallogels obtained, it is applied further for some selected catalytic reactions.

Chapter 2: This chapter discusses previous work in the same field as well as the reason and motivation for the project's work done.

Chapter 3: Materials, instruments, and experimental procedures for the production of gelator molecules and the generation of metallogels are covered in this chapter. This chapter also covers the synthesis of the catalyst using the fabricated metallogel system and its use in a chemical reaction.

Chapter 4: This chapter comprises of the results obtained after the synthesis of gelator molecule and formation of metallogel system.

Chapter 5: This chapter summarizes the work completed as well as potential future scope and uses.

CHAPTER 2

Review of past work and project motivation

2.1 Sensing

One of the most researched areas of supramolecular chemistry is analyte sensing. Optical sensing is one of the extensively used types of sensing, in which the interaction of analyte with sensor molecule results in a change in absorbance or fluorescence characteristics. This is an extremely sensitive approach since it can detect very low concentrations of the analyte. A tiny change in concentration causes a huge variation in the optical response, allowing for a more thorough investigation of sensing and its process. Analyte sensing is applicable in various fields, including biological systems.^{41–43} Weak interactions such as π - π stacking, H-bond formation, Vander Waals force, and others enable low molecular weight gelators (LMWG) to create self-assembled structures. Because of the phenomena of AIEE or ACQ, these molecules can serve as excellent sensors.⁴⁴ Malviya et al., reported two gelator molecules G2 and G3 where both the organogelators did not show any fluorescence peak in solution, but after gel formation fluorescence peak appeared due to AIEE phenomena. The addition of various metal ions enhances the gel characteristic without significantly altering the fluorescence behaviour. The AIEE, on the other hand, was entirely turned off in the presence of Ag^+ , Fe^{2+} , and Fe^{3+} , causing the molecule to sense silver and iron in the gel state. G3 also detects ferrous ions by shutting off fluorescence in the gel state²⁴.



Figure 2.1 Organogelators G2 and G3.



Figure 2.2 Studies of G2 and G3 in DMF under Fluorometer²⁴

Many gels capable of sensing anions have been described in recent years. Cd-based gel⁴⁵, bis(benzimidazole)-based gels^{46,47}, trimesic amide-based gels⁴⁸, trisamide tripodal derivatives ⁴⁹, aminopyridine- urea molecules⁵⁰ have been reported with similar applications.

2.2 Catalytic activity

Supramolecular metallogels are suitable candidates for unique kind of catalysts with distinct advantages, such as well-defined shapes and morphologies, recyclic utilization, and simple separation, due to the presence of metal center and active organic functional groups in the gelator molecules.⁵¹ However, their potentials in organic transformations and catalysis, has remained largely untapped. Moreover, Supramolecular gels may also be used as a variety of templates to access different metal

nanoparticles (MNPs) as active catalysts, which has triggered scientists' curiosity.^{52,53}

Malviya *et al.* reported a copper-based metallogel with G2 which can operate as a reaction media and a catalyst for oxidation of catechol. This reaction was monitored using UV-vis spectroscopy for the production of the oxidized product, quinone. The investigations demonstrated that when catechol was added to the gel, a peak at roughly 402 nm formed very immediately, suggesting catechol oxidation. With time, the peak become more intense, and a minor red shift was noted, which eventually get stabilized at approximately 410 nm.²⁴



*Figure 2.3 Study of oxidation of catechol using UV-Vis spectroscopy and colour changes during the course of time.*²⁴

Kyarikwal *et al.* synthesised various metallogels with gelator molecule **G7**. Out of these metallogels, **Fe (III)-G7** metallogel was chosen for the formation and stabilisation of the silver nanoparticles (**AgNPs**). The nanocomposite was utilised as a catalyst for the reduction of nitrosubstituents to the amines. UV-Vis, GCMS, and ¹H NMR methods were used to analyse the reduction reactions of nitro compounds, and the procedure was completed in 35 minutes.⁴⁰



Figure 2.4 G7 and its metallogels formation and applications in metal absorption, AgNPs synthesis, and nitro substituent reduction⁴⁰

Lee *et al.* synthesized ligand **1** as a tri-connected linker that shows the tendency to form gel in the presence of various metal ions, notably Cd^{2+} and Zn^{+2} . SEM, TEM, rheology, and single XRD crystallography were used to characterize the gels. It was further used in a Knoevenagel condensation process catalysed by this xerogel to determine its base-type characteristics. Xerogel accelerated the reactions of benzaldehyde with the various active methylene compounds. In the catalytic reaction, the heterogeneity and recyclability of xerogel were also investigated and its catalyst ability exhibited high recyclability.³



Figure 2.5 Metallogel formation trials of Ligand **1** with (a) CdSO₄, (b) ZnSO₄, (c) CuSO₄, (d) CoSO₄, (e) NiSO₄, and (f) MnSO₄, use of Cd-metallogel in Knoevenagel condensation³

Over the past few years many metallogels have been reported and utilized for the catalysis reaction. Pd-metallogel⁵⁴, Cd-cyclohexane based metallogel, Cu-triazolyl-based metallogel⁵⁵, Cu-glutamic acid-based metallogel⁵⁶, Calcium-cholate hydrogel⁵⁶ have also been reported.

2.3 Self-healing Property

Self-healing is one of the most interesting and fascinating property of the gels. Metallogels' inherent self-healing ability is similar to that of plant and animal biomaterials. Malviya *et al.* synthesised four lanthanoid based metallogels. Out of these metallogels, **M1G6Cl** (La³⁺-metallogel) exhibited self-healing behaviour. **M1G6Cl's** self-healing properties are attributed to the existence of noncovalent interactions during the metallogel formation.⁵⁷


Figure 2.6 Self-healing behaviour of M1G6Cl metallogel⁵⁷



Figure 2.7 Thixotropic experiment for M1G6Cl⁵⁷

2.4 Drug Delivery

The idea of delivering drugs to cancer cells via collapsing metallogel is interesting. Malviya *et al.* synthesised a Ru-Metallogel with **G5** gelator molecule with an IC₅₀ value of 10.53 M for the A549 cancer cell line, the **Ru(II)G5** metallogel exhibits an intrinsic anticancer capability. When this metallogel is treated with lactic acid to replicate the acidic environment of a cancer cell, the gel collapses and the ruthenium metal ion is released. This free ion bonds to the derivative of lactic acid, releasing **G5** and forming **Ru(II)L**, which is also an anticancer molecule.⁴



Figure 2.8 Gelator G5 molecule



Figure 2.9 Release of drug monitored by UV-Visible spectroscopy⁴

Biswas *et al.* synthesized metallogels form a sequence of Zn-NSAID-based complexes. Out of four metallogels formed, the **DINAP** had tendency to act as a strong anti-cancer agent against the B16–F10 cell line, a model cell line used to research skin cancer. Antibacterial activity was found in all metallogels against Gram-positive and Gram-negative bacteria. It was observed that around 60% of the loaded drug could be released from a **DINAP** gel to the bulk solvent (phosphate-buffer saline – PBS) in 24 h.⁵⁸



Figure 2.10 Drug released from a DINAP gel⁵⁸

CHAPTER 3

Experimental Section

3.1 Reagents and Chemicals

All of the chemicals and solvents used were purchased from commercial sources and utilized without additional purification. All of the experiments were conducted in the open atmosphere. Cyanuric chloride, 2-aminopyridine, tri-ethylamine, dry DCM, DMF, chloroform, nitrobenzene, 4-nitrophenol, 4-nitro toluene, 4-nitro aniline, 4-nitro benzyl alcohol, sodium borohydride, iron perchlorate, silver perchlorate and silver nitrate were purchased from Sigma Aldrich. Copper perchlorate salt was prepared in the laboratory.

3.2 Methods and Instrumentation

The microTOF-Q II mass spectrometer from Bruker-Daltonics was utilized for electrospray ionization mass spectrometry (ESI-MS). The FT-IR TENSOR 27 BRUKER instrument was used to measure infrared spectra (IR) in the range of 4000-500 cm⁻¹ across 64 scans at 1 s intervals with a resolution of 4 cm⁻¹. NMR spectra were acquired using an AVNACE NEO500 Ascend Bruker BioSpin International AG at room temperature equipment with tetramethylsilane as an internal standard. A Varian Carry 100 Bio UV-Vis spectrophotometer was used to record absorption spectra, and samples were obtained in a quartz cuvette (10×10 mm²). The gel's morphological data were captured using a Supra55 Zeiss field emission scanning electron microscope (FE-SEM). The strength of organogels and metallogels were investigated by rheological experiment. The rheological tests were performed on a PP50 mm parallel plate with a true gap of 0.5 mm using an Anton Paar physica MCR 301 rheometer at 25 °C. The G' and G" were measured at 0.5 percent strain to determine viscoelasticity. PXRD was performed using a Empyrean, Malvern Panalytical, with Cu K α source (the X-ray wavelength was 0.154 nm), a 2 θ range of 4-90°. Varian carry 100 Bio UV-vis spectrophotometer was used to monitor the reduction process of nitro substituents using a quartz cuvette (10 x 10 mm²). ¹ H NMR data from an AVNACE NEO500 Ascend Bruker BioSpin International AG were used to analyze reduced products of nitro substituents. Thermogravimetric analysis was performed in Mettler Toledo TGA/ DSC1.

3.3 <u>Synthesis of gelator, metallogels and nanocomposite</u> <u>catalyst</u>

3.3.1 Synthesis of Gelator Molecule (G7)

The synthesis of gelator molecule **G7** was done according to a previously reported procedure⁴⁰. 1.44 g (14 mmol) of 5-aminotetrazole monohydrate and 1.95 mL (14 mmol) of triethylamine were mixed in 40 mL of dry DCM and dropwise added into a CHCl₃ solution (40 mL) of trimesoyl chloride (1.06 g, 4 mmol) at 0 °C to make **G7**. After overnight stirring, the reaction mixture was then filtered and the residue obtained was washed with methanol and water. It was then left to dry under vacuum at room temperature and white colored ionic G7 was obtained.

3.3.2 Synthesis of gelator molecule (PN2)

Synthesis of **PN2** was done by adding 1.645 g (17.5 mmol) of 2aminopyridine and 2.089 mL (17.5 mmol) of triethylamine in dry dichloromethane (DCM) (30 mL) and the mixture was added dropwise into a CHCl₃ solution (30 mL) of cyanuric chloride (0.920 g, 5 mmol) at 0 °C. The reaction mixture was allowed to stir for 12 hr. The obtained precipitate was filtered off and washed with acidic water followed by water. After washing, the pinkish-white compound (**PN2**) was collected, dried and the final product was obtained.

3.3.2.1 Formation of Organogel from G7PN2

Organogel of **G7PN2** was formed in DMSO: H_2O (1:1 v/v) solvent combination. For this purpose, 41 mg (0.1mmol) of **G7** and 36 mg (0.1 mmol) of **PN-2** were dissolved in DMSO. Then 1 mL milli-Q water was added to it. A stable organogel was obtained spontaneously when the solution was left undisturbed for a few minutes which was confirmed by inverted test tube approach.

3.3.2.2 Formation of metallogels from G7PN2

The metal salt and combined gelator molecule (1:1 molar ratio) in DMSO and H₂O (1:1 v/v), metallogels of Fe (III) (M^1 G7PN2), Cu (II) (M^2 G7PN2), and Ag(I) (M^3 G7PN2) were obtained. For this purpose, 41 mg (0.1mmol) of G7 and 36 mg (0.1 mmol) of PN-2 were dissolved in DMSO and corresponding metal perchlorate salt were dissolved in 1 mL milli-Q water. Mixing both the solutions gave stable metallogels spontaneously within few minutes. Inversion test confirmed the formation of stable metallogel.

3.3.3 Synthesis of silver Nanoparticles (AgNPs)

Synthesis and stabilization of the Ag nanoparticles was done by adding 34 mg (0.04 M) of a DMF solution of AgNO₃ to the 1 g of metallogel (**M¹G7PN2**), which was then refluxed at 80 °C for 12 hours. Finally, a reddish-brown precipitate was generated. After filtration AgNPs containing

powdered precipitate was obtained. The PXRD, UV-Vis and FE-SEM analysis was used to characterize and investigate the synthesized silver nanoparticles inside gel matrix.

3.3.4 Synthesis of metallogel from silver Nanoparticles (AgNPs) composite

A very tiny amount of nanocomposite powder (2-3) mg was taken in 1 mL MQ-water and then added to a 1 mL solution of **G7PN2** (41 mg **G7**, 0.1 mmol) and 36 mg **PN2**, 0.1mmol) in DMSO. A stable brownish yellow-colored nanostructured metallogel was formed in less than a minute which was primarily confirmed by inversion test tube method.

3.4 Melting temperature of Gels (T_{gel})

The sol-gel transition behaviour were measured using a silicon oil bath. A glass vial was utilized for this experiment, and the temperature was recorded using a thermometer. The system was immersed in the oil bath after a steel ball was placed on the gel surface. The melting temperature of the gel was recorded when the temperature began to rise and the gel began to melt (as evidenced by the steel ball movement toward the gel surface) (T_{gel}). At this moment, the heating was turned off. The sol was found to be transformed back into a gel after 5 minutes. The sol-gel transition temperature for organogels and metallogels is shown by the gel melting point.

3.5 <u>Catalysis Reactions</u>

With the help of M¹G7PN2AgNPs catalyst, reduction reaction of nitrosubstituent to corresponding amine product was investigated. For this purpose, in 10 mL of milli-Q water, 0.1 mmol nitro-substituent, 1 mmol NaBH₄, and 6 mg catalyst were suspended and stirred at room temperature. UV-Vis spectroscopy is used to track reduction processes. The distinctive nitroaromatic peaks have been shown to fade with time, whereas a new peak for comparable amine compounds emerges. Also ¹H NMR was utilized to confirm the reduction process.

CHAPTER 4

Results and Discussion

4.1 Synthesis and Characterization

A) G7 was synthesized by previously reported method. In dry DCM, 5aminotetrazole monohydrate and triethylamine were mixed and added into a CHCl₃ solution of trimesoyl chloride at 0 °C. After overnight stirring, the precipitate was obtained which was filtered and then washed with water and methanol, and dried under vacuum. Product was confirmed by ESI-MS and NMR spectroscopy data.

B) The synthesis of **PN-2** was carried out by mixing 2-aminopyridine and triethylamine in dry DCM and addition of the mixture into a CHCl₃ solution of cyanuric chloride at 0 °C. After 12 hours stirring, the precipitate was filtered and washed with acidic water before being rinsed with water. The compound was collected and left to dry under vacuum. The confirmation of the structure was supported by mass spectra showing a peak at 358.27 m/z in positive mode. The compound was further characterized by NMR spectroscopy.

C) The Ag nanoparticles were synthesized and stabilized by adding AgNO₃ and metallogel to the DMF solution, which was then refluxed at 80 °C and after 12 hours, a reddish-brown precipitate was formed, which was filtered to get the AgNPs inside nanocomposite powder. It was investigated by the FE-SEM, PXRD, and UV-VIS spectroscopy.

4.2 <u>Reaction Schemes</u>

4.2.1 Synthesis of G7



Scheme 4.1: Synthesis of G7

4.2.2 Synthesis of PN-2



Scheme 4.2: Synthesis of PN2

4.2.3 Synthesis of MG7PN2AgNPs

Metallogels + AgNO₃ <u>DMF</u> Silver nanoparticles@metallogels Silver nanoparticles@metallogels

Scheme 4.3: Synthesis of AgNPs

4.3 Mass Spectrum

The formation of gelator molecule **PN2** has been confirmed by ESI-MS spectrometry. The electrospray ionisation mass (ESI-MS) spectra gave convincing evidence for the development of the indicated structures. The molecular ion peak appears at 358.27 m/z in the gelator spectra (in positive mode). (Figure 4.1)



Figure 4.1 ESI-MS spectra of PN2

4.4 NMR Spectrum

The structure for the gelator **PN2** was in complete accordance with ¹H NMR data. DMSO-d₆ was used for NMR. ¹H NMR of **PN2** (400.13 MHz, 298 K, DMSO-d6): δ 7.71 (3H, pyridine ring, d), 7.64 (3H, pyridine ring, m), 7.33 (3H, pyridine ring, m), 6.46 (3H, pyridine ring, m), 5.88 (3H, amine, s) (Figure 4.2)



Figure 4.2 NMR spectrum of PN2

4.5 Formation of Organogels and Metallogels

G7PN2 gelation behaviour was investigated in many organic solvents. **G7** and **PN2** are found to be soluble in DMSO and DMF, respectively (Table 4.1). The organogel was obtained by dropping 1 mL of water into a 1 mL solution containing 50 mM of **G7PN2** in DMSO or DMF. In DMSO and Milli-Q water combination (1:1 by volume), the critical gel concentration for the **G7PN2** was found to be 30 mM. (Table 4.2). The traditional "test tube inversion method" was used to confirm gel formation (Figure 4.3). The gel **G7PN2** heating-cooling experiment revealed that the gel-sol conversion's transition temperature (T_{gel}) was 100 °C, showing that it is stable at ambient temperature.



Figure 4.3 Inversion test of metallogels of (a) G7PN2 organogel (b) $M^{1}G7PN2$ (c) $M^{1}G7PN2AgNPs$ gel (d) $M^{2}G7PN2$ (e) $M^{3}G7PN2$

Table 4.1 Solubility of Gelator molecule in various solvents (G: Gel; S:Soluble; I: Insoluble)

Solvent	Solubility (G7PN2)	Gelation	Solvent	Solubility (G7PN2)	Gelation
Cyclohexane	Ι	-	Chloroform	Ι	-
Methanol	Ι	-	DCM	Ι	-
THF	Ι	-	DMSO	S	G
Toluene	Ι	-	Ethanol	Ι	-
n-Hexane	Ι	-	Benzene	Ι	-
DMF	S	Weak G	Ethyl Acetate	Ι	-
Acetone	Ι	-			

Table 4.2 Optimization Table for gelation

Concentration	DMSO	H ₂ O	Gelation
50 mM	500	1500	No gel
	1500	500	Weak gel
	1000	1000	Strong gel

Concentration	DMSO/H ₂ O	Gelation	
10 mM	1 mL/1 mL	No gelation	
20 mM	1 mL/1 mL	No gelation	
30 mM	1 mL/1 mL	Weak gel	
40 mM	1 mL/1 mL	Weak gel	
50 mM	1 mL/1 mL	Strong gel	

With Fe (III), Cu (II), and Ag((I), **G7PN2** was evaluated for the creation of metallogels. In all instances, it creates stable metallogels. Metallogels are formed by dropping 1 mL metal perchlorate (40 mM in water) solution into 1 mL **G7PN2** solution (50 mM in DMSO). The T_{gel} from the sol to the gel in these metallogels were found to be in the range of 115-120 °C, showing tha stability of all the fabricated metallogels at ambient temperature.

4.6 Formation of AgNPs

The **M¹G7PN2AgNPs** catalyst has resulted in a novel metallic system that can be used as an efficient catalyst in composite form for the reduction reaction. UV-vis spectroscopy was used to monitor the formation and stability of AgNPs in the nanocomposite. According to published data, AgNPs have an absorption peak in the region of 410-480 nm, with larger nanoparticles absorbing at longer wavelengths^{59,60}. The synthesized nanoparticles have shown peak at 463 nm (Figure 4.4). The best conditions for forming and stabilizing **M**¹**G7PN2AgNP** were determined to be 12 hours of heating at 80 °C of a combination of 0.5 g of gel and 5 mL AgNO₃ solution in DMF. FE-SEM validated the formation of AgNPs under these conditions.



Figure 4.4 UV-Vis Spectra of M¹G7PN2NPs

Further this nanocomposite can again be converted to the nano-metallogel. (Figure 4.5)



Figure 4.5 (a) M^1G7PN2 gel, (b) nanocomposite suspension and (c) $M^1G7PN2NPs$ gel

4.7 Rheological data

The viscoelastic characteristics of **G7PN2** metallogels were studied using rheological techniques. The storage modulus (G') for the organogel was discovered to be about 3091 Pa, and G' was always larger than the loss modulus (G''). In the linear Viscoelastic experiment (LVE) both values (G' and G'') deviated from linearity as the strain increased. The storage modulus of **M¹G7PN2**, **M²G7PN2** and **M³G7PN2** were found to be around 4574 Pa, 3074 Pa and 2883 Pa respectively. The storage modulus of **M¹G7PN2AgNP** gel, which are generated from the synthesized silver nanocomposite **M¹G7PN2AgNP**, was found to be around 2734 Pa. The synthesized **M¹G7PN2AgNP** gel also shows thixotropic behavior (sol-gelsol transition) which has been confirmed by time oscillation sweep (TOS) experiment done in rheometer at minimum 0.1 % strain and maximum 100 % strain values. After one cycle the storage modulus value decreases which might be due to the release of solvent molecules from gel matrix because of the high storage value of gel i.e. 2734 Pa.



Figure 4.6 (*a*) *Linear viscoelastic behaviour for G7PN2 organogel* (*b*) *Dynamic frequency sweep for the G7PN2 organogel*



Figure 4.7 (a) Linear viscoelastic behaviour for M^1G7PN2 gel (b) Dynamic frequency sweep for the M^1G7PN2 gel



Figure 4.8 (a) Linear viscoelastic behaviour for M^2G7PN2 gel (b) Dynamic frequency sweep for the M^2G7PN2 gel



Figure 4.9 (a) Linear viscoelastic behaviour for *M*³*G7PN2* gel (b) Dynamic frequency sweep for the *M*³*G7PN2* gel



Figure 4.10 (a) Linear viscoelastic behaviour for M¹G7PN2AgNPs gel (b) Dynamic frequency sweep for the M¹G7PN2AgNPs gel



Figure 4.11 Time oscillation sweep (TOS) experiment of M¹G7PN2AgNPs gel

4.8 Thermogravimetric Analysis

The organogel **G7PN2** has been synthesized from **G7** and **PN2** gelator component in which **G7** act as a trigger gelator molecule to gelate **PN2** in 3-D network. The thermogravimetric analysis (TGA) of the powder **G7**,

powder PN2 and xerogel of organogel G7PN2 have been performed in the range of 25-400 °C and found the variability in combustion temperature under decomposition steps. In the case of G7, the slow removal of solvent molecules found at 100°C and the weight loss percentage was 2.34 %. After that the weight start to decrease slowly and at 299°C the 35.54 % weight loss was observed (Figure 4.12a). In the case of powder PN2, the weight loss occurred in three steps till 400 °C. At 65, 201 and 302 °C the weight loss are 0.84, 3.25 and 23.63 % respectively (Figure 4.12b). When the TGA was done for xerogel of organogel G7PN2, removal of solvents molecule has been found at 64 °C with 1.56 weight percentage loss while the slow combustion of compound was observed and at 291 °C the weight loss was 37.88 %. It is observed that at 400 °C, the remaining weight percentage for G7, PN2 and G7PN2 were 44.81, 51.31 and 36.79 %, respectively (Figure 13b). The analysis indicated that after the gel formation there were noncovalent interaction between G7 and PN2 molecules which were removed by increasing temperature.



Figure 4.12 TGA data for (a) G7 powder (b) PN2 powder



Figure 4.13 (a) TGA data for G7PN2-Xerogel (b) Comparative TGA data for G7 powder, PN2 powder and G7PN2-xerogel

4.9 PXRD Analysis

The PXRD analysis shows the presence of physical state and non-covalent interactions within gelator molecules. In the xerogel of organogel G7PN2, an intense peak was observed at 27.35° with d value of 3.35 Å, indicating the presence of $\pi - \pi$ stacking between aromatic rings while the peak at $2\theta =$ 22.21° (d value 4.07 Å) and $2\theta = 39.10^{\circ}$ (d value 2.44 Å) showing the presence of intercolumnar stacking and hydrogen bonds, respectively. When the Fe(III) perchlorate introduce with G7PN2 and metallogel M¹G7PN2 has been formed, the PXRD data shows the conversion of amorphous organogel into crystalline Fe(III) metallogel (Figure 4.14). The synthesized metallogel used for synthesis and stabilization of silver nanoparticles (AgNPs) from AgNO₃ and the silver nanocomposite M¹G7PN2AgNPs was obtained. The synthesis of AgNPs inside gel matrix has been confirmed by PXRD analysis of M¹G7PN2AgNPs and found the PXRD peaks at 27.83° (d=3.29 Å), 32.31° (d=2.88 Å), 46.24° (d=2.13 Å), 54.84° (d=1.88 Å), 76.56° (d=1.58 Å) and 85.67° (d=1.57 Å) indicating the presence of silver nanoparticles. This silver nanocomposite again converted

into **M¹G7PN2AgNPs** nano-metallogel and the PXRD data shows the presence of AgNPs inside nanogel matrix (Figure 4.15).



Figure 4.14 PXRD data for (a) G7PN2 Xerogel (b) M¹G7PN2 Xerogel



Figure 4.1 PXRD data for (a) M¹G7PN2AgNPS nanocomposite (b) M¹G7PN2 Xerogel

4.10 SEM Analysis

The morphological study helps to understand the internal structure transformation of organogels and metallogels. The FE-SEM analysis has been done for **G7PN2** organogel, **M¹G7PN2** (Fe (III) metallogel, silver nanocomposite **M¹G7PN2AgNPs** and nano-metallogel **M¹G7PN2AgNPs**. The SEM image of organogel shows the fibrous morphology while in the case of metallogel, the morphology converted into 3-D leaf like structure connected with each other like threads. When the **M¹G7PN2AgNPs**

nanocomposite has been synthesized from M^1G7PN2 and $AgNO_3$, the FE-SEM images show the presence of AgNPs inside gel matrix. The formation of nano-metallogel from $M^1G7PN2AgNPs$ nanocomposite was also confirmed by FE-SEM technique in which the AgNPs particles can be seen inside gel matrix. Therefore, the conversion from organo- to metallo- and metallo to nano-metallo gels can be confirmed by FE-SEM analysis.



Figure 4.16 FE-SEM image of (a) G7PN2 organogel (b) M¹G7PN2



Figure 4.17 FE-SEM image of $M^1G7PN2AgNPs$ nanocomposite in (a) 1 μm and (b) 300 nm scales



Figure 4.18 FE-SEM image of $M^1G7PN2AgNPs$ nano-metallogel at (a) 1 μm and (b) 300 nm scales

4.11 FT-IR Analysis

The FTIR of **G7PN2** organogel displays the typical band for carboxamide -NH at 1578 cm⁻¹ and -C=O at 1653 cm⁻¹, as well as the C=N stretching at 1699 cm⁻¹ and the presence of the tetrazolic group at 1219 and 1394 cm⁻¹. While for **M¹G7PN2**-Xerogel the peaks are observed at 1594, 1675, 1247, and 1439 cm⁻¹ respectively (Figure 4.19). The FT-IR of **M¹G7PN2AgNPs** shows peaks at 1565, 1656, 1297 and 1359 cm⁻¹ and for the **M¹G7PN2AgNPs**-Xerogel the peaks are observed at 1579, 1664, 1241, and 1386 cm⁻¹ (Figure 4.20). The shifting in IR bands for different group shows that these groups are participating in non-covalent interactions for gel formation.



Figure 4.19 FT-IR of (a) G7PN2 organogel (b) M¹G7PN2-Xerogel



Figure 4.20 FT-IR of (a) M¹G7PN2AgNPs (b) M¹G7PN2AgNPs-Xerogel

Table 4.3 FT-IR analysis for xerogels and nanocomposite

Compound	-C=O	-NH-	Tetrazole C-N	Tetrazole - N=N-	Cyanuric ring -C=N-
G7PN2-xerogel	1653	1578	1219	1394	1699
M ¹ G7PN2- xerogel	1675	1594	1247	1439	-
M ¹ G7PN2AgNP- nanocomposite	1656	1565	1296	1359	-
M ¹ G7PN2AgNP- xerogel	1664	1579	1241	1386	-

4.12 Catalysis Reactions

Nitro-group reduction is a crucial and difficult process. Nitro-substrates are used in a broad range of fields, including insecticides, herbicides, dyes, and so on. As a consequence of their vital function in agricultural, dyes, and textile industries, these substrates harm or poison the environment following their final application. Therefore, degradation or reductions of these compounds that result in the production of safer products are thus critical. However, the degradation of various nitro-substrates has not been well investigated. In this work, we screened several aromatic nitrocompounds for reduction reactions and investigated the catalytic activity of M¹G7PN2AgNPs in nitro-group reduction. At room temperature, all reduction processes were monitored using a UV-Visible spectrophotometer.

4.12.1 <u>Reduction of 4-Nitrophenol</u>



Scheme 4.4 Reduction of 4-Nitrophenol

The nitro-compound has a UV-Vis peak at 317 nm, which changes toward 400 nm with the addition of NaBH₄ due to the conversion to the phenolate ion. The reduction process is started by adding a little amount of **M¹G7PN2AgNPs**. With the development of a new peak at 295 nm corresponding to the production of p-aminophenol, the intensity of the peak at 400 nm slowly declines.⁶¹ p-nitrophenol gets completely reduced in less than 30 minutes, as demonstrated by the plateau at 400 nm (Figure 4.21).



Figure 4.21 UV-Vis Spectrum for reduction of 4-Nitrophenol

4.12.2 <u>Reduction of 4-nitroaniline</u>



Scheme 4.5: Reduction of 4-Nitroaniline

In the presence of NaBH₄, the absorbance of p-nitroaniline is observed at 380 nm. The strength of the peak at 380 nm steadily decreases during the reduction process after addition of the nano-catalyst. The disappearance of the peak at 380 nm and the development of a new peak at 239 nm indicate that 4-nitroaniline has been completely reduced to 4-aminoaniline⁴⁰. The reaction gets completed within 25 minutes (Figure 4.22).



Figure 4.22 UV-Vis Spectrum for reduction of 4-Nitroaniline

4.12.3 <u>Reduction of Nitrobenzene</u>



Scheme 4.6: Reduction of Nitrobenzene

In the presence of NaBH₄ solution, nitrobenzene exhibits a distinctive peak at 270 nm in a UV-Visible spectrophotometer. After the addition of the catalyst, the absorbance band at 270 nm gradually diminished, followed by a shift to 230 nm, which corresponded to the production of aniline. Completion of reaction takes place in about 25 minutes (Figure 4.23).



Figure 4.23 UV-Vis Spectrum for reduction of Nitrobenzene

4.12.4 <u>Reduction of 4-nitro benzyl alcohol</u>



Scheme 4.7 Reduction of 4-Nitrobenzyl alcohol

The disappearance of a peak at 276 nm and the emergence of additional peaks at 239 and 285 nm indicate that the reduction of 4-nitrobenzyl alcohol to 4-aminobenzyl alcohol has been completed.⁴⁰ (Figure 4.24).



Figure 4.24 UV-Vis Spectrum for reduction of 4-Nitrobenyl alcohol

4.13 NMR Study for Catalysis reaction

The catalytic conversion process is also monitored using proton NMR spectroscopy. In the case of 4-Nitrophenol, the aromatic protons produced two doublets at 6.94 and 8.13 ppm, respectively, when the ¹ H NMR spectra was recorded in DMSO. The signal for 4-NP grows weaker as the reaction time increases, but the signal for 4-AP becomes greater. After 30 minutes, the spectrum included solely signals for 4-aminophenol, suggesting that 4nitrophenol had been nearly completely converted to 4-aminophenol. The aromatic protons of 4-aminophenol (6.46-6.42 ppm) are detected in the spectrum, with a signal at 4.38 ppm is due to the existence of the aromatic Ar-NH₂ proton. (Figure 4.25). Also, for 4-nitrobenzyl alcohol peaks for aromatic proton and benzyl-CH₂ proton are observed at 8.21, 7.60 and 4.65 respectively when NMR spectra was recorded in DMSO. The signal for 4-NBA got weaker as the reaction time increased and after 25 minutes, the spectrum shows that 4- nitro benzyl alcohol has completely converted to 4aminobenzyl alcohol. The aromatic protons of 4-amino benzyl alcohol (6.99-6.50 ppm) are detected in the spectrum, with a signal at 5.72 ppm is due to the existence of the aromatic Ar-NH₂ proton (Figure 4.26). Similarly, Nitrobenzene and 4-Nitro aniline reduction was also confirmed by ¹H NMR analysis. (Figure 4.27 and 4.28)



Figure 4.25 ¹H NMR spectrum for reduction of 4-Nitrophenol



Figure 4.26 ¹*H NMR spectrum for reduction of 4-Nitrobenyl* alcohol



Figure 4.27 ¹H NMR spectrum for reduction of 4-Nitroaniline



Figure 4.28 ¹H NMR spectrum for reduction of Nitrobenzene

CHAPTER 5

Conclusion and Future Scope

Designing and fabricating innovative smart materials based on low molecular weight gelators has shown to be an intriguing method with several applications. The non-covalent interactions are widely recognized as the driving force underlying the development of supramolecular selfassembly. The major purpose of this present research is to develop low molecular weight gelator molecule and examine its applications in some catalytic reaction. Keeping this in focus, a gelator molecule PN2 is synthesized which on addition of a G7 shows gelation. Metallogels with G7PN2 were fabricated and were well characterized with various techniques. Out of various metallogels, M¹G7PN2 was utilized for the synthesis of nanocomposite M¹G7PN2AgNPs, which was further utilized as the catalyst for the reduction of nitro aromatic compounds. UV-vis and ¹H NMR methods were used to evaluate the reduction processes of nitro compounds and the reactions were almost completed in 30 minutes. Also, the nanocomposite M¹G7PN2AgNPs transforms into the M¹G7PN2AgNP nanometallogel in the presence of G7 and PN2.

Various physical and chemical properties such as conductivity, colour, rheological behaviour, catalytic activities, redox activities, and self-healing can be tuned by the addition of various metal ions in the gels. As a future prospective, the metallogels of **G7PN2** could be utilized for applications other than the catalysis. A more thorough investigation of metal ion induced gelation, as well as tailoring the numerous weak interactions to make the gels suitable for a wide range of applications, is envisaged.

References

(1) Wang H., Xu W., Song S., Feng L., Song A., Hao J. (2014), Hydrogels Facilitated by Monovalent Cations and Their Use as Efficient Dye Adsorbents, J Phys Chem B, 118, 4693-4701. (DOI:10.1021/jp500113h)

(2) Hu Y., Xie D., Wu Y., Lin N., Song A., Hao J. (2017), Hydrogels Based on Ag⁺-Modulated Assembly of 5'-Adenosine Monophosphate for Enriching Biomolecules, Chem – Eur J, 23, 15721-15728.
(DOI:10.1002/chem.201703180)

(3) Lee HH., Jung SH., Park S., Park KM., Jung JH. (2013), A Metal– Organic Framework Gel with Cd²⁺ Derived from Only Coordination Bonds Without Intermolecular Interactions and Its Catalytic Ability, New J Chem, 37, 2330-2335. (DOI:10.1039/C3NJ00164D)

(4) Malviya N., Sonkar C., Ganguly R., Bhattacherjee D., Bhabak KP., Mukhopadhyay S. (2019), Novel Approach to Generate a Self-Deliverable Ru(II)-Based Anticancer Agent in the Self-Reacting Confined Gel Space, ACS Appl Mater Interfaces, 11, 47606-47618.
(DOI:10.1021/acsami.9b17075)

(5) Lin Q., Lu T.T., Zhu X., Sun B., Yang Q.P., Wei T.B., Zhang Y.M.,
(2015), A Novel Supramolecular Metallogel-Based High-Resolution Anion Sensor Array, Chem Comm, 51, 1635-1638. (DOI:10.1039/C4CC07814D)

(6) Fang W., Zhang Y., Wu J., Liu C., Zhu H., Tu, T. (2018), Recent Advances in Supramolecular Gels and Catalysis, Chem Asian J, 13, 712-729. (DOI:10.1002/asia.201800017)

(7) Malviya N., Das M., Mandal P., Mukhopadhyay S. (2017), A Smart Organic Gel Template as Metal Cation and Inorganic Anion Sensor, Soft Matter, 13, 6243-6249. (DOI:10.1039/C7SM01199G) (8) Nagarajan V., Pedireddi VR. (2014), Gelation and Structural Transformation Study of Some 1,3,5-Benzenetricarboxamide Derivatives, Cryst Growth Des, 14, 1895-1901. (DOI:10.1021/cg500026t)

(9) Thool G. S., Narayanaswamy K., Venkateswararao A., Naqvi S., Gupta V., Chand S., Vivekananthan V., Koner R. R., Krishnan V., Singh S. P. (2016), Highly Directional 1D Supramolecular Assembly of New Diketopyrrolopyrrole-Based Gel for Organic Solar Cell Applications, Langmuir, 32, 4346–4351. (DOI: 10.1021/acs.langmuir.6b00846)

(10) Datta S., Bhattacharya S. (2015), Multifarious Facets of Sugar-Derived Molecular Gels: Molecular Features, Mechanisms of Self-Assembly and Emerging Applications, Chem Soc Rev, 44, 5596-5637.
(DOI:10.1039/C5CS00093A)

(11) Sangeetha NM., Maitra U. (2005), Supramolecular Gels: Functions and Uses, Chem Soc Rev, 34, 821-836. (DOI:10.1039/B417081B)

(12) Yi T., Sada K., Sugiyasu K., Hatano T., Shinkai S. (2003), Photo-Induced Colour Generation and Colour Erasing Switched by the Sol–Gel Phase Transition, Chem Commun, 3, 344-345. (DOI:10.1039/B210741D)

(13) Shi C., Huang Z., Kilic S., Xu J., Enick R.M., Beckman E.J., Carr A.J., Melendez R.E., Hamilton A.D. (1999), The Gelation of CO₂: A Sustainable Route to the Creation of Microcellular Materials, Science, 286, 1540-1543.
(DOI: 10.1126/science.286.5444.1540)

(14) Wang R., Geiger C., Chen L., Swanson B., Whitten DG. (2000), Direct Observation of Sol–Gel Conversion: The Role of the Solvent in Organogel Formation, J Am Chem Soc, 122, 2399-2400. (DOI:10.1021/ja993991t)

(15) Terech P., Weiss RG. (1997), Low Molecular Mass Gelators of Organic Liquids and the Properties of Their Gels, Chem Rev, 97, 3133-3160. (DOI:10.1021/cr9700282)

(16) Jung JH., Lee JH., Silverman JR., John G. (2013), Coordination Polymer Gels with Important Environmental and Biological Applications, Chem Soc Rev, 42, 924-936. (DOI:10.1039/C2CS35407A)

(17) Segarra-Maset MD., Nebot VJ., Miravet JF., Escuder B. (2013),
Control of Molecular Gelation by Chemical Stimuli, Chem Soc Rev, 42,
7086-7098. (DOI:10.1039/C2CS35436E)

(18) Moniruzzaman M., Sahin A., Winey KI. (2009), Improved Mechanical Strength and Electrical Conductivity of Organogels Containing Carbon Nanotubes, Carbon, 47, 645-650. (DOI: 10.1016/j.carbon.2008.10.046)

(19) Tam AYY., Yam VWW. (2013), Recent Advances in Metallogels, Chem Soc Rev, 42, 1540-1567. (DOI:10.1039/C2CS35354G)

(20) Saha S., Das G., Thote J., Banerjee R. (2014), Photocatalytic Metal– Organic Framework from CdS Quantum Dot Incubated Luminescent Metallohydrogel, J Am Chem Soc, 136, 14845-14851.
(DOI:10.1021/ja509019k)

(21) Hamley IW. (2003), Nanotechnology with Soft Materials, Angew Chem Int Ed, 42, 1692-1712. (DOI:10.1002/anie.200200546)

(22) Chung YM., Simmons KL., Gutowska A., Jeong B. (2002), Sol-Gel Transition Temperature of PLGA-G-PEG Aqueous Solutions, Biomacromolecules, 3, 511-516. (DOI:10.1021/bm0156431)

(23) Yu G., Yan X., Han C., Huang F. (2013), Characterization of Supramolecular Gels, Chem Soc Rev, 42, 6697-6722.(DOI:10.1039/C3CS60080G)

(24) Malviya N., Sonkar C., Kundu BK., Mukhopadhyay S. (2018),
Discotic Organic Gelators in Ion Sensing, Metallogel Formation, and
Bioinspired Catalysis, Langmuir, 34, 11575-11585.
(DOI:10.1021/acs.langmuir.8b02352)
(25) Draper ER., Adams DJ. (2017), Low-Molecular-Weight Gels: The State of the Art, Chem, 3, 390-410. (DOI:10.1016/j.chempr.2017.07.012)

(26) Mei J., Leung NLC., Kwok RTK., Lam JWY., Tang BZ. (2015), Aggregation-Induced Emission: Together We Shine, United We Soar, Chem Rev, 115, 11718-11940. (DOI:10.1021/acs.chemrev.5b00263)

(27) Hong Y., Lam JWY., Tang BZ. (2009), Aggregation-Induced Emission: Phenomenon, Mechanism and Applications, Chem Commun, 29, 4332-4353. (DOI:10.1039/B904665H)

(28) Castilla AM., Dietrich B., Adams DJ. (2018), Using Aggregation-Induced Emission to Understand Dipeptide Gels, Gels, 4.(DOI:10.3390/gels4010017)

(29) Liu Y., Tikunov Y., Schouten R.E., Marcelis L.F., Visser R.G. and Bovy A. (2018), Anthocyanin Biosynthesis and Degradation Mechanisms in Solanaceous Vegetables: A Review, Front Chem, 6, 52. (DOI:10.3389/fchem.2018.00052)

(30) Fan B., Zhang K., Liu Q., Eelkema R. (2020), Self-Healing Injectable Polymer Hydrogel Via Dynamic Thiol-Alkynone Double Addition Cross-Links, ACS Macro Lett, 9, 776-780. (DOI:10.1021/acsmacrolett.0c00241)

(31) Fang Y., Wang CF., Zhang ZH., Shao H., Chen S. (2013), Robust Self-Healing Hydrogels Assisted by Cross-Linked Nanofiber Networks, Sci Rep, 3, 2811. (DOI:10.1038/srep02811)

(32) César V., Bellemin-Laponnaz S., Gade LH. (2004), Chiral N-Heterocyclic Carbenes as Stereodirecting Ligands in Asymmetric Catalysis, Chem Soc Rev, 33, 619-636. (DOi:10.1039/B406802P)

(33) Jun CH. (2004) Transition Metal-Catalyzed Carbon–Carbon Bond Activation, Chem Soc Rev, 33, 610-618. (DOI:10.1039/B308864M)

(34) Seregin IV., Gevorgyan V. (2007), Direct Transition Metal-CatalyzedFunctionalization of Heteroaromatic Compounds, Chem Soc Rev, 36, 1173-1193. (DOI:10.1039/B606984N)

(35) Allen CL., Williams JMJ. (2011), Metal-Catalysed Approaches to Amide Bond Formation, Chem Soc Rev, 40, 3405-3415.(DOI:10.1039/C0CS00196A)

(36) Knowles JR. (1991), Enzyme Catalysis: Not Different, Just Better, Nature, 350, 121-124. (DOI:10.1038/350121a0)

(37) Trost B.M. (2004), Asymmetric Catalysis: An Enabling Science, Proc Natl Acad Sci U.S.A, 101, 5348-5355.

(38) Escuder B., Rodríguez-Llansola F., Miravet JF. (2010), Supramolecular Gels as Active Media for Organic Reactions and Catalysis, New J Chem, 34, 1044-1054. (DOI:10.1039/B9NJ00764D)

(39) Díaz DD., Kühbeck D., Koopmans RJ. (2010), Stimuli-Responsive
Gels as Reaction Vessels and Reusable Catalysts, Chem Soc Rev, 40, 427448. (DOI:10.1039/C005401C)

(40) Kyarikwal R., Malviya N., Chakraborty A., Mukhopadhyay S. (2021),
Preparation of Tris-Tetrazole-Based Metallogels and Stabilization of Silver
Nanoparticles: Studies on Reduction Catalysis and Self-Healing
Property, ACS Appl Mater Interfaces, 13, 59567-59579.
(DOI:10.1021/acsami.1c19217)

(41) Beatty M.A., Borges-González J., Sinclair N.J., Pye A.T., Hof F.
(2018), Analyte-Driven Disassembly and Turn-On Fluorescent Sensing in Competitive Biological Media, J Am Chem Soc, 140, 3500-3504.
(DOI:10.1021/jacs.7b13298)

(42) Lubken RM., Bergkamp MH., de Jong AM., Prins MWJ. (2021), Sensing Methodology for the Rapid Monitoring of Biomolecules at Low Concentrations over Long Time Spans, ACS Sens, 6, 4471-4481. (DOI:10.1021/acssensors.1c01991)

(43) McNerney MP., Piorino F., Michel CL., Styczynski MP. (2020),
Active Analyte Import Improves the Dynamic Range and Sensitivity of a
Vitamin B12 Biosensor, ACS Synth Biol, 9, 402-411.
(DOI:10.1021/acssynbio.9b00429)

(44) Gao M., Tang BZ. (2017), Fluorescent Sensors Based on Aggregation-Induced Emission: Recent Advances and Perspectives, ACS Sens, 2, 1382-1399. (DOI:10.1021/acssensors.7b00551)

(45) Roy S., Katiyar AK., Mondal SP., Ray SK., Biradha K. (2014), Multifunctional White-Light-Emitting Metal–Organic Gels with a Sensing Ability of Nitrobenzene, ACS Appl Mater Interfaces, 6, 11493-11501.
(DOI:10.1021/am502146m)

(46) Peng ZW., Yuan D., Jiang ZW., Li YF. (2017), Novel Metal-Organic
Gels of Bis(Benzimidazole)-Based Ligands with Copper(II) for
Electrochemical Selectively Sensing of Nitrite, Electrochimica Acta, 238,18. (DOI:10.1016/j.electacta.2017.03.121)

(47) Panja S., Bhattacharya S., Ghosh K. (2018), Pyridine Coupled Mono and Bisbenzimidazoles as Supramolecular Gelators: Selective Metal Ion Sensing and Ionic Conductivity, Mater Chem Front, 2, 385-395. (DOI:10.1039/C7QM00505A)

(48) Ghosh D., Deepa., Damodaran KK. (2020), Metal Complexation Induced Supramolecular Gels for the Detection Of Cyanide in Water, Supramol Chem, 32, 276-286. (DOI:10.1080/10610278.2020.1751845)

(49) Ghosh A., Das P., Kaushik R., Damodaran KK., Jose DA. (2016),
Anion Responsive and Morphology Tunable Tripodal Gelators, RSC Adv,
6, 83303-83311. (DOI:10.1039/C6RA16345A)

(50) Ghosh K., Panja S., Bhattacharya S. (2015), Naphthalene Linked Pyridyl Urea as a Supramolecular Gelator: A New Insight Into Naked Eye Detection of I– in the Gel State with Semiconducting Behaviour, RSC Adv, 5, 72772-72779. (DOI:10.1039/C5RA11721F)

(51) Xing B., Choi M.F., Xu B., (2002), Design of Coordination Polymer
Gels as Stable Catalytic Systems, Chem Eur J, 8, 5028-5032.
(DOI:10.1002/1521-3765(20021104)8)

(52) Lee JH., Kang S., Lee JY., Jung JH. (2012), A Tetrazole-Based Metallogel Induced with Ag⁺ Ion and its Silver Nanoparticle in Catalysis, Soft Matter, 8, 6557-6563. (DOI:10.1039/C2SM25316J)

(53) Paul M., Sarkar K., Dastidar P. (2015), Metallogels Derived from Silver Coordination Polymers of C3-Symmetric Tris(Pyridylamide) Tripodal Ligands:Synthesis of Ag Nanoparticles and Catalysis, Chem Weinh Bergstr Ger, 21, 255–268. (DOI:10.1002/chem.201404959)

(54) Liu Y.-R., He L., Zhang J., Wang X., Su C.-Y. (2009), Evolution of Spherical Assemblies to Fibrous Networked Pd(II) Metallogels from a Pyridine-Based Tripodal Ligand and their Catalytic Property, Chem Mater, 21, 557–563. (DOI:10.1021/cm802841r)

(55) Araújo M., Díaz-Oltra S., Escuder B. (2016), Triazolyl-Based Molecular Gels as Ligands for Autocatalytic 'Click' Reactions. Chem–Eur J, 22, 8676–8684. (DOI:10.1002/chem.201600594)

(56) Maity M., Maitra U. (2014), An Easily Prepared Palladium-Hydrogel Nanocomposite Catalyst for C–C Coupling Reactions, J Mater Chem A, 2, 18952–18958. (DOI:10.1039/C4TA04200J)

(57) Malviya N., Ranjan R., Sonkar C., Mobin S. M., Mukhopadhyay S. (2019), Self-Healable Lanthanoid-Based Metallogels: Dye Removal and Crystallization in the Confined Gel State, ACS Appl Nano Mater, 2, 8005–8015. (DOI:10.1021/acsanm.9b02064)

(58) Biswas P., Datta H. K., Dastidar P. (2022), Multi-NSAID-Based Zn(II)
Coordination Complex-Derived Metallogelators/Metallogels as Plausible
Multi-Drug Self-Delivery Systems, Chem Commun, 58, 969–972.
(DOI:10.1039/D1CC05334E)

(59) Gogoi N., Babu P. J., Mahanta C., Bora U. (2015), Green Synthesis and Characterization of Silver Nanoparticles Using Alcoholic Flower Extract of Nyctanthes Arbortristis and in Vitro Investigation of Their Antibacterial and Cytotoxic Activities, Mater Sci Eng C Mater Biol Appl, 46, 463–469. (DOI: 10.1016/j.msec.2014.10.069)

(60) Bonsak J., Mayandi J., Thøgersen A., Marstein E., Umadevi M. (2011),
Chemical Synthesis of Silver Nanoparticles for Solar Cell Applications,
Phys Status Solidi C, 8, 924–927. (DOI:10.1002/pssc.201000275)

(61) Sharma M., Sarma P. J., Goswami M. J., Bania K. K. (2017) Metallogel Templated Synthesis and Stabilization of Silver-Particles and Its Application in Catalytic Reduction of Nitro-Arene, J Colloid Interface Sci, 490, 529–541. (DOI: 10.1016/j.jcis.2016.11.065)