# Chapter 1

# Introduction to Metal-Organic gels (Metallogels)

## 1.1 General introduction to the gels

In early twentieth century, an archaic type of gel *i.e.;* organogel attracted the attention of scientific community due to its potential applications in chemo sensors [1], drug delivery [2], tissue engineering [3], oil spill recovery agents [4], biomaterials [5], jelly greases [6], optoelectronic materials [7], pollutant capture/removal [8], in general life as hair gel, face wash, cold creams, suns cream, sanitary products [9] and jelly *etc*.. Initially, organogels were mostly derived from high molecular weight gelators like; polymer derived from polyallylammonium carbamate [10], polyisobutylene [11], polyurethane [12], polybutadiene [13], polyorthocarbonate [14], polyoctadecylacrylate [15] and tetra-alkylammonium tetraphenylborate [16] *etc*. These polymers based 3-D network of fibre entraps the solvent molecules in the matrix and yield the gels. But only from last decade, low molecular weight gelators (LMWGs) are most appealing candidate for gel synthesis across the globe owing to their small structure with easy prediction of mechanism behind gelation. Due to involvement of small gelator molecule in gel synthesis, a stimuli responsive material could easily be achieve through reversible weak interactions between small molecules (Figure 1.1).[17-19]

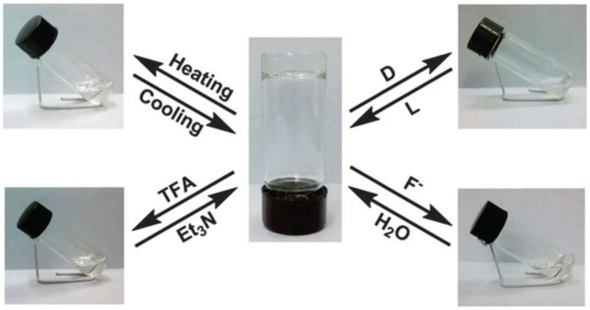
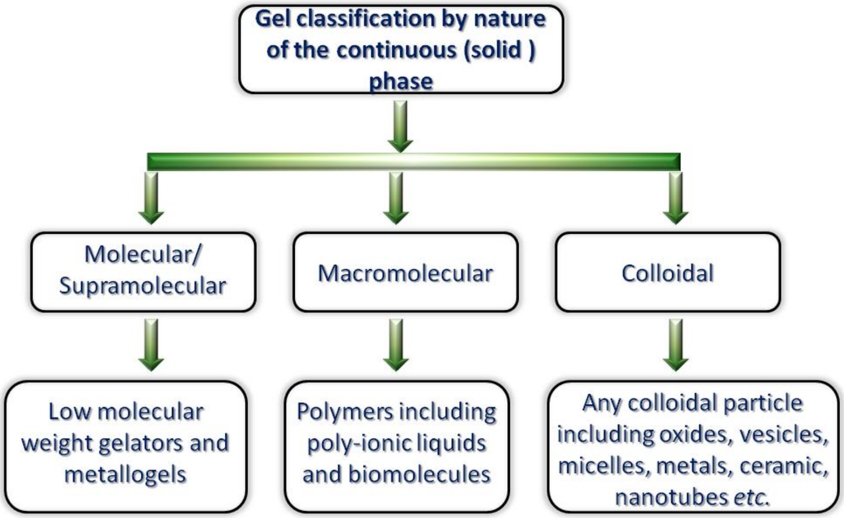


**Figure 1.1** Liu *et al.* synthesized a stimuli responsive strong organogel. [18] – Reproduced by permission of The Royal Society of Chemistry

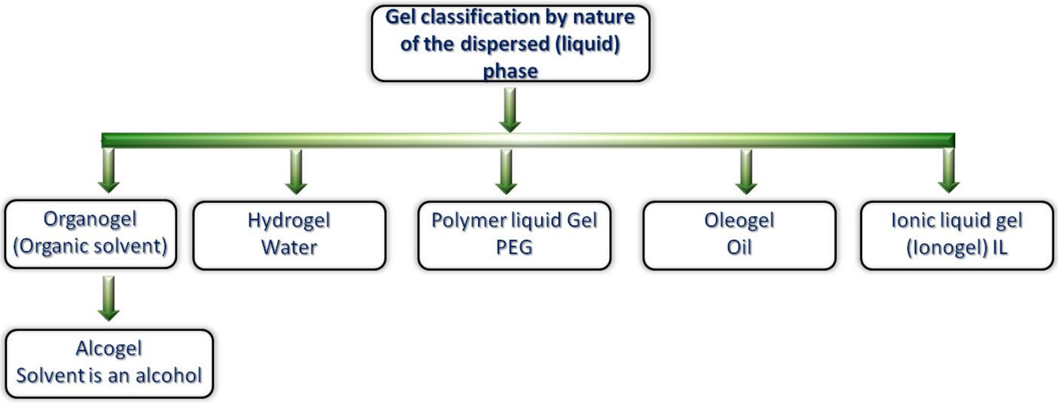
## 1.2 GEL CLASSIFICATION BASED ON SOLID AND LIQUID PHASE

Under this head, gels are classified into two parts, such as;

### 1.2.1 Based on solid phase



### 1.2.2 Based on liquid phase



## 1.3 GEL CLASSIFICATION BASED ON INVOLVEMENT OF METAL

On this basis, gels may be of two types again:

**1.3.1 Organic gel:** The gel which does not contain any metal component inside gel matrix and gelation takes place usually with the help of H-bonding Van der Waals interactions,

$\pi-\pi$ stacking and solvophobic forces *etc*.

**1.3.2 Metal-Organic gel (Metallogel):** The gels which contain metal as an essential structural component for gel formation are known as metallogels. The main driving force for metallogels formation is usually a strong co-ordination of metal to the gelator molecule (ligand). Further, addition of a metal to the organic gels may lead to additional fascinating properties such as; colour, charge transfer, fluorescence, rheological, magnetism, helicity, stimuli responsiveness, nanofabrication, conductance and catalysis *etc*. Later stage, metallogels offered the wide variety of applications in interdisciplinary fields also such as catalysis, electronics and sensors *etc*. Designing has been the main difficulty for metallogelators which already limits its broad range of applications. In general, scientist extend their experience of organic-gelator designing to metallogelators with some modifications as metal binding sites and metals are added to these binding sites using various methodologies. Notably, present thesis focuses towards synthesis of multi-functional metallogels and their possible applications.

## 1.4 IMPORTANT APPLICATIONS OF METALLOGELS

### 1.4.1 Electronic devices

Due to presence of metal ions, metallogels, usually shows self-healing and electrically conducting behaviour which have promising application in the field of electronic devices such as diodes, transistors, solar cells etc.[20] Recently, Dey *et al.* developed a Schottky barrier diode using metallogel thin film.[21] The thin film of as-synthesized metallogel was grown on conducting oxide coated glass substrate followed by annealing at 80°C for 45 min to evaporate the solvent, thickness of the film was ~1 µm . They designed the device by making a sandwich-like configuration of different layers of Indium tin oxide (ITO), metallogel and Aluminium. Electrical characterizations were performed on developed device to explore its electrical behaviour. I-V characteristic of the device revealed the non-linear behaviour of the device which is typical characteristic of a diode (Figure 1.2). The metallogel was synthesised from oxalic acid incorporating Mn(II) *via* coordination complexation.

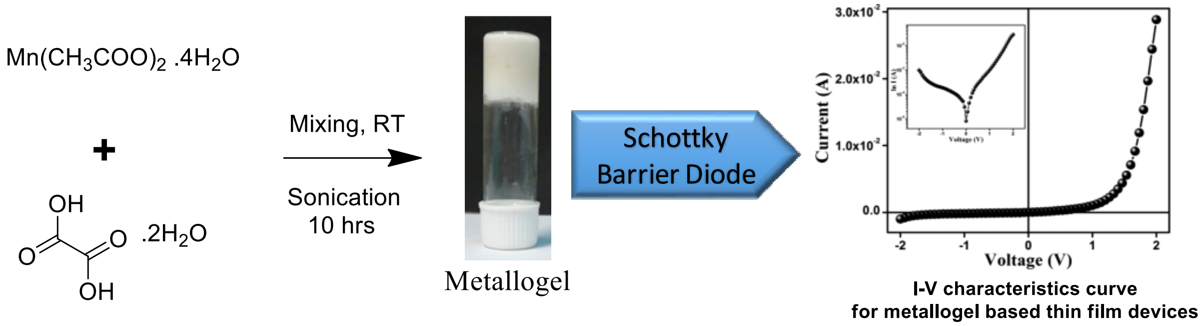


**Figure 1.2** Schematic of synthetic procedure of metallogel followed by application in Schottky barrier diode. [21] – Adapted by permission of The Royal Society of Chemistry

Huo and co-workers synthesized a metallogel *via* $Fe^{2+}$ coordination-driven complexation with trimesic acid as gelator and further applied the metallogel in dye-sensitized solar cell (DSSC) application as an electrolyte.[22] Traditionally, the DSSCs are fabricated by developing photoelectrode and counter electrode plates separated by liquid electrolyte, in this work, they replaced liquid electrolyte with gel electrolyte in order to prevent leakage. The photovoltaic characterization was conducted on fabricated DSSC, current density (J)–voltage curves (V) of DSSCs with various concentration of electrolyte exhibits a typical solar cell characteristic. Metallogel–based DSSC provided an appreciable photoelectric conversion efficiency of 5.31%. (Figure 1.3)

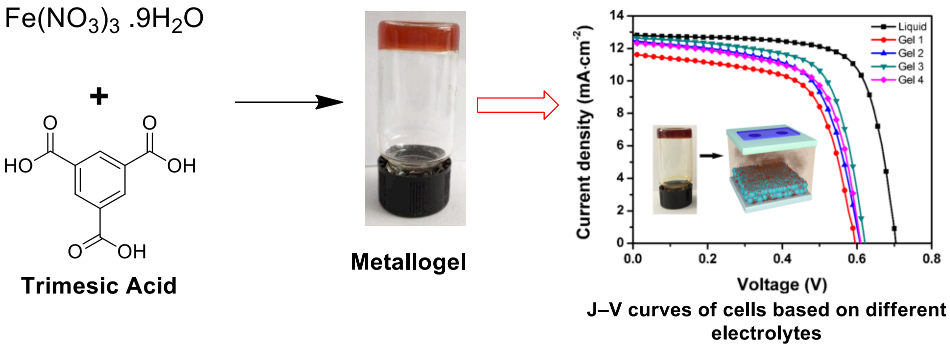


**Figure 1.3** Schematic of synthetic procedure of metallogel and application in solar cell. Adapted by permission from [Springer Nature]: [Springer] [Journal of Solid State Electrochemistry][22] [COPYRIGHT] 2019

### 1.4.2 Electrolytic material

Metallogels as an electrolyte have important application in supercapacitors, solid oxide fuel cells (SOFC) and batteries.[23] Since liquid electrolytes faces problems such as leakage, internal corrosion, volatilization *etc*., therefore metallogel based electrolytes are of immense interest to resolve the problem associated with liquid electrolytes.[24] Recently,

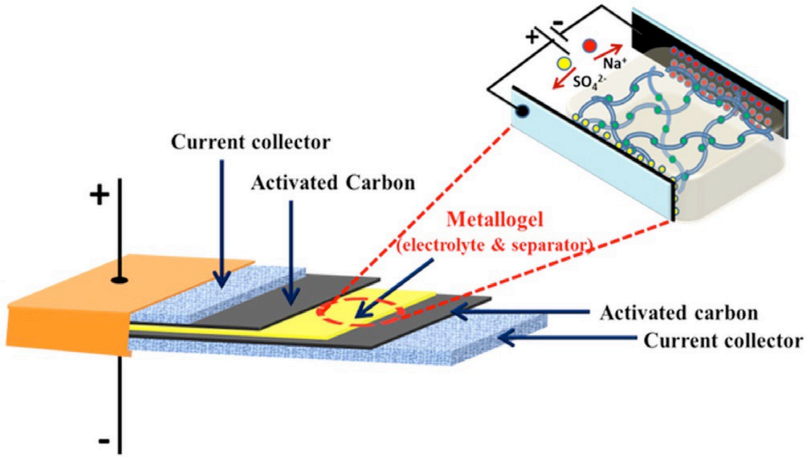


**Figure 1.4** Metallogel as an electrolyte utilized in solid-state supercapacitor. Copyright (2019) Wiley. Used with permission from ref 24.

Bhattacharjee *et al.* synthesized a metallogel from l-2-(3,5-ditert-butyl-2-hydroxybenzyl amino)-succinic acid with $ZnSO_4$ and successfully utilized the metallogel in the application of super capacitor (Figure 1.4).[24]

Kurungot *et al.* proposed the metallogel solid electrolyte as proton conductor and employed the pellets of xerogel obtained from metallogel in fuel cells to complete the electrical circuit between electrodes.[25] The prepared solid electrolyte provided an open circuit voltage (OCV) of 1.02 V with proton conductivity of $2.4 \times 10^{-2}$ S $cm^{-1}$ at 120 °C. The metallogel was synthesized by immobilization phytic acid with $Fe^{2+}$ *via* coordination complexation. (Figure 1.5)

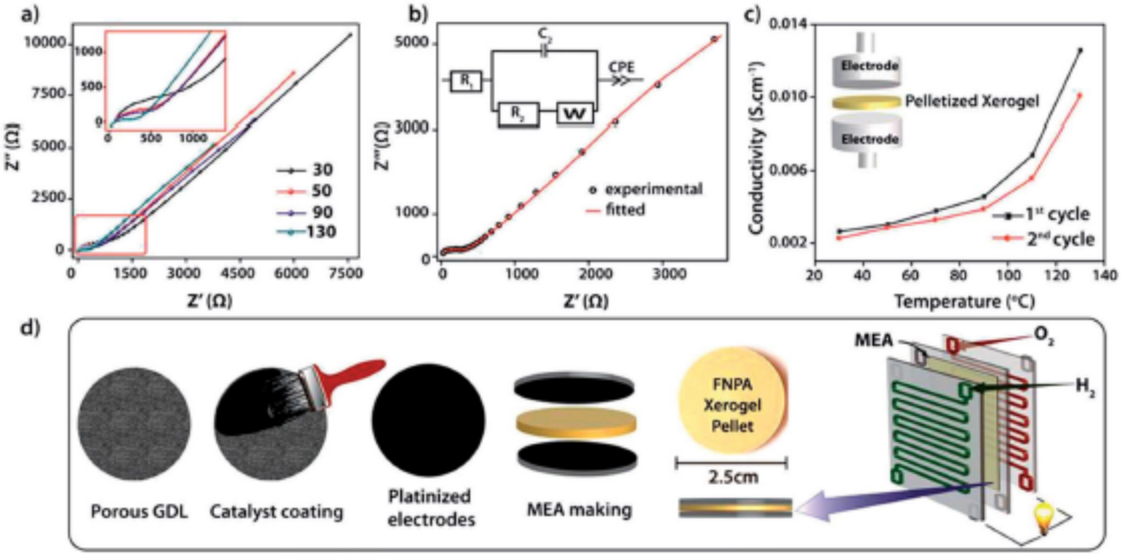


**Figure 1.5** (a) Nyquist impedance plots at various temperatures, (b) equivalent circuit model fitted for Nyquist impedance plot obtained at 130 °C, (c) Conductivity *v/s* temperature graph along with electrode schematic and (d) schematic of membrane electrode assembly (MEA) designed using pelletized xerogel. [25] - Reproduced by permission of The Royal Society of Chemistry

### 1.4.3 Sensor

Multi-stimuli responsive feature of metallogel makes it suitable candidate to be used as sensors, particularly as chemo-sensors as well as biosensors.[26] Pal *et al.* developed a redox-responsive Cu(I) metallogel for removal of Cr(VI) from aqueous solution (Figure 1.6). The metallogel exhibits its redox-responsive behaviour due to the availability of Cu(I) metal centers in entire structural backbone which makes the metallogel to be utilized in removal of Cr(VI) ions. The metallogel was synthesized from 2-mercaptobenzimidazole and $CuCl_2$ in ethanolic medium.[26]

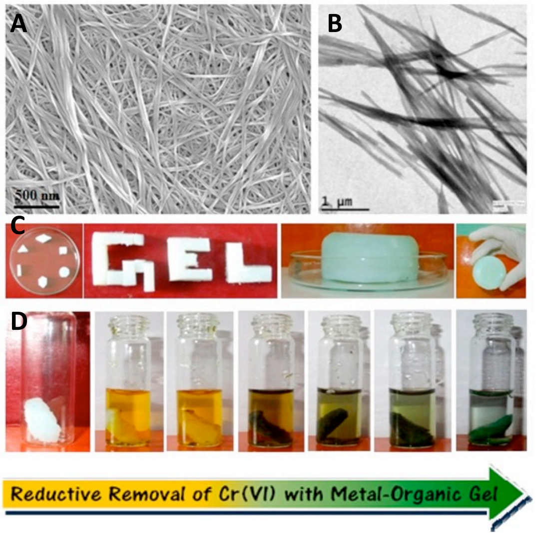


**Figure 1.6** (A) FE-SEM images of diluted metallogel, (B) TEM images of metallogel, (C) images showing metallogel properties and (D) Subsequent reduction of Cr(VI) to Cr(III). Reprinted with permission from [26]. Copyright [2014] American Chemical Society.

Mukhopadhyay and co-workers reported cobalt induced metallogel for sensing L-Tryptophan among amino acids.[27] The metallogel synthesized from 1,3,5-tricarboxamide-based gelator molecule, exhibits Aggregate-Induced Enhanced Emission (AIEE). The metallogel was utilized for sensing of L-Tryptophan through quenching of AIEE. Limit of detection of metallogel for sensing of L-Tryptophan was measured to be $2.4\times10^{-8}$ M (Figure 1.7).

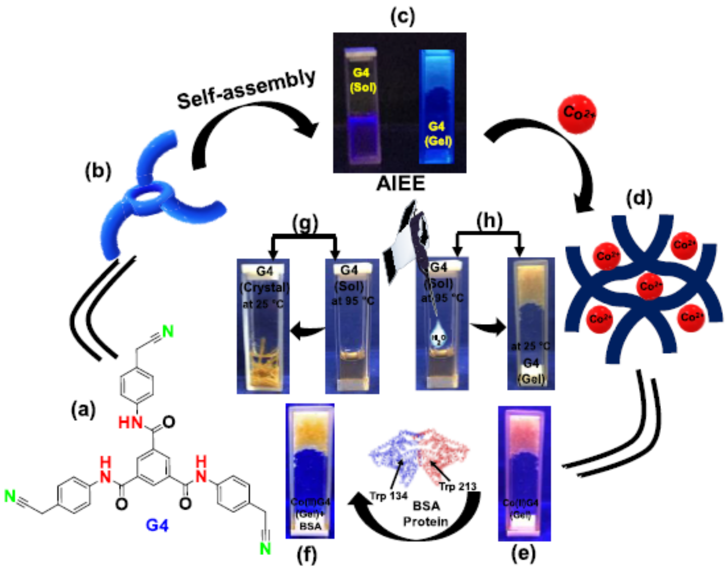


**Figure 1.7** (a) Chemical structure of metallogel (**$G_4$**), (b) Schematic representation of $G_4$, (c) AIEE scheme of $G_4$ after self-assembly under UV-light, (d) Self-assembly of Co(II) and gelator molecule, (e) Photograph of metallogel, (f) Photograph of metallogel incorporated with L-Tryptophan, (g) Cooling of the gelator solution leading towards crystallization and (h) Addition of $H_2O$ to the $G_4$ solution leading towards gel formation. Reprinted with permission from [27]. Copyright [2019] American Chemical Society.

### 1.4.2 Catalytic material

Being a smart material, metallogel are also utilized for catalyzing important organic molecule transformations. Few of the important results are summarized in this section. Yamada *et al.* synthesized a tripodal ligand which upon coordination with Pd metal forms a self-assembly and lead to a novel metallogel formation (Figure 1.8).[28] The freshly prepared metallogel is shown as an active catalytic material for Suzuki-Miyaura coupling reaction of aryl halides with arylboronic acids (Scheme 1.1).

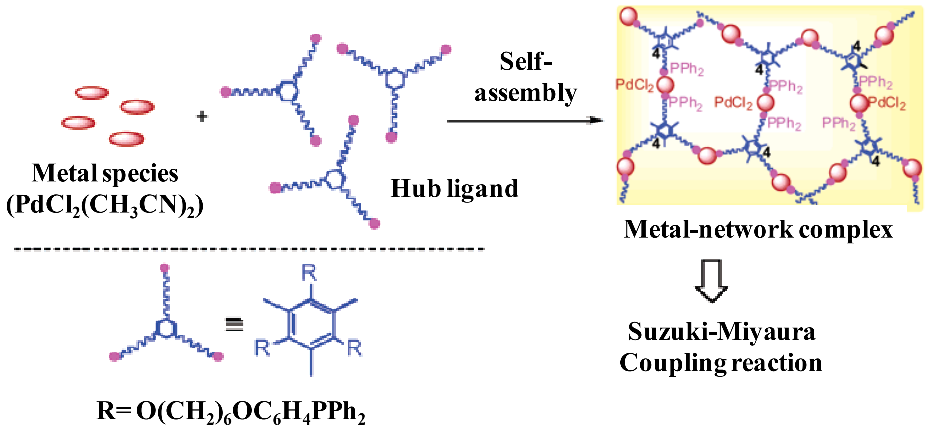
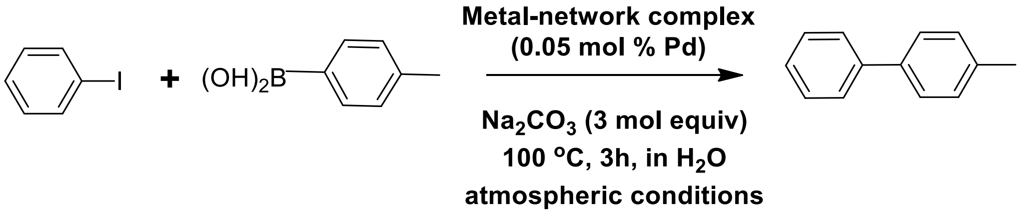


**Figure 1.8** Schematic presentation of self-assembly *i.e.* metallogel formation and its use for Suzuki-Miyaura coupling reaction. Adapted with permission from [28]. Copyright [2006] American Chemical Society.



**Scheme 1.1** Suzuki-Miyuara coupling reaction using metallogel complex. Adapted with permission from [28]. Copyright [2006] American Chemical Society.

First ever utilization of metallogel as a catalytic material is reported by Xing *et al.* in 2002.[29] Novel coordination polymeric metallogel was obtained by mixing of Pd-salt with a tripodal type ligand in dimethylsufoxide (Figure 1.9). The synthesized metallogel was reported to be useful for controlled oxidation of benzyl alcohol to benzaldehyde in good yield (Scheme 1.2). Metallogel as a catalytic material shows recyclability with moderate loss in catalytic activity possibly due to the remaining amount of benzaldehyde in the gel network.

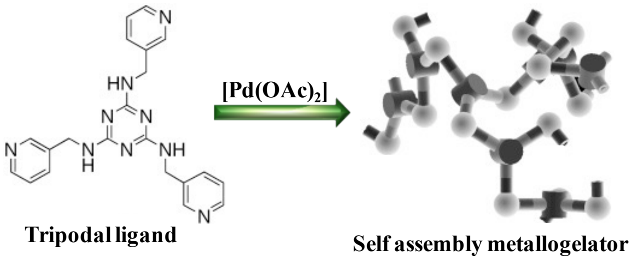
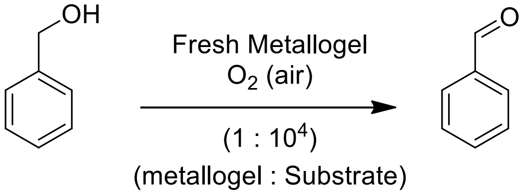


**Figure 1.9** Self-assembly formation from tripodal ligand *via* coordination of Pd-metal. Copyright (2002) Wiley. Used with permission from ref 29.



**Scheme 1.2** Oxidation of benzyl alcohol to benzaldehyde using fresh metallogel in presence of molecular oxygen. Copyright (2002) Wiley. Used with permission from ref 29.

## 1.5 Recent advancements in gels and metallogels

Taking all this into consideration, scientist developed an enhanced vision for synthesis and application of such smart organic gels and fascinating metal-organic gels (*i.e.* metallogels). We discussed in earlier section (section 1.3.2) that the metallogels might be equipped with some interesting additional properties which are discussed here in detail.

### 1.5.1 Charge transfer

Charge transfer at supramolecular level *i.e.* in gel state created new dimensions to this material due to its exciting photophysical properties which ultimately made them useful materials in devices such as bulk-heterojunction solar-cells, organic transistors *etc.*[30] Based on presence of donor (D) and acceptor (A) units either within a molecule or different molecules, charge transfer can be divided into two types; Intermolecular charge transfer and Intramolecular charge transfer (ICT) (Figure 1.10). In the past decades, a considerable amount of research has been carried out over synthesis of intermolecular charge transfer gel due to their class performance towards optoelectronics application.[30,31] Charge transfer interactions generally derive strong interaction between a donor and acceptor molecule which may lead to stacking into a regular alternate order, in turn, produced the charge transfer gel.

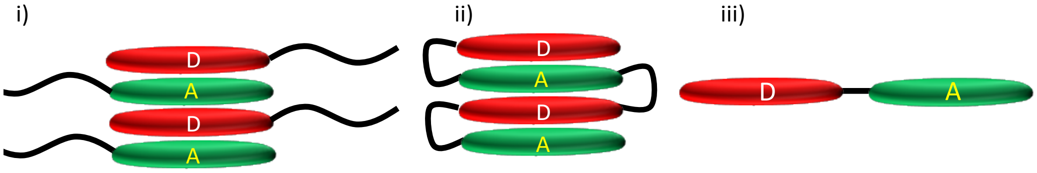


**Figure 1.10** Schematic presentation of arrangement of donor (D) and acceptor (A) units from (i) different molecules (*i.e.* intermolecular charge transfer) or (ii-iii) the same molecule (intramolecular charge transfer).

In early 2000s, Wang *et al.* designed and synthesized an excellent tetrathiafulvalene (TTF) appended urea based ligand and its charge transfer organic gel using 7,7,8,8-tetracyanoquinodimethane (TCNQ), respectively.[32] Strategically, they placed a well-known urea moiety as an electron as well as H-bonding donor centre in the ligand along with the TTF moiety which produced an organic gel in cyclohexane. Further, the synthesized gel is subjected to react with TCNQ in cyclohexane which lead to the formation of intermolecular charge transfer based dark green colored organic gel (Figure 1.11).

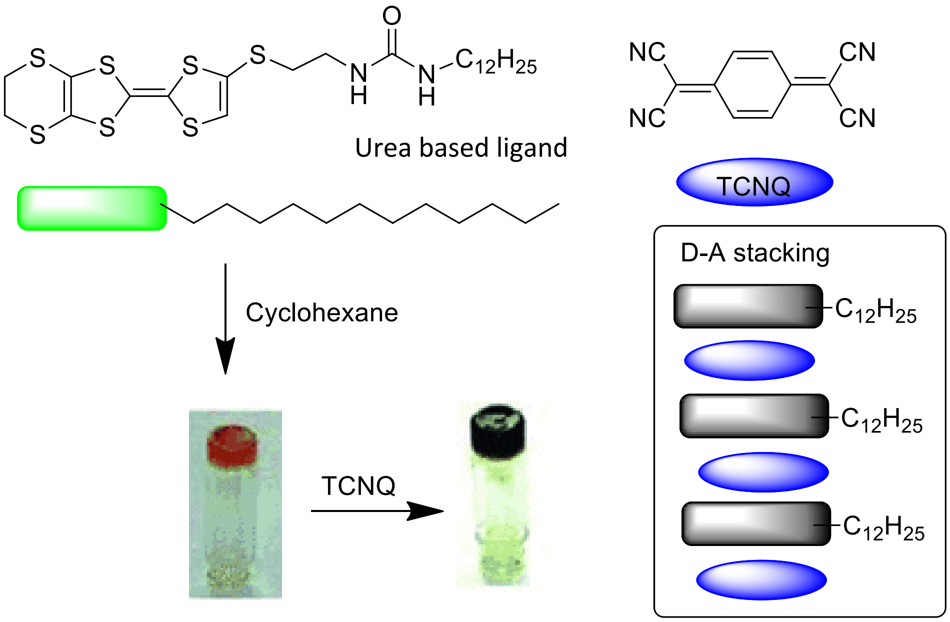


**Figure 1.11** Schematic presentation of gel synthesis using urea-based ligand with and without TCNQ. (inset) Possible donor and acceptor stacking for intermolecular charge transfer gel formation. Adapted with permission from [32]. Copyright [2005] American Chemical Society.

Nalluri *et al.* also reported a chiral supramolecular organic gel using enzymatic condensation of a NDI-functionalized tyrosine (NDI-Y) and phenylalanine-amide (F-$NH_2$).[33] Further, these building blocks produce a charge transfer interaction by mixing of any of the mentioned hydroxyl or alkoxy donor compounds; 1,5-dialkoxy naphthalene (1,5-DAN), 2,6- dialkoxy naphthalene (2,6-DAN), 1,5-dihydroxy naphthalene (1,5-DHN) and 2,6-dihydroxy naphthalene (2,6-DHN). Addition of these donor molecules would lead to the development of 1D D-A stacks in turn charge transfer interaction (Figure 1.12).

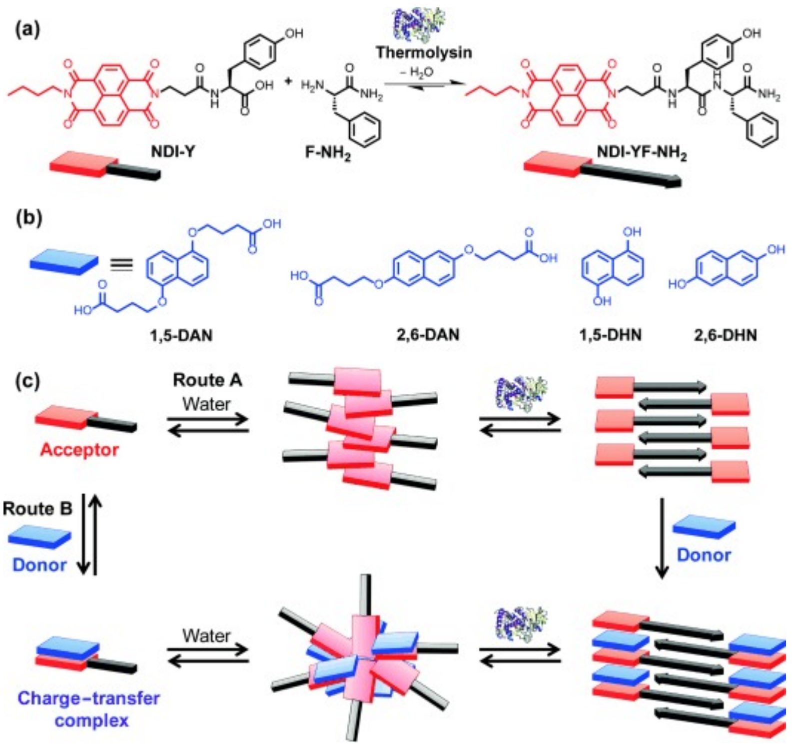


**Figure 1.12** (a) Thermolysin-catalyzed condensation to form n-type naphthalenediimide–dipeptide conjugate acceptor (NDI-YF-$NH_2$), (b) Molecular structures of various di-alkoxy/hydroxy–naphthalene (DAN/DHN) donors used in this study and (c) Schematic illustration of the proposed differential supramolecular organization of NDI-Y/NDI-YF-$NH_2$ acceptors in the absence and presence of various DAN/DHN donors. Copyright (2014) Wiley. Used with permission from ref 33.

### 1.5.2 Stimuli responsive materials

Chen *et. al* explored the luminescence properties of metallogel as well as its tunability using lanthanide(III) metal-polymeric ligand system.[34] In their work, they synthesized light emitting metallogels using Eu(III) and Tb(III) metals and terpyridyl-end-capped PEG polymer. A white light emitting metallogel was achieved by adjusting Eu:Tb molar ratio to 4:96, while the single metal component based metallogels using Eu(III) and Tb(III) exhibited red and green luminescencent metallogels, respectively (Figure 1.13). Considering one step further, this white emissive gel exhibited responsive behavior towards multiple external stimuli (mechanical, chemical, pH triggered vapochromism and thermal stimuli). Reason behind such extensive stimuli responsiveness were accredited to the utilization of dynamic Ln-N^N^N interactions and competing interaction between Ln(III) cations and stimulating anion (F$^-$) inside the gel generating system. Applicative experiments were also performed by examining the stimuli responsiveness of their also corresponding solid thin films which also proved to be highly thermo-responsive, changing color from green-white-red transformation, strongly indicative of intrinsic energy transfer from Tb to Eu centered luminescent chromophores with increasing temperature (Figure 1.13).

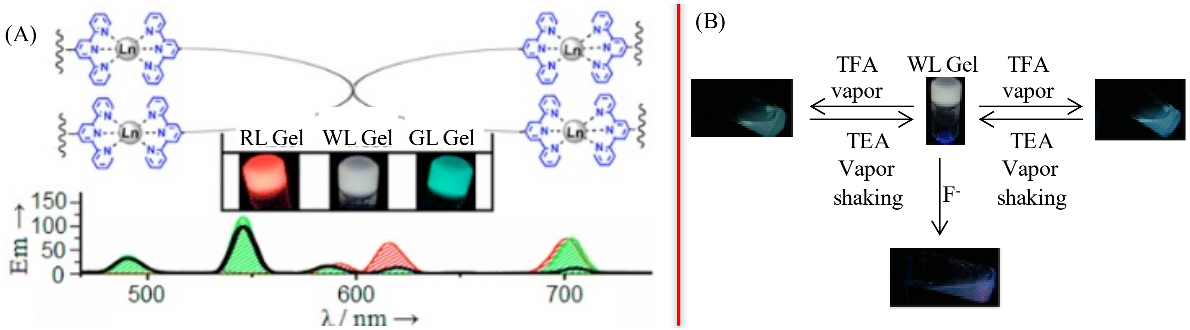


**Figure 1.13** (A) Three different light emitting metallogels using Eu (RL Gel), Tb (GL Gel) and Eu:Tb (WL Gel) metal salts and (B) Stimuli-responsive behavior of WL Gel against TEA vapor, TFA vapor and F$^-$ ion. Adapted with permission from [34]. Copyright [2015] American Chemical Society.

Zhang *et al.* recently reported a host-guest induced polymeric metallogel using Pt(II), Zn(II) metal ion and finally benzo-21-crown-7.[35] Metallogel shows high grade of self-healing property and stimuli responsiveness towards stimuli like temperature, K$^+$ and Cyclen (Figure 1.14).

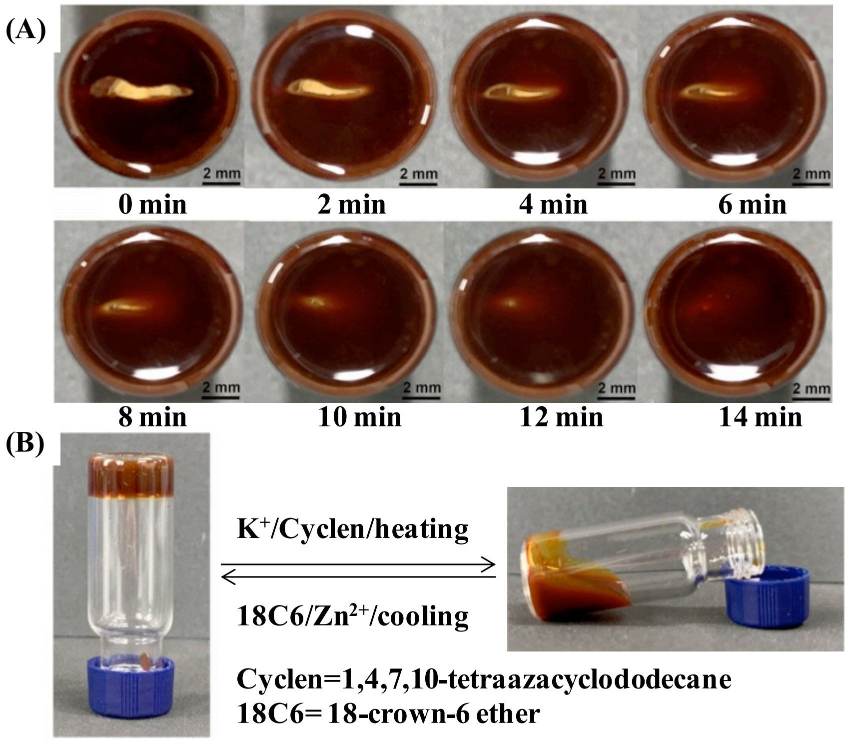


**Figure 1.14** (A) Self-healing and (B) multi-stimuli responsive property of metallogel. Adapted with permission from [35]. Copyright [2019] American Chemical Society.

### 1.5.3 Chiral metallogels

Introduction of chirality in to the metallogelator may lead to interesting alteration in the morphology such as twisting/helicity into the fibres as well as optical properties of metallogel.[36] In addition to this, chiral metallogel are very recently being analyzed as potential and rare chiral discriminator.[37]

Sun *et al.* reported a alanine based chiral ligand which upon metal coordination leads to aggregation and produces chiral organoplatinum(II) metallacycles rhomboids $1^D/1^L$ and hexagons $2^D/2^L$ (Figure 1.15).[36] Further, under suitable conditions, these metallacyles would first lead to fine nanospheres which will further aggregate *via* H-bonding and $\pi-\pi$ stacking to generate chiral metallogel. Interestingly, the chiral metallogel shows helical morphology under TEM analysis.

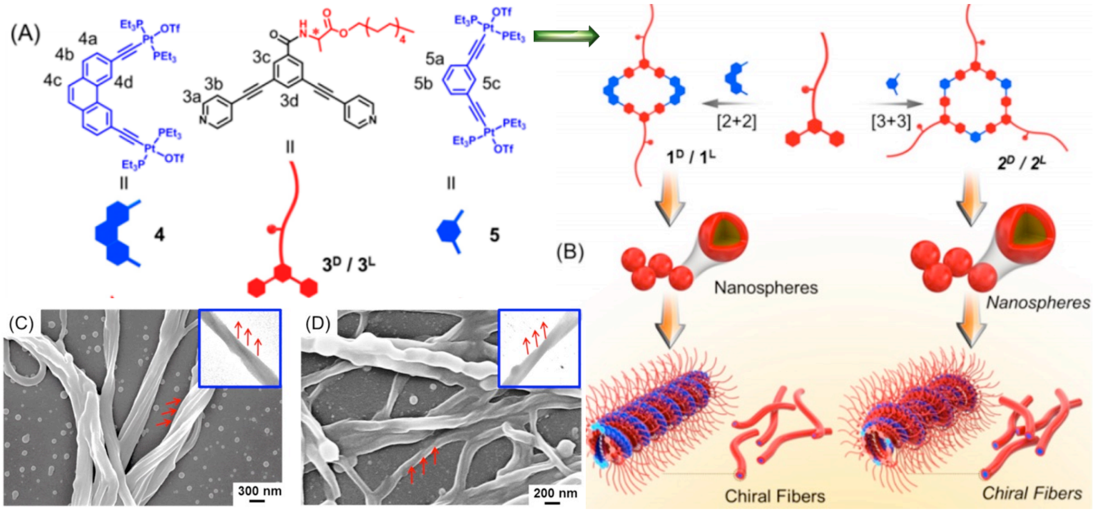


**Figure 1.15** Self-Assembly of (A) rhomboids $1^D/1^L$ and hexagons $2^D/2^L$ , and (B) $1^D/ 1^L$ and $2^D/2^L$ to give nanospheres and nanofibers SEM images of (C) rhomboids 1D and (D) rhomboids $1^L$ in the metallogel state. Inset: TEM images of rhomboids $1^D$ and rhomboids $1^L$ in (C) and (D). Adapted with permission from [36]. Copyright [2018] American Chemical Society.

Tu *et al.* reported an interesting chiral metallogel which was found to be helpful in recognizing (R)- or (S)-binap.[37] Metallogel specifically collapsed in the presence of (R)-binap and showed unchanged architecture of metallogel after mixing of (S)-binap (Figure 1.16 and 1.17).

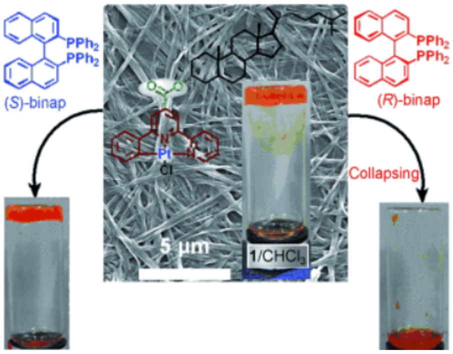


**Figure 1.16** Chiral metallogel resist to the presence of (S)-binap (left side) and gets collapsed in presence of (R)-binap (right) along with SEM image of original metallogel. Copyright (2011) Wiley. Used with permission from ref 37.

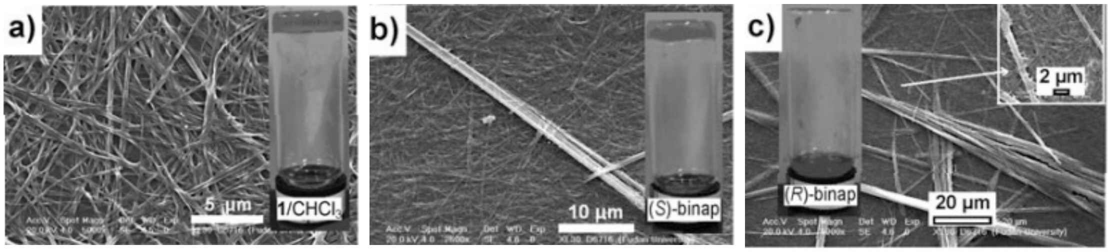


**Figure 1.17** SEM images of (a) gel 1/$CHCl_3$, (b) gel (1+0.1 equiv (S)-binap)/$CHCl_3$ and (c) collapsing sol of (1+0.1 equiv (R)-binap)/$CHCl_3$ along with their respective SEM images. Copyright (2011) Wiley. Used with permission from ref 37.

### 1.5.4 Fluorescent Metallogels

By strategically implementing AIE phenomena into self-assembled gel network, X. Ma and coworkers were able to synthesize a simple yet intelligent multiple pseudoamide based fluorine-gelator, where intermolecular rotation, vibration was deliberately inhibited to increase the radiative decay of excited state species *via* self-assembly achieved by non-covalent interactions.[38] Multiple H-bond donors-acceptors functionalities as well as metal coordinating sites were the main driving force to trigger the necessary self-assembly for the gel formation. Specialty of this ligand lied in intelligent sensing of $Al^{3+}$ in competition with all the other cations *via* strong luminescence enhancement of the entity. Keeping this interesting result in the mind, they successfully suggested a new writable gel material which can be almost immediately erased by $F^-$ ion solution due to precipitation of $AlF_3$ and thus immediate quenching of fluorescence through the recovery of PET phenomena (Figure 1.18).

Chen *et al.* synthesized a tunable fluorescent single metal ion as well as mixed metal ion appended metallogel by the coordination of 5-boronisophthalic acid (**5-bop**) with Eu(III), Tb(III) and/or Dy(III).[39] As we observed in section 1.4.3, emission color tuning of metallogels could be achieved through the mixed lanthanide metal ions. Similarly, in present study, Chen *et al.* synthesized a white light emitting metallogel by mixing of Eu(III), Tb(III) and Dy(III) in 1:1:1 ratio with **5-bop** (Figure 1.19).

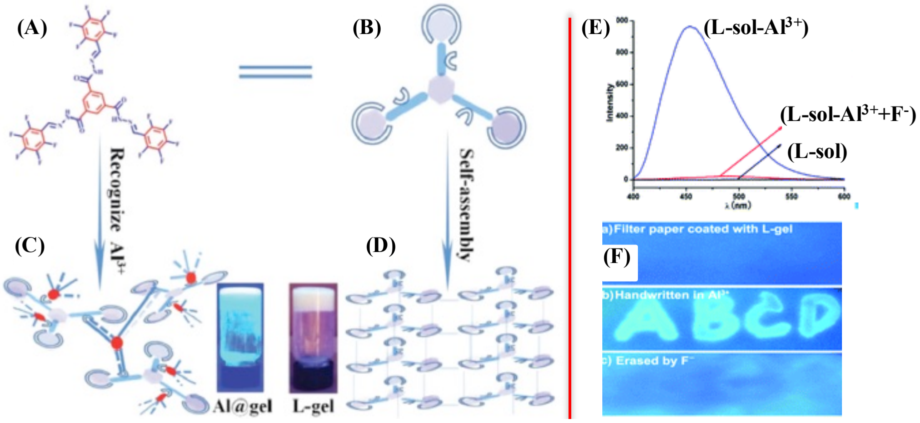


**Figure 1.18** (A) Gelator with its (B) representative model and self assembly process of gelator for the formation of (C) organic gel and (D) metallogel along with photographs under UV at 365 nm, (E) Fluorescence spectra of L-sol, L-sol+Al$^{3+}$ and L-sol+Al$^{3+}$+F$^{-}$ and (F) photos of filter paper strip coated with L-gel (a), handwriting of Al$^{3+}$ (b), handwriting of Al$^{3+}$ erased by F$^{-}$ (c). [38] - Reproduced by permission of The Royal Society of Chemistry

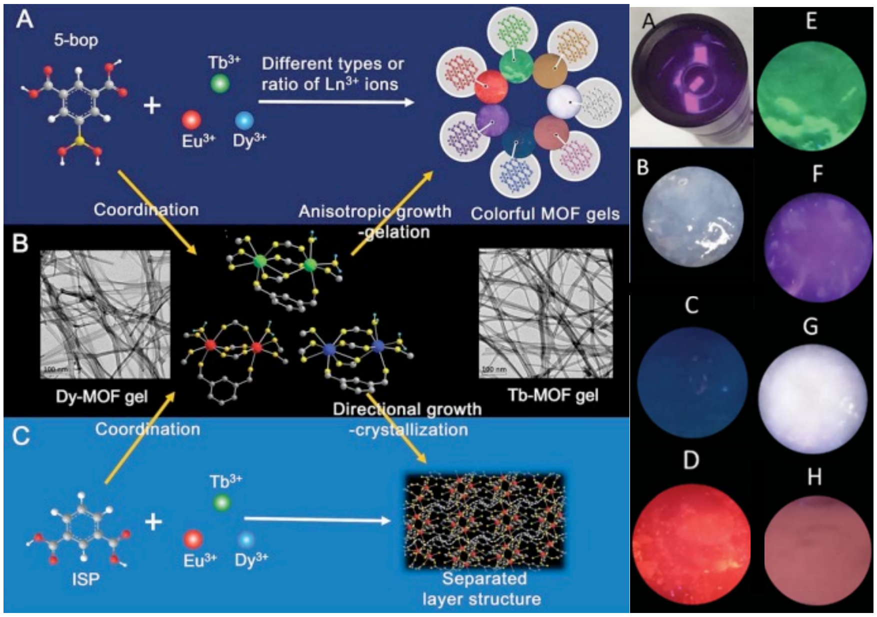


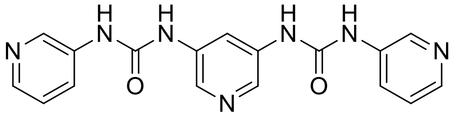
**Figure 1.19** (A) Eu$^{3+}$, Tb$^{3+}$ and Dy$^{3+}$ reacted in different proportions to obtain variety of metallogels. (B) Metallogel formation using Tb and Dy metal ions gels. (C) Layered crystal structure obtained from metal coordination further supported the fiber growth for entrapment

of solvent leading to gelation. Metallogel under (D) UV light with wavelength of 275 nm and (E) visible light irradiation. MOF gels with single and mixed metal ions under UV light (F) Dy, (G) Eu/Tb of 1:1, (H) Tb/Dy of 1:1, (I) Eu/Dy of 1:1, (J) Eu/Tb/Dy of 1:1:2, (J) Eu/Tb/Dy of 2:1:1. [39] - Reproduced by permission of The Royal Society of Chemistry

### 1.5.5 Nanofabrication and nanocatalysis

Directional and controlled nanofabrication of various metal nanoparticles inside gel matrix is started gaining attention in recent past owing to their promising application towards catalysis using ultra-small metal nanoparticles. Besides the early discovery of nanofabrication inside gel media, there are very few reports available which were able to obtain a fine sized and controlled growth of metal nanoparticles.[40,41] Particularly in metallogel, there are only three reports available where the researchers were able to produce the gold (Au) or silver (Ag) nanoparticles inside metallogel matrix without adding any external stabilizing agent.

Piepenbrock *et al.* proposed a *bis*(urea) pyridyl type ligand which upon addition of $AgBF_4$ form a slightly transparent metallogel in THF/water mixtures (Scheme 1.3).[40] Interestingly, the metallogel could further be utilized as *in situ* nanofactory for nanofabrication of silver nanoparticles (AgNPs). ‘N’ atom present in the ligand possibly helps in the directional growth of AgNPs majorly over the nanofiber’s platform (Figure 1.20).



**Scheme 1.3** A bis(urea) pyridyl type ligand used for metallogelation. [40]-Adapted by permission of The Royal Society of Chemistry

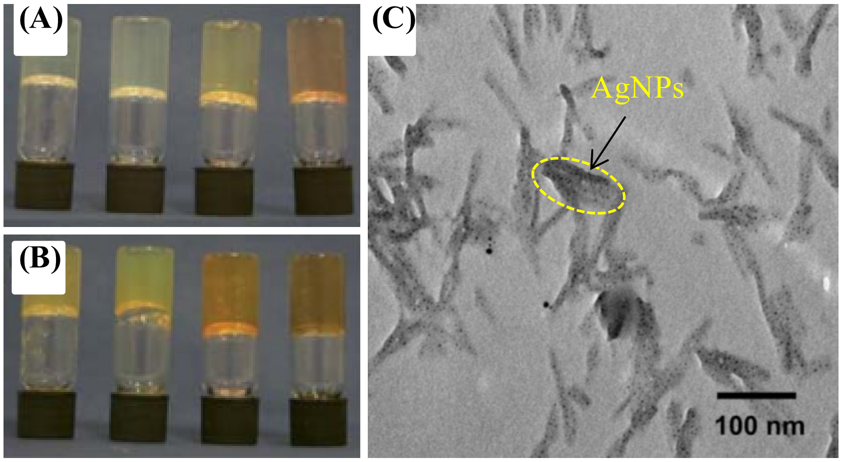


**Figure 1.20** Gels of *bis*(urea) pyridyl type ligand with 0.5, 1.0, 2.0 and 3.0 equivalent (left to right in (A) and (B)) of $AgBF_4$ produce a yellowish to orange colored metallogel in (A) 1-2 weeks and (B) 2-3 weeks. (C) TEM images of 1.0 equivalent of $AgBF_4$ added metallogel. [40]-Adapted by permission of The Royal Society of Chemistry

The idea of *in situ* synthesis of AgNPs is further extended by Lee and co-workers.[41] They synthesized a metallogel by coordination of Ag(I) metal with tetrazole based symmetrical ligand as shown in figure 1.21 which was capable of *in situ* generation of AgNPs in side gel matrix For the first time metallogel chemistry, this group was able to use the synthesized AgNPs for catalytic reduction of 4-nitrophenol to 4-aminophenol in presence of $NaBH_4$. (Figure 1.21)

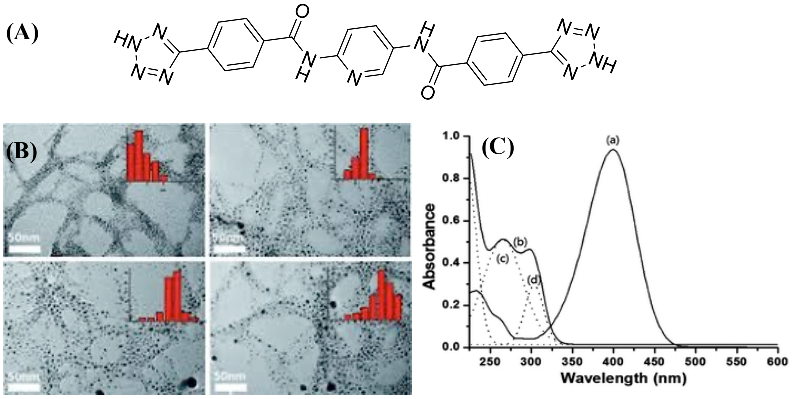


**Figure 1.21** (A) Structure of ligand utilized for metallogelation with silver salt, (B) TEM images of AgNPs embedded metallogel, (C) UV-vis spectral monitoring of (a) 4-

nitrophenolate reduction to (b) 4-aminophenolate in presence of AgNps loaded metallogel in catalytic amount. [41] - Reproduced by permission of The Royal Society of Chemistry

Similarly, in 2015, Paul *et al.* designed and synthesized few $C_3$-symmetric *tris*(pyridylamide) ligands which could fix a DMSO/water mixture upon coordination with variety of silver salts.[42] The synthesized coordination polymeric metallogel was able to produce *in situ* AgNPs upon simple irradiation of metallogel under sunlight. Further, the AgNPs were utilized as a catalytic material for a model reduction reaction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) in presence of excess $NaBH_4$ (Figure 1.22).

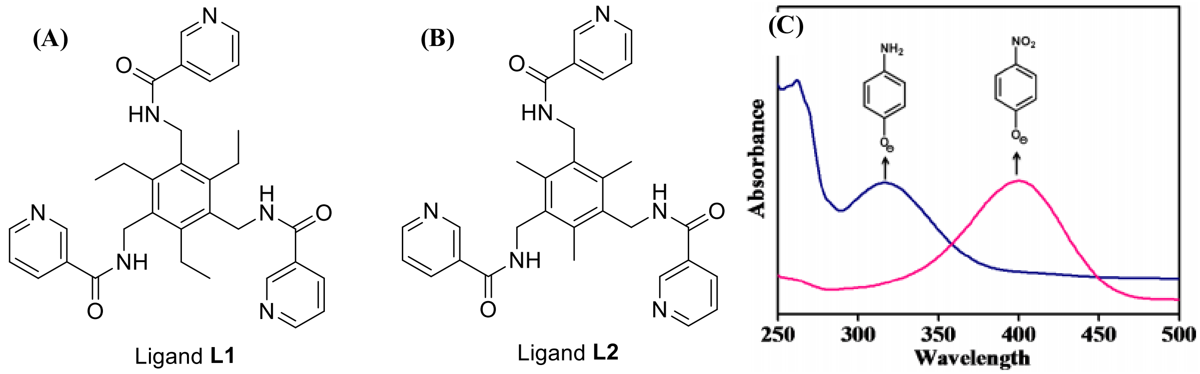


**Figure 1.22** (A) and (B) Ligands used for metallogelation with Ag salts. (C) Catalytic activity of *in situ* synthesized AgNPs inside gel matrix for reduction of 4-NP to 4-AP in presence of excess $NaBH_4$. Copyright (2015) Wiley. Used with permission from ref 42.

## 1.6 Findings of the literature

During the literature survey regarding the synthesis and application of metallogel, we find few lacks which is discussed below;

**(A)** Highly emissive metallogels were usually synthesized by coordination of costly lanthanide metal ions (such as; Eu, Tb and Dy etc.) with pincer-based ligand. Thus, we focused the present thesis work towards synthesis of highly fluorescent metallogel in a very cost-effective way using organic ligand using simple organic synthetic procedure and cheap metal ions (like alkali meta ions and metal ion from 3d-transition series).

**(B)** Interestingly, only few reports are available for *in situ* nanofabrication of metal nanoparticles inside metallogel matrix. Moving towards application of metallogel, we find a severe lack of information towards complete kinetic study for reduction of 4-nitrophenol to 4-amnophenol in presence of Sodium borohydride. Either, only rate constant or no kinetic parameter is provided for the abovementioned reduction reaction. Keeping this lack in the mind, this thesis also focused to synthesize a chiral fluorescent coordination polymeric metallogel which possibly be able to control the growth of metal nanoparticles inside gel matrix. These metal nanoparticles would be further used for mentioned reduction reaction with full analysis of kinetic parameters.

**(C)** Literature survey towards charge transfer metallogel reveals that there is no report available towards chiral intramolecular charge transfer metallogel till date. Thus, we aimed for designing of a ligand with chiral core and suitably placed donor-acceptor moieties for intramolecular charge transfer (ICT) which possibly induce gelation through dipole-dipole interaction under suitable conditions.