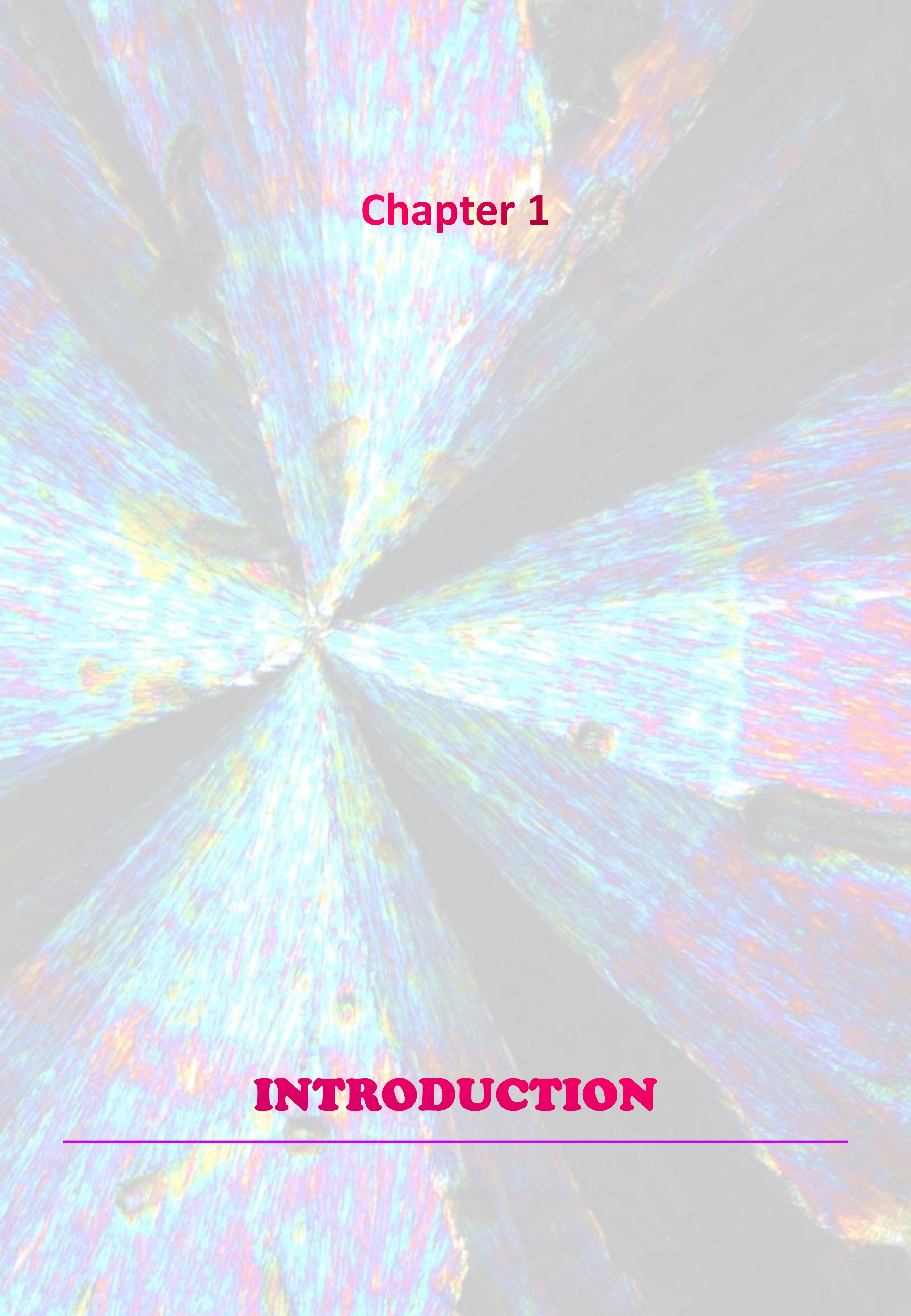

Chapter 1

INTRODUCTION

CHAPTER 1 INTRODUCTION

1.1 Introduction to gels

Gels have encompassed our everyday life in a variety of forms. The wet soft solids that we run into in the form of commercial products such as toothpaste, hair gel, soap, shampoo, and other cosmetics, as well as contact lenses and gel pens etc. are all gels derived from polymeric compounds. In spite of so many common and diverse applications of the gels, there has been no proper definition of a gel. There have been various efforts to define the term ‘gel’.

The term gel was first coined by a Scottish chemist Thomas Graham from the word gelatin.

“**While the rigidity of the crystalline structure shuts out external expressions, the softness of the gelatinous colloid partakes of fluidity, and enables the colloid to become a medium for liquid diffusion, like water itself. The colloid possesses ENERGIA. It may be looked upon as the probable primary source of the force appearing in the phenomena of vitality**” *Thomas Graham (1861)*[1]

This indistinctness was first pointed out by Jordan-Lloyd; who in 1926 stated that – “**the colloidal condition, the gel, is one which is easier to recognize than to define**”.[2]

Since then, the scientific understanding about what comprises a gel has shown a major improvement. Supramolecular gels belong to the field of interdisciplinary science and scientists from various fields like chemistry, physics and even biology have been working on it. Still, it remains difficult to have a proper definition for gels. A more suitable understanding of the gels was given by Flory that included s**tructural criteria, such as the formation of an infinite entangled network, or a 3-dimensional (3D) structure in exhibiting properties such as coherence and connectedness.**

A recent definition was given by Murphy which states that the gels are viscoelastic solids.[3] Both these definitions were accepted and later on modified by Almdal *et al* who stated that – “**gels are soft, solid-like materials that are composed of 2 or more materials, one of which is a gelator molecule responsible for gel formation and the other is a liquid that is usually present in substantially more quantity as compared to the gelator**”.[4]

From the recent understanding of the gels, it has been observed that gels are a system in which at the gelation point, an infinite cluster is created that spans the whole system.

A 3-dimensional assembly is important in imparting the mechanical strength to the structure of the gels. Another important property characteristic to the gels is the sol-gel transition temperature (T_{gel}).[5] Sol-gel transition is the temperature at which macroscopic properties of the gel change abruptly from solid-like gel to an isotropic liquid.

In general, after studying and interpreting various definitions it can be concluded that for a material or a substance to be classified as a gel, it should have 2 important properties –

- they should consist of atleast 2 or more components, one of which is a liquid and is in a fairly higher proportion, and
- they should have solid-like characteristics.[4]

According to IUPAC, ***a gel can be defined as a nonfluid colloidal network or polymer network that is expanded throughout its whole volume by a fluid***. It is a heterogeneous system which consists of immobile network of solid gelator and a mobile solvent trapped by the gelator. Gel has solid-like property that allows it to sustain shear stress.

According to rheological analysis, gels are viscoelastic materials which exhibit the properties of both solid as well as a liquid. [6–13] Gels are non-Newtonian fluids and they display flow characteristics that resemble to that of viscoelastic materials. The storage modulus (G’) of the gels is larger than the loss modulus (G’’). Gel is a substance/material that should appear solid-like and there should be no flow with time under its own weight.[14]

The gels are usually prepared dissolving a gelator in a given solvent and heating the system at a higher temperature, which is further followed by cooling the system slowly. The heat provides the activation energy which is required to arrange and organize the gelator molecules in a 3-dimensional network through non-covalent interactions which traps the solvent molecules. This results into a liquid-solid transition which is called gelation leading to a stable gelator system. At gelation point, an infinite cluster is created that extends in the entire system and the properties of the system drastically change from a liquid-like system to a consistent solid.

The formation of the gel is characterized by inverting the vial or test-tube in which the gel is formed. A stable gel resists the gravitational force and does not fall even on inverting the vial or test-tube, which is a characteristic of stable gel. This is also called an inversion test. T_{gel} is another important characteristic of a gel, T_{gel} is the temperature at which the gel transforms from a solid gelator system to a flowy liquid system, also known as sol-gel transformation. T_{gel} is also referred as the sol-gel transformation temperature. These kinds of gels are called thermoreversible gels and such thermoreversible change can take place several times without disrupting the gelator system. The T_{gel} temperature is dependent on the strength of the interaction between the gelator molecules and the solvent as well as the amount of solvent immobilized in the gelator system.[15]

Earlier the formation of the gels was more of a chance or an accident rather than a properly designed experiment. However, since the past 3 decades many groups have worked on designing the gelators and made this process more design-oriented and scientific rather than just a chance discovery.[16–25]

The gelator system can be formed by covalent as well as non-covalent interactions between the gelator molecules. If the assembly forming the gels is held by non-covalent or supramolecular interactions like hydrogen bonding, halogen bonding, π-π stacking, hydrophobic interactions, charge transfer, donor–acceptor interactions, metal–ligand coordination, etc. – the gels are termed as ***physical gels***.[14] When the formation of gels is followed by covalent interactions – such gels are called ***chemical gels*** or ***polymer gels***.[26]

Silica gel, polymer gels and gels formed by proteins like gelatin are the examples of chemical gels which involve chemical bonds. Some of the polymer gels act as super absorbent gels which can absorb tremendous amount of water/solvent.[27] Gelatin which is formed of collagen forms a thermoreversible gelator system when mixed with water.

1.2 Classification of gels

There are various ways of classifying gels (Figure 1.2.1)

1. The source

The gels can be classified on the basis of source as **artificial** and **natural** gels.

2. The type of solvent incorporated by the gels

Supramolecular gels are also classified on the basis of solvent entrapped by the gels. If the gels immobilize organic solvents, they are called **organogels** whereas if they incorporate water in their structure they are termed as **hydrogels**.

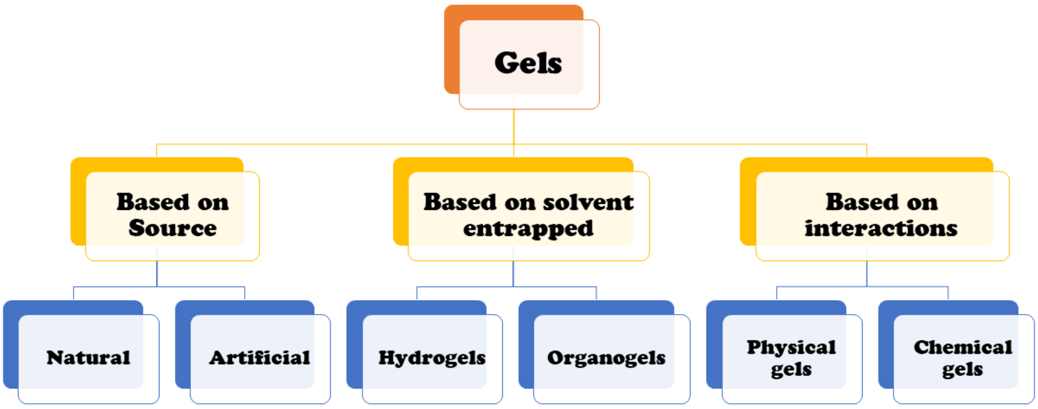

Figure 1.2.1 Classification of the gels on the basis of interactions.

3. The type of interactions/ bonding present between the gelator molecules

Physical gels are composed of a gelator and the solvent which is entrapped by the gelator. It also has a third component which has no chemical interaction with the gelator, but it affects the properties of the gel (rheological properties, T_{gel}). The gelator is capable of forming the gel by itself. The third component does not play any role in gelation, it only modifies or affects the properties of the gel.

Composite liquid crystalline physical gels of photochromic azobenzene moieties as gelators and typical rod-like liquid crystalline (LC) molecules like 4-butyl-4'-cyanophenyls as a third component have been reported.[28] These are hybrid or composite gels because they have combined properties of both: the gelator as well as the LC molecules.

Chemical gels are the ones in which 2 or more components react chemically to form a gelator which forms gel.

The gels can be both, (i) consisting of only organic moieties or (ii) involving metal ions either physically held in the network of gels or held in the gel-forming network through coordinate bonds. The latter are usually termed as metallogels, though the term can be more appropriately used for the gels where the metal ions are a part of the gel-forming network, typically by coordination. The focus in the present work is more on this latter type of metallogels.

A bis(pyridylurea) ligand forms metallogels in methanol in the presence of up to 0.5 equivalent of copper(II) chloride.[29] Properties of the gel depend on the type of counter anion and the concentration of copper ions. Gelation is favored by the presence of counter anions like chloride whereas nitrate and sulphate hinder the process of gel formation. Also, the T_{gel} temperature increases with the increase in the concentration of copper(II) chloride.

Metallogel formed by a methanolic solution of $NiCl_2.6H_2O$ with N-methylmorpholine has been reported.[30] Ag(I)–melamine coordination polymer which forms a metastable hydrogel at 1:1 molar ratio and 1:2 molar ratio has also been reported.[31] The gel exhibits chiral behavior owing to the helical nature of the assembly. Both these gels are chemical gels as there is chemical interaction between the metal and the ligand.

Low Molecular Weight Gelators (LMWGs) / Low Molecular weight Organic Gelators (LMOGs): These are the components of a recent category of gels that are formed by comparatively smaller molecules in contrast to the macromolecular gels / polymeric gels.

The molecular mass of the gelator molecules here is usually ≤ 3000.[32]

When the gels are formed by LMWGs on incorporation of a metal ion/atom into their structure, ***metallogels*** are formed. As discussed earlier, the metallogels are also composed of a gelator and a solvent, which is entrapped by the gelator. The metallogels can be of two main types, the ones which are formed by interaction of the LMWGs and a metal ion where no discrete complex is formed or characterized, results in the formation of a gel. It is a combination of the gelator molecules and the metal ions that are responsible for gel formation, where the metal ion does have an influence on the properties of the gels but its binding with gelator is not well defined. On the other hand, the metallogels that are formed by discrete coordination complexes have also been reported, in which the gel forming complex has been isolated and properly characterized. A detailed discussion of these kind of metallogels along with examples are included latter in this chapter.

1.3 Low molecular weight gelators (LMWGs)

Low molecular weight gels are a specific class of gels that are formed by comparatively smaller molecules in contrast to the macromolecular gels. The molecular mass of such gelators is usually ≤ 3000.[32] These molecules result into a self-assembly that extends in three dimensions. The assembly is held together by non-covalent interactions such as H-bonding, π-π stacking, electrostatic interactions, metal-ion coordination, solvophobic forces (hydrophobic forces for gels in water) and van der Waals interactions. These gels can be more specifically called Low molecular weight supramolecular gels (LMWSGs) as it is the supramolecular assembly of small molecules formed due to the non-covalent interactions that extends in 3-D space resulting in the formation of gels.

1.3.1 Synthesis and Designing of LMWGs

Supramolecular assemblies formed by LMWGs are held together by non-covalent interactions. Thus, the primary condition for a molecule or complex to behave as a gelator is that it should have functionalities which can get involved in non-covalent interactions like H-bonding, π-π stacking, coordinate covalent bonds etc. The gelator should be soluble in a solvent which it incorporates to form a gel. Molecules or complexes forming a 1-Dimensional assembly have more chances of behaving as a gelator and form a gel. If the assembly extends in 2 or 3 dimensions then the molecular weight increases and there are chances that it will either crystallize or precipitate instead of forming a gel.

Gels of low molecular mass compounds are usually prepared by heating the gelator in an appropriate solvent and cooling the resulting isotropic supersaturated solution to room temperature. When the hot solution is cooled, the molecules start to condense and then three situations can arise:

- A highly ordered aggregation giving rise to crystals i.e., crystallization
- A random aggregation resulting in an amorphous precipitate
- An aggregation process intermediate between these two, yielding a gel

Formation of a supramolecular assembly which ends up in a gel is a multistep event.[33] The general mechanism of any gelation can be simplified into 3 steps (Figure 1.3.1.1).

1. The formation of the fibrils because of the non-covalent interactions like H-bonding and π-π stacking
2. Self-assembly of fibrils to form nanoscale bundles which are termed as fibers
3. Eventually all the fibers intertwine and result into the formation of a 3-dimensional supramolecular assembly which has the capability of entrapping the solvent.

Figure 1.3.1.1 How the gel formation is thought to occur. (Image has been adapted from the reference[34]).

Gel formation can be achieved by dissolving the solid molecule (gelator) in the desired solvent as mentioned previously. Sometimes sonication, heating by providing higher temperature or subjecting the system to UV light is also done in order to achieve gelation.

Gel formation is strongly dependent on 2 factors:

1. The concentration of the gelator molecules in the solvent
2. Temperature

The minimum amount of the gelator molecules required to achieve gel formation is called ***critical gelator concentration*** (CGC). It is also termed as ***minimum gelator concentration*** (MGC), a concentration below which gel formation does not take place. Higher the concentration of gelator molecules, higher is the chance of gel formation. The morphological and viscoelastic properties of the gels can be varied and controlled by changing the gelator concentration.

Temperature is another critical factor that decides the gel formation, as a higher temperature leads to a disruption in the non-covalent interactions, thus destabilizing the supramolecular assembly and deforming the gel. However, some minimum heat or temperature is usually required in order to provide sufficient energy to the molecules which enables them to arrange and form a supramolecular assembly. The temperature at which the gel converts to a flowy liquid from a solid-like substance is called T_{gel} temperature. Gelator concentration and the T_{gel} are both inter-related.

1.3.2 Structural Requirements for Supramolecular Gelators

The last 3 decades have seen an ever-increasing interest in low-molecular-weight gelators (LMWG).[5] It is now beginning to be possible to move from the discovery of gelators by chance to attempting a more rational design of molecules for specific gel applications.

"To gel or not to gel: A prior prediction of gelation in solvent mixtures''

The above-mentioned phrase clearly shows the development in understanding the process of gel formation. The process of gelation can be made from chance to design if the non-covalent interactions of the system can be studied and controlled. Though π-π stacking and H-bonding are the main interactions present in the gel-forming supramolecular assemblies, it is not possible to point out the exact functional groups and molecules that would result in the formation of gels. There can be certain moieties that would potentially act as gelators, however, their ability to exhibit gelation depends on the solvent, temperature, pH and a lot of other conditions prevalent in the system.

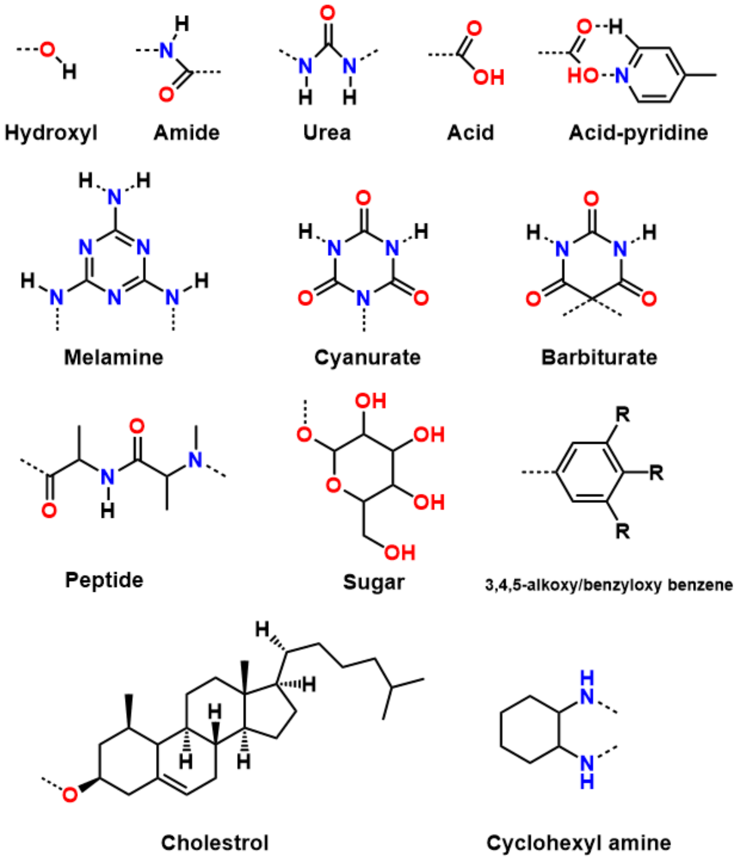

Figure 1.3.2.1 Structures of few of the commonly known gelator molecules.

The moieties shown in the Figure 1.3.2.1 are known to exhibit gel forming capabilities. Presence of functional groups such as hydroxyl, amide, carboxylic acid, urea, amino groups, etc. makes the formation of H-bonding possible that can lead to the construction of supramolecular assemblies. The presence of hydrocarbon chain also helps in van der Waals interactions while the presence of aromatic rings increases the possibility of π-π stacking which can contribute to gel formation. Yet, the above-mentioned molecules and criteria do not guarantee gel formation as it is quite a complex process involving numerous factors. However, the in-depth knowledge of such potential gelator molecules is definitely a stepping stone in this vast and exciting field of supramolecular chemistry - **'Gels'!**

1.3.3 Advantages of Low-molecular weight gelators (LMWGs) over traditional & polymer gels

Since the LMWGs are formed using smaller molecules it is easier to probe and understand the kind of interactions that lead to the development of the nano-scale fibrous network which eventually results in the formation of gels. Since the molecules leading to the formation of gels are simpler and smaller, their synthesis and modifications post synthesis are both easier and more convenient. Thus, after the formation of such low molecular weight gelators, modifications can be done in the structure and the structure-activity relationship can be studied and established.

Polymer gels or metal oxide gels like silica gel find applications in very limited areas as they are rigid, more like solid and it is usually very difficult to attain the sol-gel transitions in these types of gels. As a result, their main uses have been limited to absorbents or hydrogelators. Whereas on the other hand, supramolecular assemblies that result into gels are governed or held together by non-covalent interactions[6,33,35–39] like H-bonding, π-π stacking, coordinate covalent bonds etc. [40–42] As the extent of these non-covalent interactions can be controlled, it is possible to tune the properties of the gels and design them for specific uses. Many of the LMWGs are biocompatible molecules. This gives the low molecular weight gelators an advantage when it comes to biological applications. The low-molecular weight enables easy degradation as they are also usually expected to have fast metabolic rates. These gels can be programmed to be stimuli responsive (pH, temperature, solvent and radiation) which make them suitable candidates for numerous applications.

1.3.4 Applications of LMWGs

The world of nanosciences has attracted a lot of attention because of their potential and versatile nature of applications. Particularly, the synthesis of one-dimensional nano-assemblies has attracted special attention because of their interesting electronic, optical and chemical properties. Small molecules can be used to form these highly ordered nanostructured assemblies with the help of non-covalent interactions. The balance between these non-covalent interactions is very delicate and these supramolecular assemblies can be tuned by controlling the extent and nature of such non-covalent interactions. Any insight and discussion about ***'Supramolecular Chemistry'*** is incomplete without mentioning the names of Cram, Lehn and Pedersen who were awarded with a noble prize in 1987 for their outstanding contribution in this field and accelerated the research in the area of supramolecular chemistry tremendously.

Recently, Low Molecular Weight Gelators (LMWGs) have attracted ever increasing attention and interest amongst various fields[15] and there has been a great increase in the research and reports of supramolecular gels especially after 2005. This is mainly owing to their widespread applications in various fields like sensors,[43–45] drug delivery systems,[39,46,47] tissue-engineering,[48] aerospace,[49] templated nanomaterial synthesis[50] and optoelectronic devices.[51]

1.4 Incorporation of metals in the structure of LMWGs - 'METALLOGELS'

Metal ions or atoms can be incorporated in the structure of the gels formed by LMWGs. Other than the above-mentioned applications of the LMWGs, metallogels can have a broader spectrum when it comes to applications and possess several advantages because of the presence of metal ions. The recent years have witnessed immense interest in the field of ***metallogels***[5] which involves a metal in the framework of the gelator assembly. Initially, metallogels were formed by adding the metal ions in the gels and monitoring the effect and changes in the chemical, physical and morphological properties[52–54] of the metallogels thus formed. The unusual properties like catalytic activity,[55–57] redox responsive,[58,59] stimuli responsive,[60,61] photoemissive,[60,62,63] magneto-optical switching[64] properties are exhibited by the metallogels due to the presence of metal ion within the gel structures.

Metals can lead to the formation of metallogels in 2 ways –

- Metal-ligand interaction leading to the formation of metallogels by the addition of metal ions. Here the metal or metal ion can be present in the form of a nanoparticle adhered in the structure of the gel.
- Formation of a metal-ligand coordination complex which itself acts as gelator and leads to the formation of a metallogel. The metallogelator complex immobilizes the solvent and leads to the formation of metallogel through various non-covalent interactions like H-bonding, electrostatic interactions, π-π stacking, hydrophobic / lyophobic interactions exerted by the ligands as well non-conventional metal-metal interactions. Such interactions lead to interesting structural and spectroscopic properties.[26]

Metal-ligand interactions can be used to design small molecules which can act as gelators, these small molecules can be controlled to build up large assemblies that can be controlled using the unidirectional and diverse properties of metal-ligand bonding. Metal-ligand Frameworks (MOFs) are examples of metal coordination polymers in which metal-ligand interactions are used to form infinite assemblies that extend in one, two or three dimensions. In order to predict the exact structure, these MOFs are usually characterized using single crystal analysis. However, the same metal-ligand interactions can also be used to design metallogels instead of metal-organic frameworks. The properties of such gels can be varied and controlled depending on the metal ions/atoms involved, their oxidation state, coordination geometry and the nature of the coordinating ligands. It is often claimed that the metallogels have advantages over the organogels in terms of catalytic, spectroscopic and redox properties mainly owing to the presence of metal ions/atoms. Also, by employing the metal-ligand interactions, the assembly can be developed in a one dimensional array which is not usually possible by using the organic ligands alone.[15]

Metal ions form coordinate covalent bonds which are the strongest non-covalent interactions known and these interactions are capable of holding the supramolecular assembly together with required strength to enable their application in various fields. Each metal ion has a specific coordination geometry, thus assemblies with different morphologies can be designed. Metal ions can also have an effect on the T_{gel} of the gels. Thus, the tuning of the sol-gel transition temperature is also possible by varying the concentration of metal ions. Metallogels synthesized using transition metal ions can show interesting magnetic and redox properties.

Metallogels provide a diversity of architectures such as rods, ribbons, tapes, tubes, helices, etc. in nanometric dimensions. The superstructures formed by a given gelator molecule define a unique morphology, which can be used as templates for crystallization or for the synthesis of nanoparticles. Incorporation of metal ion into LMWGs and coordination directed gels display novel properties useful in adsorption, catalysis and as templates for porous materials which might find applications in gas storage. As many supramolecular hydrogels are derived from naturally occurring molecules, they are expected to be biocompatible. As a result, they are being widely explored as media for tissue engineering and 3D bioprinting owing to their structural similarity to the macromolecular components in the body. Gels are a promising media for applications involving controlled release of molecules, specifically for drug delivery.

1.5 Characterization techniques for Gels

Since gels are a supramolecular system and not just discrete molecules, it is important to develop and use techniques that not just give information about the gelator molecules and their structure but also of the various interactions present between the gelator and solvent molecules which eventually result in the formation of gels. These techniques provide knowledge and insight about intra- as well as intermolecular interactions which lead to gelation. Apart from these, the viscoelastic properties of the gels are also studied by performing the rheological analysis of the gels.

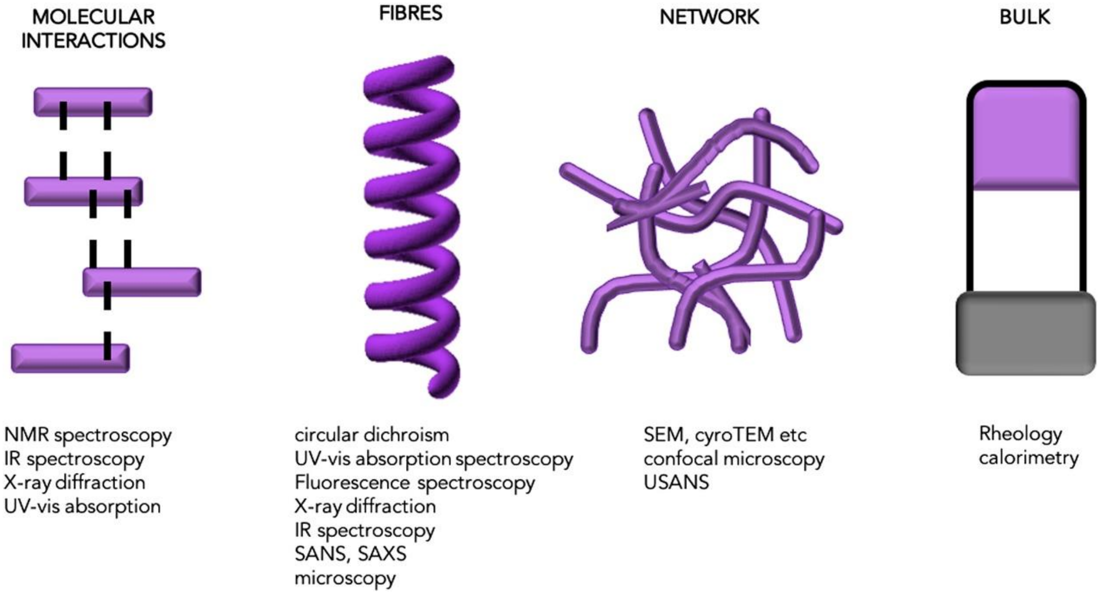

Figure 1.5.1 Various analytical techniques for the characterization of gels. (Image has been adapted from the reference [34]).

The characterization of the discrete gelator molecule/molecules can be carried out using conventional characterization techniques like NMR, IR, Mass spectroscopy, UV-visible and fluorescence spectroscopic studies **(Figure 1.5.1)**.

1.5.1 Inverted Vial Method

Inverted vial method is one of the most basic, simple and preliminary methods employed to confirm gel formation. It entirely depends on direct visualization and does not require any high-end instrumentation or technique. A known amount of gelator is taken in a vial and the solvent is added to it in required proportion. The contents in the vial are heated as the supramolecular assembly that leads to gel formation requires certain energy to be formed, the heat energy here in the form of elevated temperature provides the same. After this, the contents in the vial are allowed to cool down. The vial is then inverted and gel formation is confirmed if the contents in the vial do not flow down and resist gravity.[18] The minimum concentration or the amount of the gelator required at which gel formation takes place is called critical gel concentration (CGC).

1.5.2 Gel Morphology

Gel formation takes place when a solvent is immobilized by gel forming molecules (gelator). The morphology of the gels is controlled by the nature of the solvent immobilized, the structure & nature of the gelator molecules and the nature & extent of the non-covalent interactions existing between the gelator & solvent molecules. One common characteristic observed in all the types of gels is the presence of fibrous assemblies that extend throughout the structure of the gel in 3-dimensional space. As the fibers cannot be observed by naked eyes, several techniques and instruments are used in order to visualize the morphology existing in the gels.

The fibrous structures along with other morphological patterns can be visualized using scanning electron microscopy (SEM). SEM provides the surface morphology of the fibrous assembly and an insight about the width and the length of the fibers forming the fibrous assemblies can be obtained. However, to get an idea about the hollowness in the fibers or the height and thickness of the fibers, transmission electron microscopy (TEM) is more advantageous. High resolution TEM (HR-TEM) is useful especially for the metallogels as it can provide information about the type of the metal as well as its oxidation state existing in the metallogel.

Atomic Force Microscopy (AFM) also gives an insight about the thickness and the height of the gel fibers. Elevated temperatures to convert the gels into xerogels results in disturbing the supramolecular assemblies, hence the cryogenic electron microscopy techniques can be employed to get a more accurate information of the microscopic structures. Cryo-SEM and cryo-TEM can give information about the dimensions of the fibers without disturbing the supramolecular assemblies. Small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) in which the gel sample is hit by X-rays and energetic neutrons, respectively, can also be used in order to indirectly determine the morphology of the gels. SANS is specifically useful to study the H-bonding, if present in the supramolecular assembly leading to the formation of the gels.[65,66] The particles in the beam are scattered depending on the size and the shape of the fibers.[67]

1.5.3 Viscoelastic Properties of Gels

Since gels are non-Newtonian viscoelastic materials, they resist flow due to gravity. In order to get an idea about their viscoelastic properties, rheological studies can be performed which offer a very convenient and relatively easy way of assessing the strength of the gels. The instrument is called rheometer where the gel sample is placed and is subjected to shear stress. Viscoelastic storage modulus (G′) and loss modulus (G”) measured by a rheometer are the indicators of the viscoelastic properties of the gel.[68–70]

Frequency sweep method can be used in order to calculate the G’ and G’’ values. G’ indicates the amount of energy that a gel can store, and which is thus related to the elasticity of the gel sample; while on the other hand G’’ symbolizes the tendency of the flow of the gels. G’ is also called as storage modulus and G’’ is termed as loss modulus. For an ideal solid, the value of G’’ is 0 as solids do not have a property to flow while Newtonian liquids have a value of G’ as 0 as liquids are not elastic in nature. In viscoelastic materials like gels, G’ is greater than G’’ which indicates the dominance of elastic behavior of the system. The ratio of storage modulus (G’) with respect to loss modulus (G’’) is represented by tan δ = G”/G.

If the ratio of loss and storage moduli (tan δ = G”/G’) is less than 1 (constant, usually at lower frequencies over a wide range, i.e., from 0.1 to 5 rad s^{-1}) it is a characteristic of elastic materials. The tan δ values increase and become (>1) with a smooth transition which is an indication of a transition from elastic to viscous behavior, usually taking place at frequencies higher than 10 rad s^{-1}. This frequency dependence is a characteristic of soft materials[71]. Further, according to Hvidt's classification,[72,73] the gels that have G'>1000 Pa can be considered as hard gels.

There are two kinds of rheological measurements that are often performed on gels –

1. Determination of mechanical stress resistance
2. Dynamic moduli measurement

The dynamic moduli are mainly dependent on the frequency (time scale) of the measurement.

1.6 Examples of metallogels

The first report of a metallogel is dated way back in the mid-19th century of a lithium urate based hydrogelator.[74] However, modern research on metallogels got a tremendous boost by the work of Xu *et al*.[39] They reported the formation of palladium(II) based coordination polymer metallogel from a calix[4]arene having the metal binding sites in the form of pyridyl moieties (Figure 1.6.1) which lead to the formation of $[Pd(en)_2(H_2O)_2](NO_3)_2$ (en=ethylenediamine) in presence of DMSO as a solvent.[39]

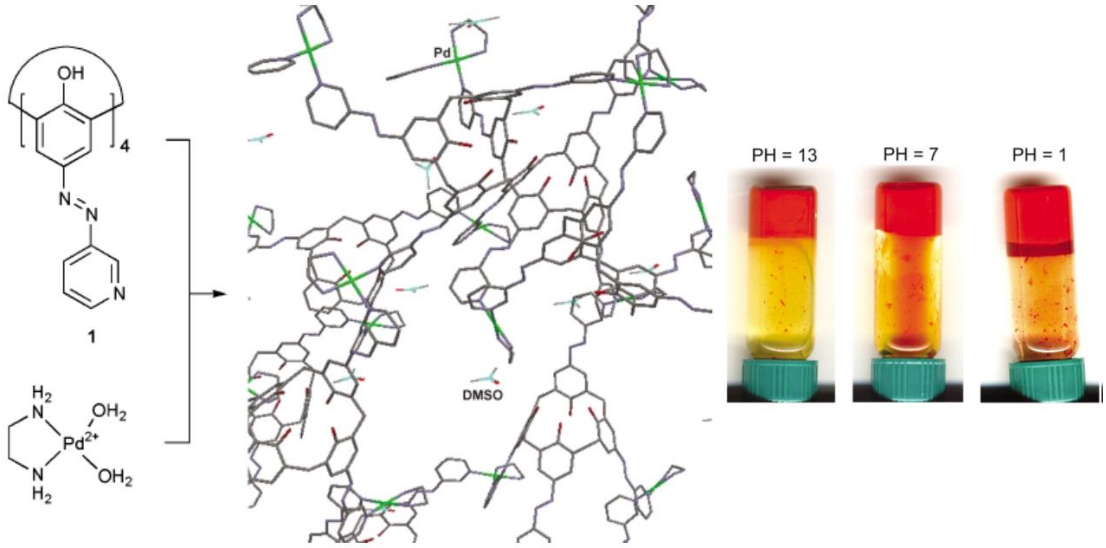

Figure 1.6.1 Formation of the possible network of the metallogels and inverted vials showing the formation of the gels at different pH values (Image adapted with permission from ref.[39] reported by Xu and co-workers. Copyright The Royal Society of Chemistry).

The metallogels can be formed as a result of the coordination polymers, crosslinked polymers or in systems where the metals are present in the form of nanoclusters in the structure of the gel. The metallogels reported in this thesis are formed by the supramolecular assembly resulting from a discrete coordination complex. Hence, the discussion here will be mainly restricted to the discrete complexes that act as metallogelators and end up forming the metallogels.

In 1997 Sohna and Fages discovered the formation of a gel with toluene as a solvent using tris(2,2'-bipyridine) ligand.[25]

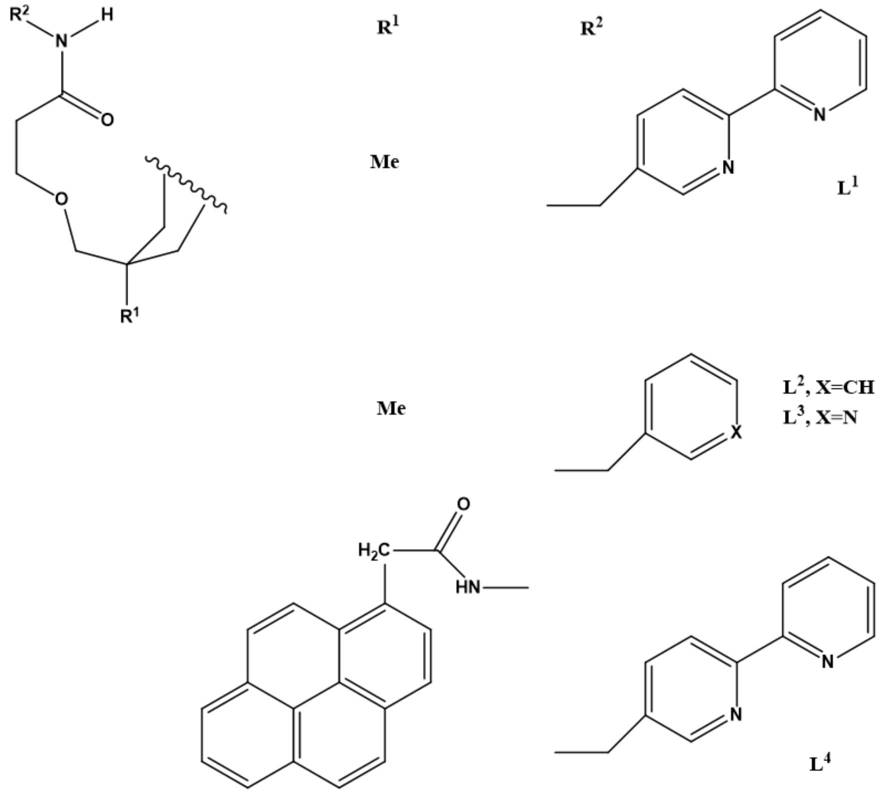

Figure 1.6.2 Structures of gelators as reported by Sohna and Fages.[25]

1 mg of the ligand L^1 was mixed in 1 mL of toluene which was followed by heating or sonicating the mixture. This mixture when cooled to room temperature resulted in the formation of a transparent gel **(Figure 1.6.2)**. Ligand L^1 was found to gelate 1 : 4 (molar ratio) CH_2Cl_2–diethyl ether and 2 : 3 CH_2Cl_2–*tert*-butyl methyl ether solvent mixtures. Gels could not be formed in presence of solvents like cyclohexane, pentane, methanol, Me_2SO, dichloromethane, chloroform, nitrobenzene, or *o*-xylene. Structurally resembling molecules L^{2-4} did not even gelate toluene. When an aqueous solution containing $FeSO_4 \cdot 7H_2O$ was placed on top of the gel L^1 formed with toluene, the ligand resisted the coordination with Iron(II). After heating the gel beyond its T_{gel} temperature the gel was found to collapse with an appearance of red color owing to the coordination of L^1 with Iron(II). This is an example where the presence of a metal ion resisted gel-formation. Gelators showing such kind of responses can be used in the development of supramolecular devices.[25]

Reinhoudt, Shinkai *et al*[75] synthesized gels using sugar-based molecules which had a *p*-aminophenyl group which are responsible for the H-bonding interactions and coordination with the metal centers. This is a first and very convenient method for incorporating a metal in an organic gel.

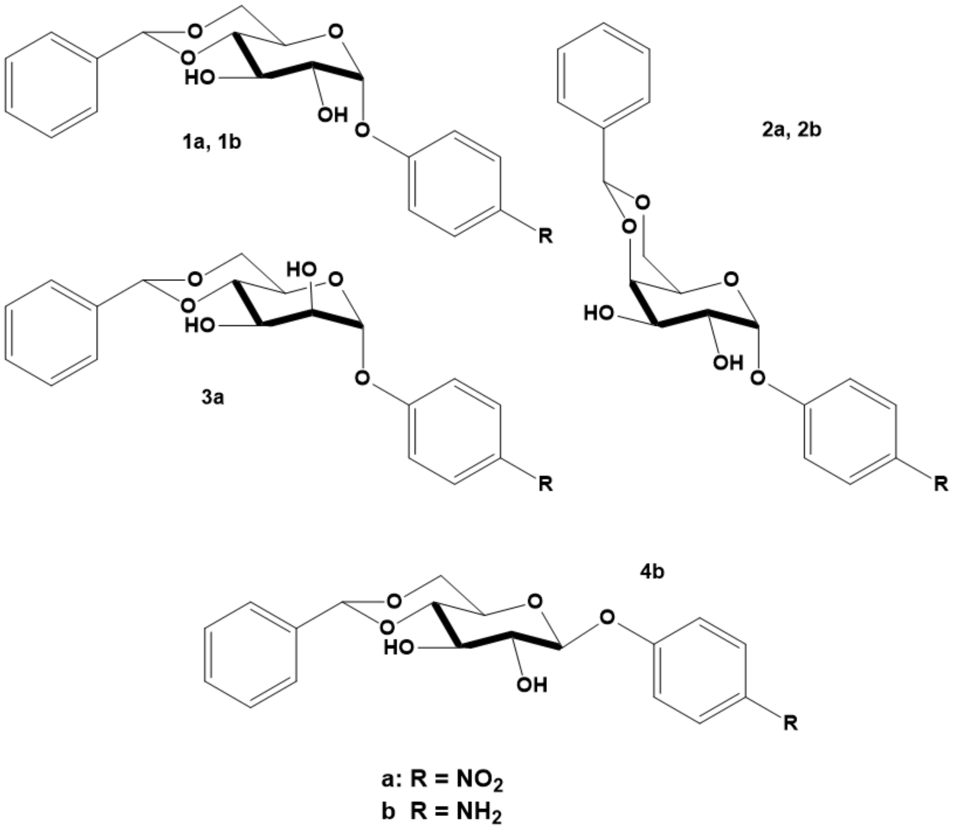

Figure 1.6.3 Structures of sugar-based gelators: R = NO_2 for **1a**, **2a** and **3a** and R = NH_2 for **1b**, **2b** and **4b** as reported by Reinhoudt, Shinkai *et al*.[75]

Reinhoudt, Shinkai *et al*[75] reported that ligand **2b** was soluble and precipitated and did not behave as a gelator (Figure 1.6.3). Ligand **4b** could gel 2 out of 15 solvents used, while ligand **1b** was the best gelator among all the molecules as it formed gels in 8 solvents. The T_{gel} values of the gel formed by **1b** with ethanol showed significant improvement by the addition of **$AgNO_3$, $CoCl_2$ or $CdCl_2$**. The gel formed by **1b** with $CoCl_2$ in ethanol is stabilized by the crosslinks formed between the amino group of ligand **1b** with cobalt(II) **(Figure 1.6.3)**.[75]

Another example of one such metallogel was reported by Steed *et al*[76] where bis(pyridylurea) ligand forms metallogels in methanol in the presence of up to 0.5 equivalent of copper(II) chloride as represented in **Figure 1.6.4**. Properties of the gel were found to be dependent on the type of counter anion and the concentration of copper ions. Gelation was favored by the presence of counter anions like chloride whereas nitrate and sulphate hindered the process of gel formation. Also, the T_{gel} temperature was found to be increasing with the increase in the concentration of copper(II) chloride.[76]

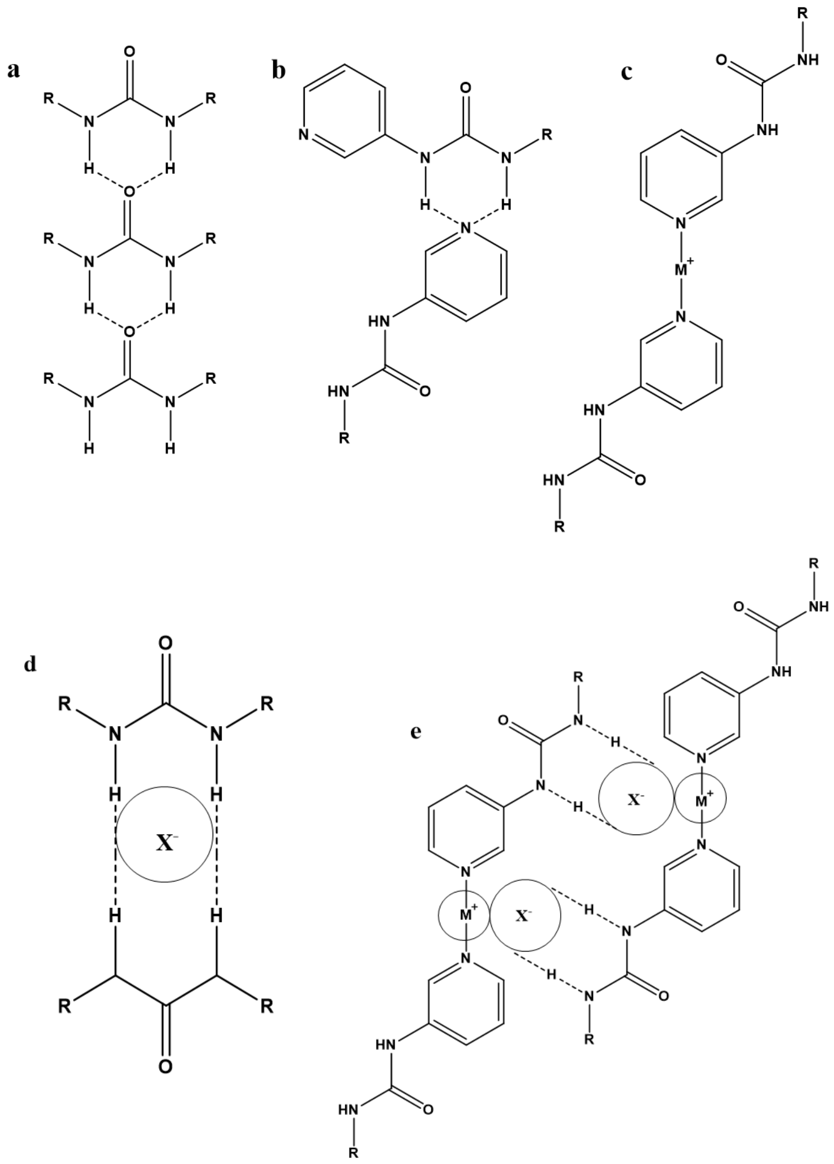

Figure 1.6.4 The structures and binding sites of ligands with the metal ions and H-bonding sites in bis(pyridylurea) ligand.

Among the stimuli-responsiveness of the LMWGs, shear responsiveness of bis(pyridyl)urea-based gelators in the presence of copper(II) bromide was found to be somewhat unusual and was found to be anion dependent;[77] whereas, the supramolecular nitrilotriacetic acid-based hydrogelator formed a magneto-rheological gel in the presence of nickel particles and a metal ion absorbent hydrogel in the presence of holmium ions.[78]

Recently, a redox assisted sol-gel transition was observed in a system where a ruthenium(II)- trisbipyridine moiety was integrated with a potential tripeptide gelator.[79]

Light-driven assembly of a coordination polymeric gelator has been reported to result in an interesting morphology,[80] while temperature driven host-guest assembly has been shown to work for controlled entrapment and release of a guest.[81] Luminescence and chirality in metallogels appear to be of special interest from the point of view of developing optical/ optoelectronic devices. The presence of metal ions in these types of gels can modify the gel formation and/or help in chirality control.[82] Luminescent metallogels made up of alkenyl rhenium complexes show rich thermotropic gelatinous behaviour upon Cu(I) or Ag(I) coordination.[83]

1.6.1 Metallogels resulting from discrete coordination complexes

The initially reported metallogels were non-stoichiometric gels in which the metal was added to a solution containing the LMWGs. The metal assisted in the formation of the gels, however, no discrete complex molecules responsible for the formation of the gel could be identified. Designing the metal complexes which lead to the formation of the gels is very tricky as the non-covalent interactions that lead to the formation of the gels should be strong enough to make sure that it holds the structure of the gel together. At the same time, it should not be too strong, otherwise the gelator system might end up in a solid form either as a crystalline material or a precipitate. On the other hand, if the interactions are too weak, it may stay in an aqueous / liquid state as the interactions would not be sufficient to convert the system in a gel. The characterization of the coordination compound/ complex that ends up in gel formation is also not easy. The metallogels are a 3-D entity held together by non-covalent interactions and leading to the formation of a supramolecular system, thus the isolation of the discrete complex responsible for the formation of a metallogel in the form of crystals or precipitates is difficult said than done.

Metallogel formed by a methanolic solution of $NiCl_2.6H_2O$ with N-methylmorpholine has been reported by Pathak *et al.*[30] UV-Vis studies indicate the formation of a square planar complex which is later transferred into a tetrahedral or octahedral complex. The theoretical studies performed by the authors show the presence of cis-$Ni(OMe)_2(MeOH)_4$ as one of the major components of the gel. The authors also highlighted the fact that preparation of chemical gels does not always require synthetically designed ligands with pre-defined coordination sites.[30]

Nandi *et al*[31] reported the formation of Ag(I)–melamine coordination polymer which formed a metastable hydrogel at 1:1 and 1:2 molar ratio. The gel was found to exhibit chiral behavior owing to the helical nature of the assembly. The gels formed in either ratio mentioned by the authors are chemical gels owing to the presence of the bond between the metal and the ligand.[31]

Copper(II) chloride with 4-(1H-pyrazol-3-yl)- pyridine and triethylamine formed a metallogel encapsulating a luminescent lanthanide cluster yielding a luminescent metallogel.[84]

1.6.2 Metallogels with Pyridyl ligands

Shinkai *et al*[85] reported the formation of a coordination complex of platinum(II) with 3,4,5-tris(n-dodecyloxy)benzoylamide of 8-quinolinol **(L-a)** **(Figure 1.6.2.1)**.

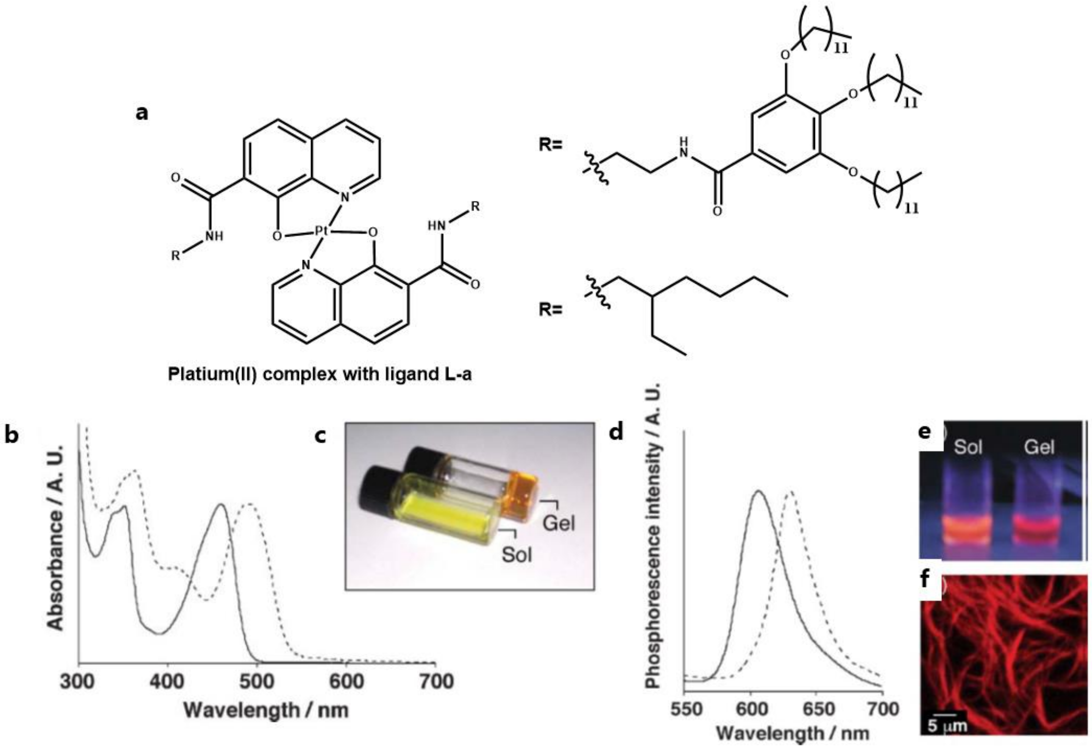

Figure 1.6.2.1 (a) Molecular structure of L-a forming a complex with platinum(II) metal, (b) UV-visible spectrum of the gel formed by the platinum(II) complex in p-xylene (dashed) and absorption spectrum of the solution of platinum(II) complex in 1,1,2,2-tetrachloroethane (solid), (c) Photograph of the xylene gel and its heated solution (sol), (d) Luminescence spectra of the xylene gel (dashed) and platinum(II) complex in 1,1,2,2-tetrachloroethane solution (solid), (e) Photograph of the xylene gel and its solution under UV light (365 nm), (f) Confocal laser scanning microscope (CLSM) image of the xylene gel. (Image adapted with permission from ref.[85] reported by Shinkai *et al.* Copyright The Royal Society of Chemistry).

Platinum(II) formed a chelate complex with the ligand **L-a** by forming a coordinate covalent bond with the nitrogen atom present in the ring as well as the -OH group. The complex was reported to have shown gelation in a number of organic solvents. The gels also showed unique thermo- and solvato-chromism of visible and phosphorescent color in response to the sol-gel transition **(Figure 1.6.2.1)**. The gels also possessed a property of inhibiting the dioxygen quenching of excited triplet states. Luminescence spectra and confocal laser scanning microscope (CLSM) was performed by the authors in order to prove the same **(Figure 1.6.2.1)**.

Steed *et al*[86] reported the formation of monourea pyridyl ligands **(L-b to L-d,** Figure 1.6.2.2). The structure of the ligands mimicked the structure of the anticancer drug *cis*-platin, with a view of development of a screening strategy for targeted, supramolecular gel phase crystallization and polymorphism. The coordination compounds were formed as a result of the reaction of the previously mentioned ligands with K_2PtCl_4. Hydrogen bonding involving the urea moiety, π-π stacking and platinum-platinum interactions were responsible for gel formation. It has been reported by the authors that the metallogels obtained from the ligand **L-d** produced high-quality DMF solvate crystals which resembled to the geometry of *cis*-platin and displayed new crystal habit **(Figure 1.6.2.2).**

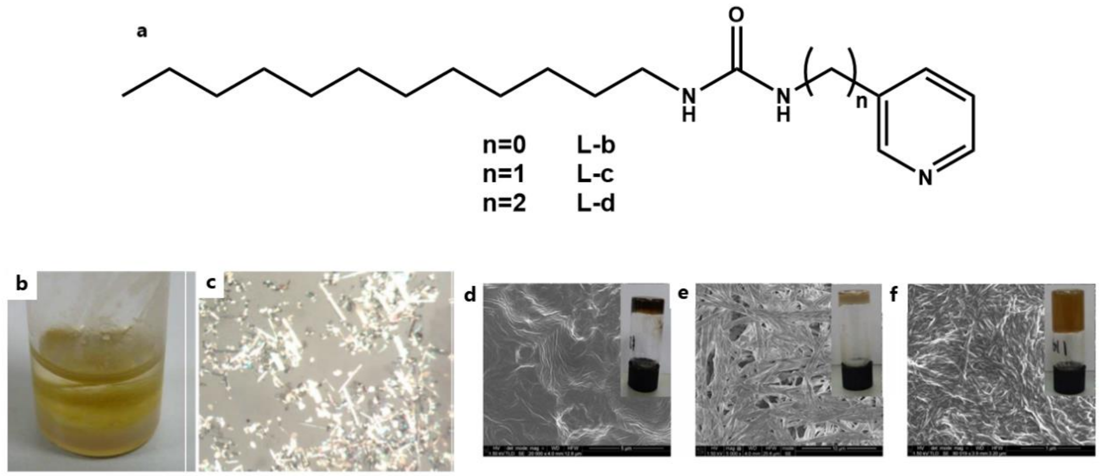

Figure 1.6.2.2 (a) Molecular structures of the ligands **L-b, L-c and L-d**, (b) Formation of yellow cis-platin crystals at the interface of the sol–gel bilayer of the gel of the platinum complex formed with the ligand **L-d**, (c) Images of cis-platin grown at the sol-gel interface obtained using optical microscope, at room temperature, (d) SEM image of the xerogel formed with ligand **L-b** in toluene, (e) SEM image of the xerogel formed with ligand **L-c** in 1-propanol. (f) SEM image of the xerogel formed with ligand **L-d** in toluene. Image adapted with permission from ref.[86] reported by Steed *et al*. Copyright The American Chemical Society.

Enantioselective metallogels containing copper(II) were reported by Pu *et al*[87] resulted from a coordination compound between copper(II), 1,1’-bi-2-napthol (BINOL) and a terpyridyl based ligand. Gel formation was reported when a dilute solution (3.13 wt% w/v) of copper(II) complex in $CHCl_3$ was briefly sonicated (1 min with a sonicator of 0.40 Wcm^{-2} and 40 kHz) and was allowed to settle at room temperature for 30 s. When

(R)- phenylglycinol (0.10 equiv) in chloroform (0.1 mL) was added to the preformed gel and the resulting solution was sonicated for 1 min, the gel remained stable. However, under similar conditions the gel collapsed when (S)-phenylglycinol was added instead of the R enantiomer. The chiral metallogel derived from the ligand **L-e** showed an enantioselective gel collapse response, which could be monitored even visually without the use of any sophisticated instrumentation (Figure 1.6.2.3).

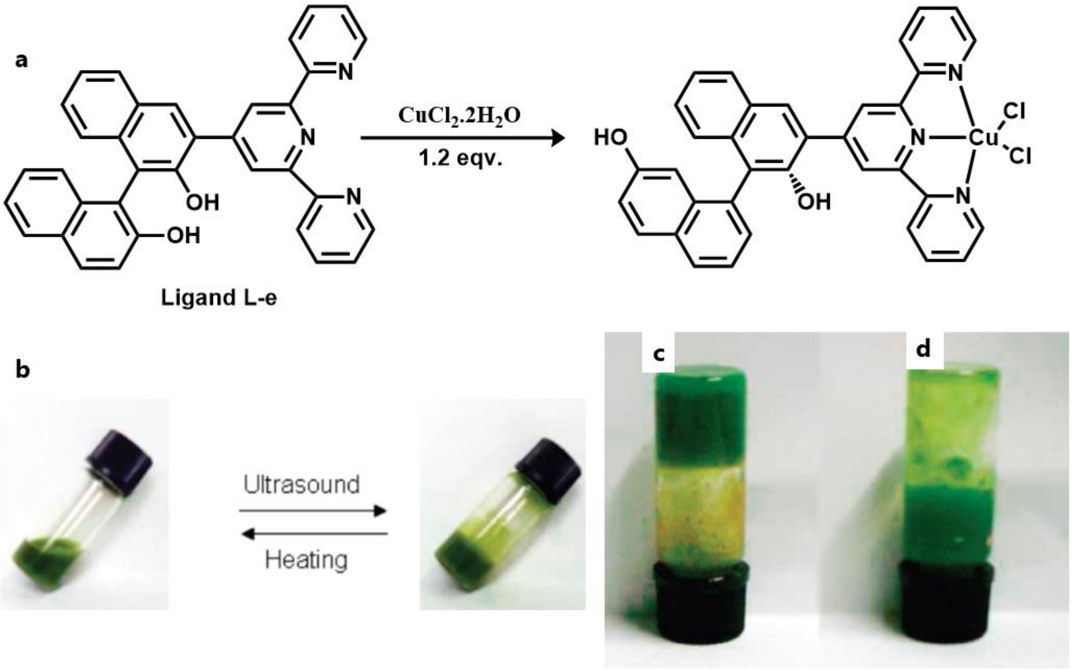

Figure 1.6.2.3 (a) Molecular structure of the ligand L-e and its copper(II) complex, (b) Images showing the ultrasound induced gelation of the copper(II) and the thermal gel collapsing, (c) Enantioselective response of the gel formed by the copper(II) complex with ligand L-e towards (R)-phenylglycinol and (d) Enantioselective response of the gel formed by the copper(II) complex with ligand L-e towards (S)-phenylglycinol. Image adapted with permission from ref.[87] reported by Pu *et al.* Copyright The American Chemical Society.

Fernandez *et al*[88] reported the formation of a hydrogel formed by the reaction of platinum(II) with an oligo(p-phenylene ethynylene) (OPE) pyridyl ligand with appended ethylene glycol chains **(L-f, Figure 1.6.2.4)**. ROESY NMR spectroscopy and single-crystal X-ray diffraction data indicated that the unconventional C-H···Cl, C-H···O, and π-π interactions were responsible for the cooperative formation of self-assembled structures of high aspect ratio resulting in the formation of metallogels in which the molecular arrangement was maintained in the crystalline state.

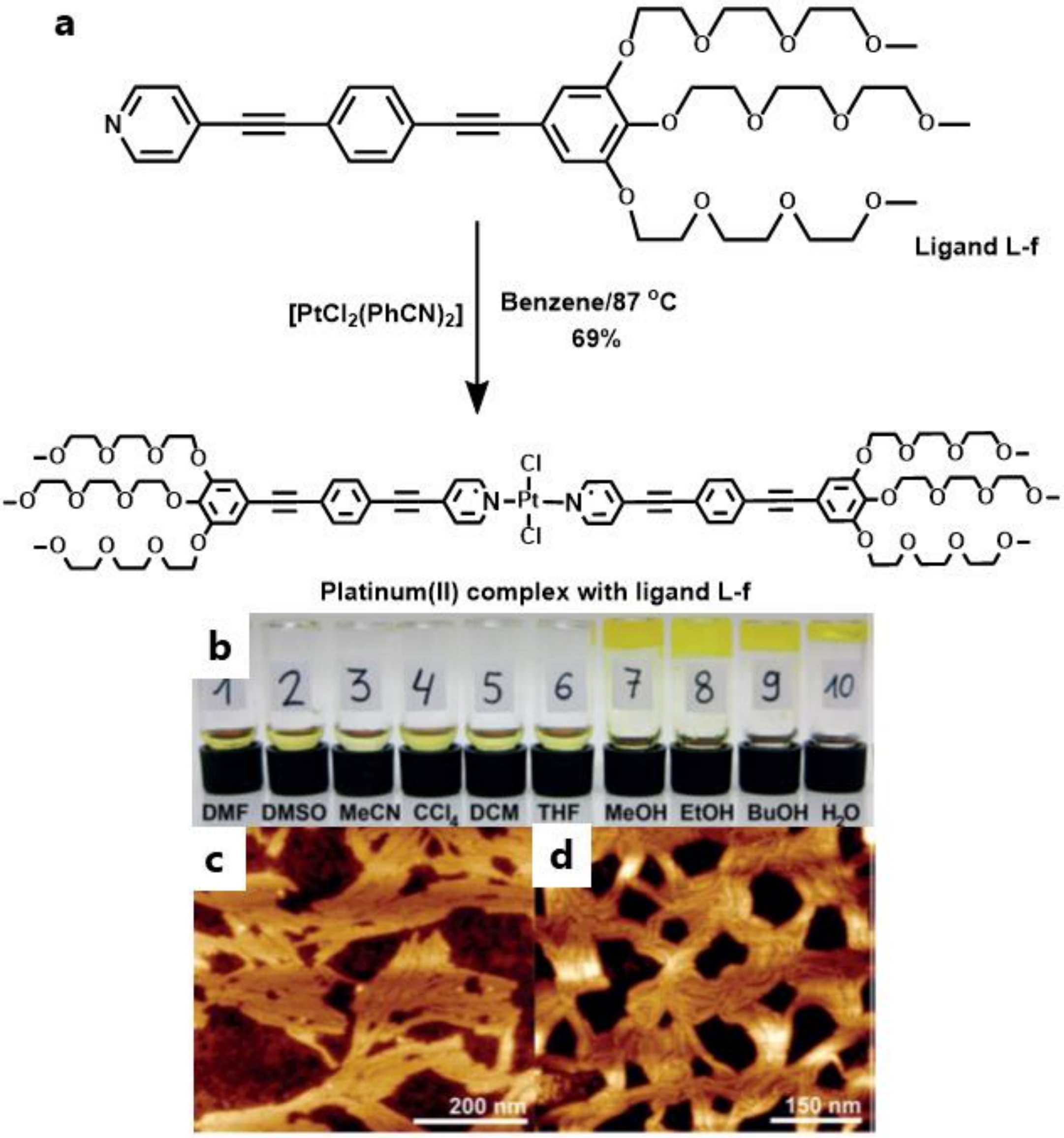

Figure 1.6.2.4 (a) Platinum(II) complex metallogelator derived from the ligand L-f, (b) The color change and gelation trials using the platinum(II) complex with ligand L-f, (c) AFM images obtained by dropcasting diluted gel solutions of the complex in water and (d) AFM images obtained by dropcasting diluted gel solutions of the complex in ethanol. (Image adapted with permission from ref.[88] reported by Fernandez *et al*. Copyright WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

1.7 Applications and future scope

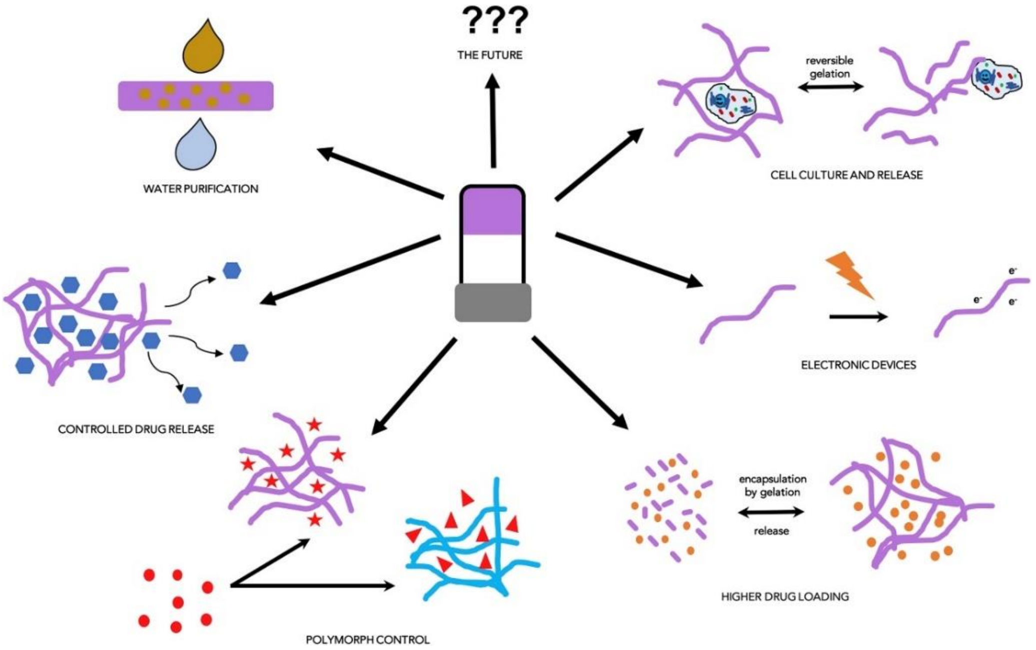

Figure 1.7.1 Schematic representation indicating different domains of the applications of supramolecular gelators.[34] (Image has been adapted from the reference [34]).

As summarized in Figure 1.7.1, gels have various applications like controlled drug release when subjected to a stimulus, water purification by removal of unwanted pollutants, cell culture and release from the gelled material and control of polymorph by providing a template surrounding. They can also be used as electronic devices if they exhibit photo-responsive behavior. Figure 1.7.1 shows the versatile nature of applications of supramolecular gels. It is very likely that **supramolecular gels may replace liquids in many of the technological applications in the not-so-distant future!**

1.8 Objective and scope of the present work

In 2009, one such metallogel was reported from our group.[89] It was formed using a well-defined trinuclear copper(II) complex involving a polypyridyl ligand in the form of 2,2'- bipyridyl and myo- inositol. The complex forms a hydrogel which was the first of its kind when reported. This report increased tremendous interest and gave momentum to the search of well-defined complex molecules capable of forming metallogels.

The above report involved gel formation at a pH of 12.[89] The present work is inspired from this report. For variety of applications, it is necessary to achieve gel-formation under neutral, mild acidic or mild basic conditions. In order to lower the pH of gel-formation, it becomes necessary to change various parameters like pH, capping ligands, metal ions present in the complex, counter anions and solvent conditions. A detailed study of these can give an insight into the parameters governing the gel formation and hence, can be a step forward in achieving the ability to design tailor made gelator molecules and tune their properties. With this objective, systematic studies have been carried out, the detailed report of which is discussed in various chapters in the thesis. Tuning the gel properties by variation in the structure of gelator molecules is a challenge and an attempt to explore in this is made in the present work. Also, some potential applications of the synthesized metallogels have been explored.

As mentioned earlier, there have been very few reports of metallogels formed by well-defined complex molecules, whereas the applications of such gels can be numerous. Also, there have been extensive studies on the morphological properties of the gels by various microscopic techniques like SEM, TEM and AFM analysis. However, the reports on birefringence of the gels have been very scarce.

The work in **chapter 2** aims at synthesizing new complex metallogelators using myo-inositol and various copper(II) carboxylates. The myo-inositol is expected to help the formation of a trinuclear complex moiety which can behave as a metallogelator complex and be responsible for the formation of a metallogel. The gel forming complex moiety, being trinuclear, should to be dissymmetric having at the most a C_3 symmetry axis. This would induce chirality in the molecule. The formation of supramolecular system because of the presence of H-bonding and π-π stacking can further enhance the chirality in the system. This can result in the birefringent properties of the metallogels.

The trinuclear copper(II) complexes, $[Cu_3(H_3ins)(bipy)_3]X_3$, with various carboxylate anions, X = $HCOO^-$, CH_3COO^- and $CH_3CH_2COO^-$ have been synthesized. The gel properties including T_{gel} were found to have significant dependence on the carboxylate anions. The metallogels were characterized by thermal analysis and spectroscopic methods. Morphological properties were studied using POM and SEM. The metallogels were found to be highly birefringent and they organize into quaternary structures which display unique patterns in the microscopic studies under polarized light.

In order to investigate the anion dependence of gel-formation and their properties, systematic variation was made in the anions and their amounts. Various simple and compound anions as well as mono- and dicarboxylate anions were used under varying conditions. Also, variation in metal ions and alkali has been attempted. Other copper like metals like manganese, nickel, cobalt and zinc and their role on gel formation was tried. The formation of metallogels was found to be highly dependent of the nature of anions, metal ions and their quantities. The details of these studies have been discussed in **Chapter 3.**

Lowering the pH of gel-formation was a challenging task and it was achieved using carbonate bases. **Chapter 4** presents the details of the synthesis of supramolecular metallogels resulting from an assembly of the trinuclear copper(II) complex $[Cu_3(H_3ins)(bipy)_3]X_3$ (X = $HCOO^-$, CH_3COO^- and $CH_3CH_2COO^-$) in presence of carbonate bases. These metallogels were found to be useful as efficient heterogeneous catalysts for the oxidation of various substrates like 3,5-di tert-butylcatechol (3,5-DTBC), 4-methyl catechol, pyrocatechol, resorcinol, hydroquinone and 2,3-dihydroxy naphthalene. The details of these studies have been discussed in this chapter.

Chapter 5 includes the results of our attempt to tune the gel properties by changing the structure of the trinuclear gelator complex by variation in the capping ligands; 1,10-phenanthroline and various derivatives of 2,2’-bipyridine and 1,10-phenanthroline have been used. These newly formed gels have been characterized by various, spectroscopic and microscopic techniques. Also, the gel-formation in presence of various organic solvents was attempted. The gels were found to incorporate variety of organic solvents. Specially, the uptake capacity for methanol was found to be exceptionally high. The details of these studies are discussed in this chapter.

The biological applications of the newly synthesized metallogels have been explored, the details of which are presented in **Chapter 6**. The gels have copper(II) which is a biologically essential and redox active metal ion. Myo-inositol being bio-molecule and the polypyridyl capping agents known to be non-toxic, it was thought worth evaluating the biological activity of the metallogels. Protein binding studies with BSA, DNA binding and superoxide dismutase activity has been studied. Also, the cytotoxicity and antimicrobial activity of the metallogels have been determined. The details of these studies are reported in chapter 6.

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