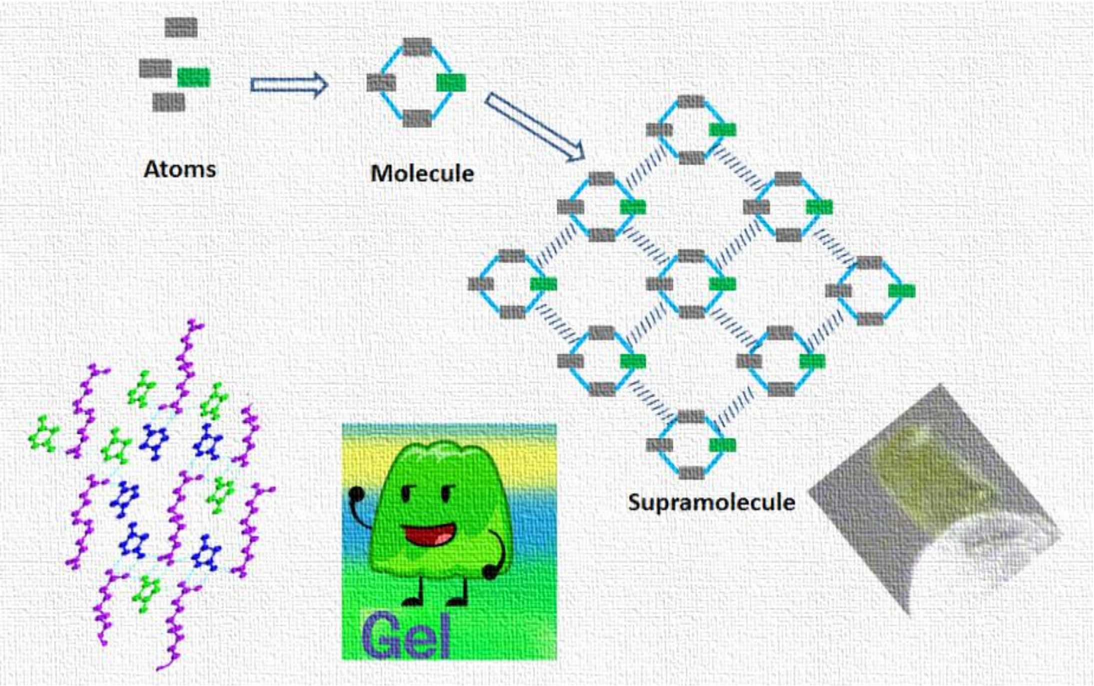
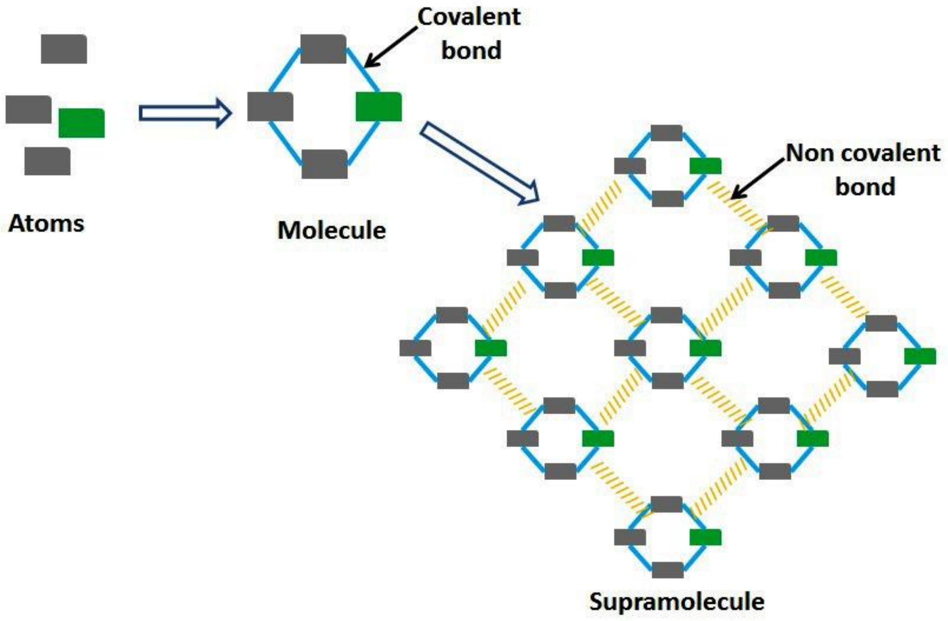
Chapter-1



Introduction

1.1 Supramolecular chemistry

Supramolecular Chemistry [1-3] is an important, interdisciplinary branch of science encompassing the idea of chemistry–biology interface. The field of Supramolecular Chemistry traces its roots to the Emil Fischer's lock and key principle, one of the most fundamental aspects of biological catalysis by means of "Enzyme," nature's own catalysts. Fischer suggested that enzyme-substrate interactions take the form of a "lock and key," the basic principles of molecular recognition[4] and host-guest chemistry. [5] This finding has inspired a new field of Chemistry whose focus is the noncovalent bond, rather than the covalent bond.Chemistry has to deal with molecules made up by covalent bond, whereas supramolecular chemistry deals with non-covalent interactions **(Scheme 1.1)**.



Scheme 1.1 Representation of periodic arrangement giving rise to supramolecule

Naturally-occurring DNA, perhaps the best known example of self-assembling structure in biological systems, where two separate strands of nucleotides connected through hydrogen bonds.[6] The two single strands are held together by a number of hydrogen bonds. In this double helix structure guanine (G) selectively forms hydrogen bonds with cytosine (C) and adenine (A) forms hydrogen bonds with thymine (T) **(Figure 1.1)** which act as glue for sticking the two strands together.

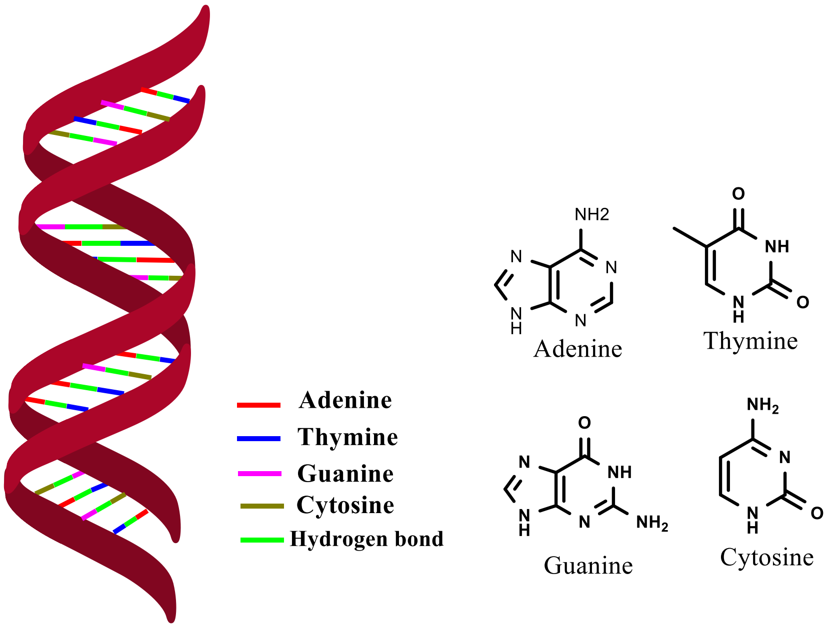


Figure 1.1 Representative DNA helical structure

Eventually, the field of supramolecular chemistry was also established by the chemists. Donald J. Cram, Jean-Marie Lehn, and Charles J. Pedersen awarded Nobel Prize in 1987 for Chemistry in recognition of their work in the area of supramolecular chemistry.

“Supramolecular Chemistry is “the Chemistry beyond the molecule; it is the chemistry of the intermolecular bond, covering the structures and functions of the entities formed by the association of two or more chemical species"

J.-M- Lehn[1]

"In contrast to molecular chemistry, which is predominantly based upon the covalent bonding of atoms, supramolecular chemistry is based upon intermolecular interactions, i.e. on the association of two or more building blocks, which are held together by intermolecular bonds"

F.Vögtle [2]

In recent years, supramolecular chemistry is recognized as one of the most active fields of science, mainly due to its dynamic nature, academic interest and real life applications. The recent progress in supramolecular chemistry, however, elongated from molecular recognition to exploring novel applications in gas/solvent storage,[7] smart materials,[8] molecular switches[9] etc.

1.2 Crystal Engineering: Crystals as Supramolecules

Crystals are a perfect example of supramolecular entity,[10] wherein thousands of molecules or ions are arranged in a periodical manner, recognizing each other through weak non-covalent interactions with high level of precision(**Figure 1.2**).

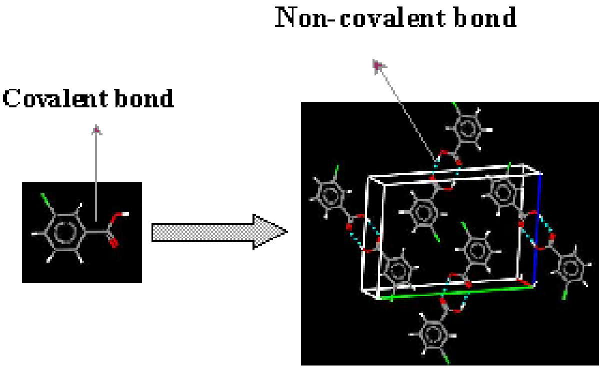


Figure 1.2 Supramolecular entity (crystals)

A crystal of an organic compound is the ultimate Supramolecule, and its assembly, governed by chemical and geometrical factors, from individual molecules is the perfect example of solid-state molecular recognition.[11-13] The crystal are glued together by weak noncovalent interactions such as Hydrogen bonding, π–π interaction, van der Waals forces, halogen-halogen interaction etc., in order to give rise to the Supramolecule. The concept of crystal engineering was introduced by R. Pepinsky.[14] Crystal engineering is an emerging discipline whereby practitioners aim to arrange molecules, both organic and metalorganic, in the crystalline phase by rational design. This challenge requires the exploitation of weaker and less directional noncovalent interactions. Hence the comprehensive understanding of supramolecule necessitates the study of crystal engineering aspects. The crystal engineering, seeks to understand intermolecular interactions and recognition phenomena in the context of crystal packing. The aim of crystal engineering is to establish reliable connections between molecular and supramolecular structure on the basis of intermolecular interactions. Few of the research area, which comes under the realm of crystal engineering, [15]are as follows:

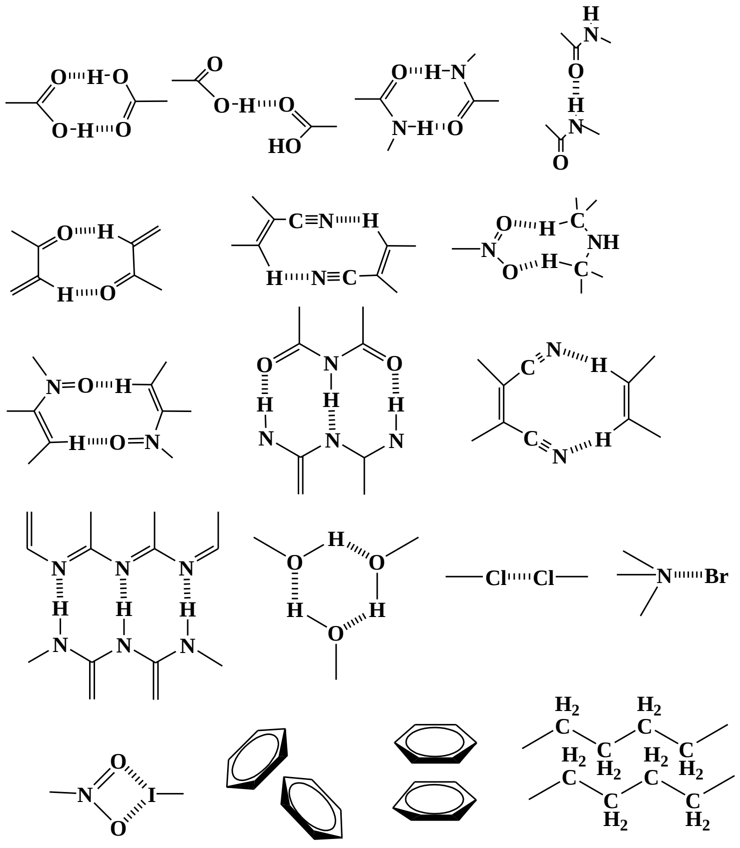
- ✓ Solid-state reactions
- ✓ Pharmaceuticals

- ✓ Polymorph
- ✓ Co-crystals formation
- ✓ Separation Science
- ✓ Catalysis
- ✓ Optical materials
- ✓ Nanotechnology
- ✓ Liquid Crystals
- ✓ Designing Low molecular mass organogelator
- ✓ Metalorganic frameworks, etc.

1.2.1 Supramolecular Synthesis

Desiraju has introduced the term supramolecular synthon in the context of crystal engineering for designing desired supramolecular assemblies. The concept of a supramolecular synthon is derived from the term “synthon”, as defined by Corey.[16] The term synthon was being used in context of covalent organic synthesis. Supramolecular synthons plays the same role in synthesis of supramolecular assemblies that synthon does in covalent synthesis.

“Supramolecular synthons can be defined as structural units within supramolecules which can be formed and/or assembled by known or conceivable synthetic operations involving intermolecular interactions.[17-18] It encapsulates a sufficient amount of critical structural information so that it serves as a model for the entire crystal.[19] Supramolecular synthon has become one of the principal synthetic tools for the supramolecular chemistry.[20-21] Synthon is the key link between molecular and crystal structure. Accordingly, one attempt to identify and then reproduce reliable supramolecular synthons so as to lead to desired crystal structures.[22]In the case of supramolecular synthesis of organic solids, various non-bonded interactions such as hydrogen bonding, π–π, C-H…π, halogen…halogen, electrostatic, van der Waals interactions etc. are the main forces in the supramolecular synthons, whereas in case of inorganic solids, the supramolecular synthon depends mainly on metal-ligand coordination bond.[23-26] Some of the representative supramolecular synthons are shown in **Scheme 1.2**.



Scheme 1.2 Representative supramolecular synthons

A non-covalent interaction differs from a covalent bond in a way that the energy released in the formation of non-covalent interactions is typically <40 kJ/mol, which is very less in comparison to covalent bond energies.

Supramolecular Interactions	
Hydrogen bond interaction	12-30 kJ/mol
Hydrophobic interaction	<40 kJ/mol
Electrostatic interaction	~20 kJ/mol
van der Waals interaction	0.4-4 kJ/mol
π-π stacking	<5 kJ/mol

Covalent bond energies	
C-O bond	340kJ / mol
C-C bond	360kJ / mol
C-H bond	430kJ / mol
C=C bond	600kJ / mol
C=O bond	690kJ / mol

Hydrogen bond is the main navigating force for the syntheses of supramolecular assemblies with specific functions. O-H…O, O-H…N and N-H…O hydrogen bonds [27-28] are frequently used to construct crystalline architectures. Supramolecular synthons involving weak hydrogen bonds (C-H…O, C-H…N)[29] have also emerged as a useful strategy.

1.2.2 Hydrogen bond

The hydrogen bond concept is almost a century old, but the debate on the nature and properties of this interaction is still heated because of its extreme importance in many fields of science.[30] A useful explanation is perhaps provided by Peter Atkins in 1989, “A hydrogen bond is a link formed by a hydrogen atom lying between two strongly electronegative atoms.”[31]

$$D^{\delta-}\text{-}H^{\delta+}\cdots\cdots A^{\delta-}$$

D-H acts as proton donor of A. Hydrogen bonding occur between a proton donor group D-H and a proton acceptor group A, where D is an electronegative atom such as O, N, S, P, Se, X (F, Cl, Br, I) or C, and the acceptor group is a lone electron pair of an electronegative atom, or a π- electron orbital of a multiple bond (unsaturated) system. Hydrogen bond Interaction is of intermediate strength, but weaker than a covalent bond.

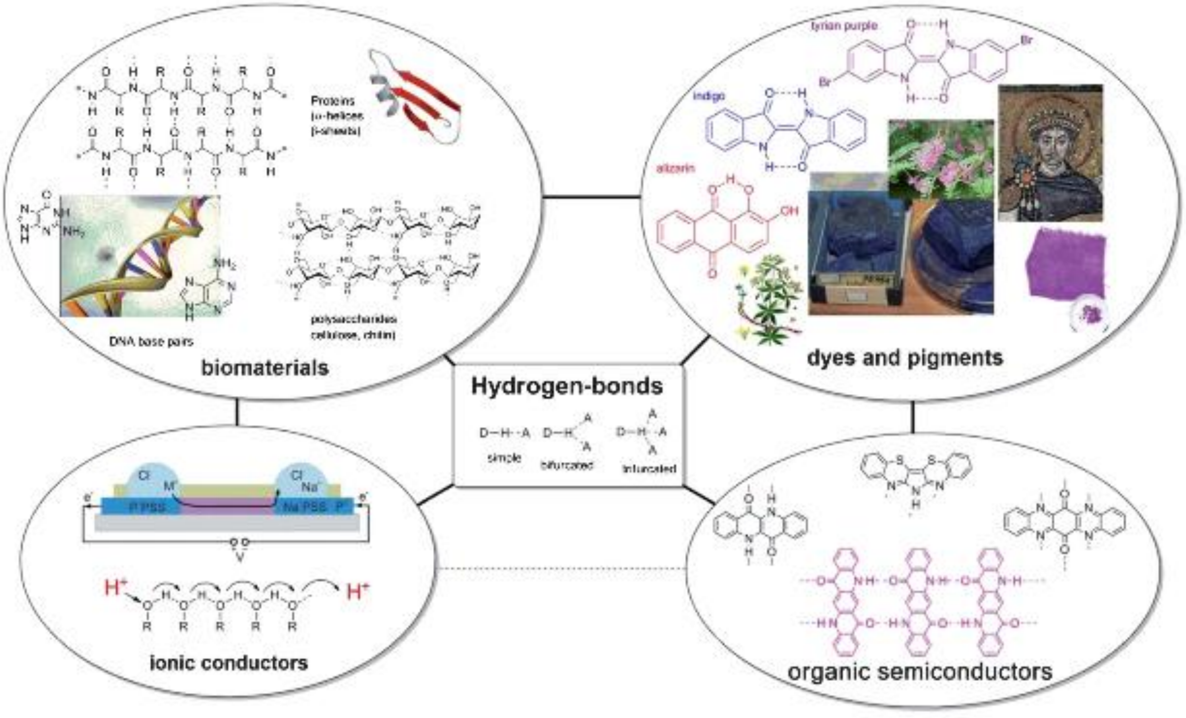
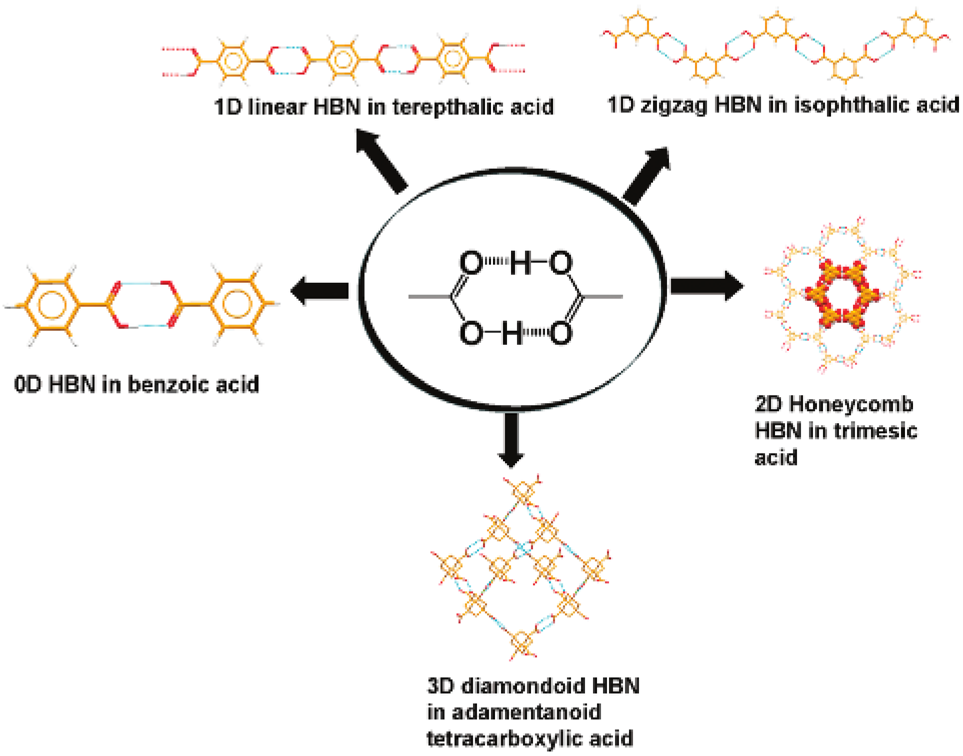


Figure 1.3 Summary of the role of hydrogen-bonding in biomaterials, dyes and pigments, ionic conductors, and organic semiconductors shown by Glowacki et al.[32]

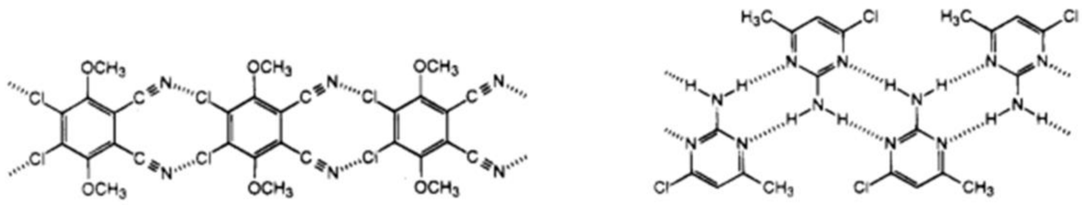
Recently, Glowacki et al.[32] have discussed significance of Hydrogen-bonds in molecular solids from biological systems to organic electronics.They have highlighted recent work on application of nature-inspired H-bonded organic molecules in organic electronic devices. They pointed up some examples where H-bonds play an important role such as biomolecules, dyes and pigments, as well as in ionic conductors and organic semiconductors **(Figure 1.3)**.Though Hydrogen bond interaction is of intermediate strength, Nevertheless, this Interaction is directional; consequently, one, two or three-dimensional structures may easily be assembled through hydrogen bonding. Das et al.[33] has considered the frequent occurrence of the -COOH dimer hydrogen bonded network as a supramolecular synthon to illustrate the crucial role of supramolecular synthon in getting easy access to supramolecular structures with various dimensionalities (0, 1, 2, or 3-dimensional).The introduction of -COOH functionality in an aromatic ring results in a 0D network in benzoic acid,[34] while terephthalic acid[35] and isophthalic acid having two -COOH functionality results in a 1D linear and zigzag network[36] respectively.



Scheme 1.3 Different Dimensionalities in the Supramolecular Structures using -COOH Dimer Synthon as illustrated by Das et al.[33]

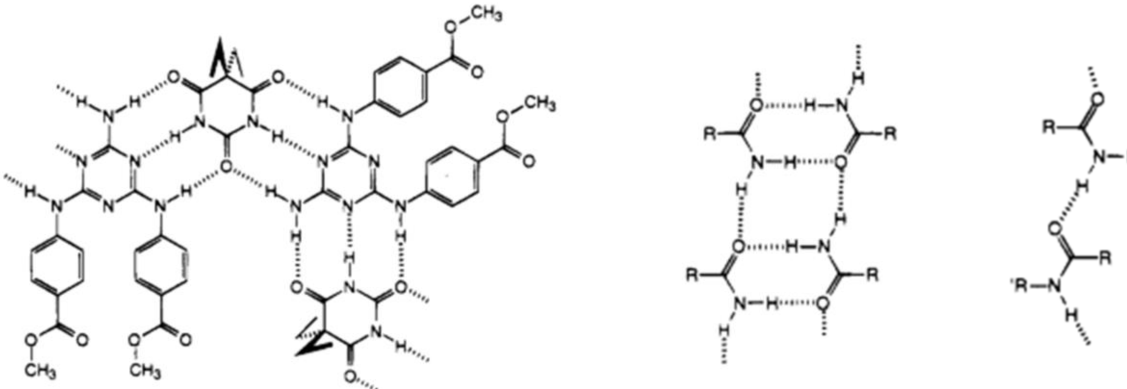
Trimesic acid [37] and Adamentanoid tetracarboxylic acid[38] with three and four -COOH functionality turns into 2D honeycomb network and a 3D diamond network respectively **(Scheme 1.3)**.

Some of the representative examples of 1-dimensional and 2-dimensional supramolecular structures were illustrated by MacDonald et al.[39] (**Scheme 1.4** and **Scheme 1.5** respectively). Similarly representative example of 3-dimensional supramolecular structure was shown by Russell et al.[40] **(Scheme 1.6)**.



5, 6-dichloro-2, 3-dicyano-l 4**,** dimethoxybenzene

2-amino-4-chloro-6-methylpyrimidin



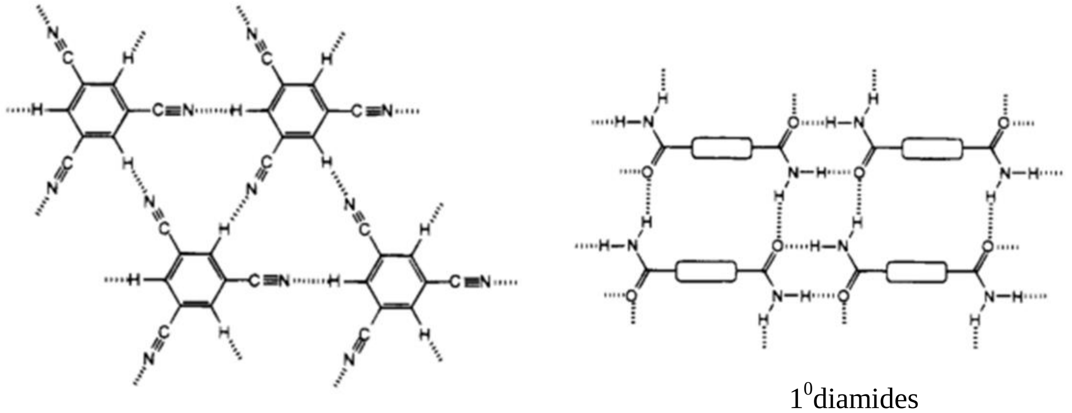
1^0 amides

2^0amides

N,N'-bis(4-carboxymethylphenyl)meIamine

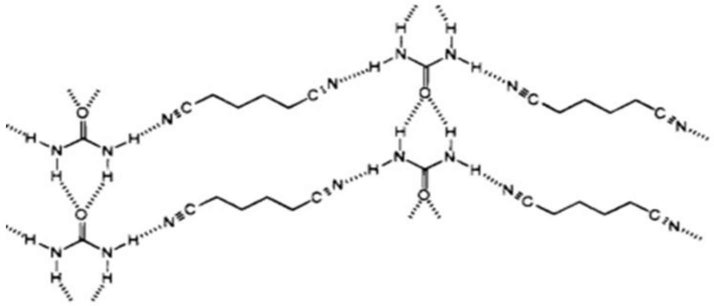
*barbital cocrystal

Scheme 1.4 Representative examples of one-dimensional network[39]



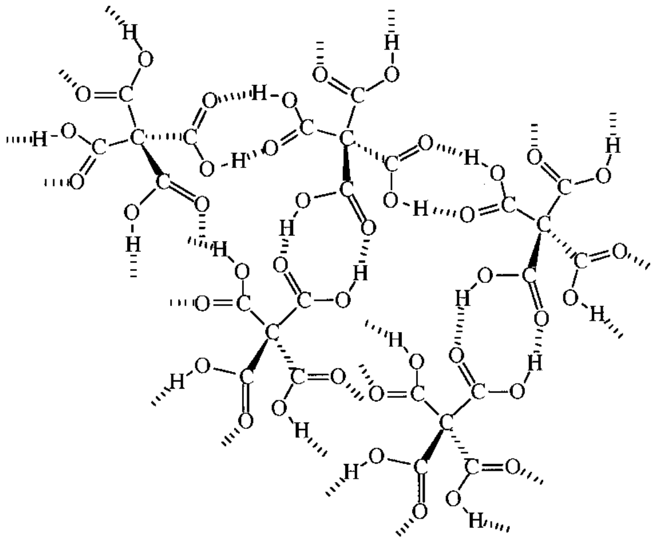
1,3,5-tricyanobenzene*hexamethylbenzene

1^0diamides
(The symbol ▭ represents a range of organic groups)



1,4-dicyanobutane*urea cocrystal

Scheme 1.5 Representative examples of two-dimensional network[39]



Scheme 1.6 Representative examples of two-dimensional network[40]

1.3 Gel

‘.........the colloid condition, the gel, is easier to recognize than to define.”

Dr. Dorothy Jordon Lloyd[41]

Gelation is one of the most intriguing phenomena in biphasic systems, which is easy to identify but difficult to explain, as stated by Dr. Dorothy Jordon Lloyd. Gel was originally detected by Scottish chemist Thomas Graham in 1861, by extracting from gelatine. [42] It is a solid, jelly-like material that can have properties ranging from soft and weak to hard and tough. Gel [43-45] is a solid-like material mainly composed of liquid phase (solvents) and small concentration of solid phase (gelator). The solid-like appearance of the gel can be attributed to the immobilization of the solvent molecules in the three-dimensional (3D) network formed by the gelator molecules. Gels can be mainly categorized in two ways depending upon the nature of the interactions involved. If chemical bond formation among gelator molecules is responsible for the formation of 3D network, the resulting gel is called a chemical gel. Inorganic oxides, silica and cross-linked polymers such as polyethylene, polyester, polyamide, poly(vinyl alcohol) etc. belong to this class of gel. On the other hand, if non-covalent interactions such as hydrogen bonding, π-π stacking, van der Waals interactions etc., are responsible for the 3D network which ultimately results to gel, then it is termed as supramolecular or physical gel. Many gels obtained from mineral clays, polymers and proteins belong to this class. One of the remarkable features of these gels is their thermo reversibility from gel phase into sol and vice versa at a moderate temperature without any decomposition.

Relatively new member of this vast family of physical or supramolecular gels is Low Molecular Mass Organic Gelators (LMOGs). LMOGs are small organic or organometallic compounds having molecular weight less than 3000. They are capable of gelling organic solvents and/or water even at extremely low concentration. Gelators capable of hardening organic solvents are popularly known as organogelators .While, gelator which shows gelation behaviour for aqueous solvent, are called hydrogelators. The gelators which are capable of hardening both organic solvents as well as water are termed as amphoteric gelator.

1.3.1 Classification of LMOGs based on structural constituent

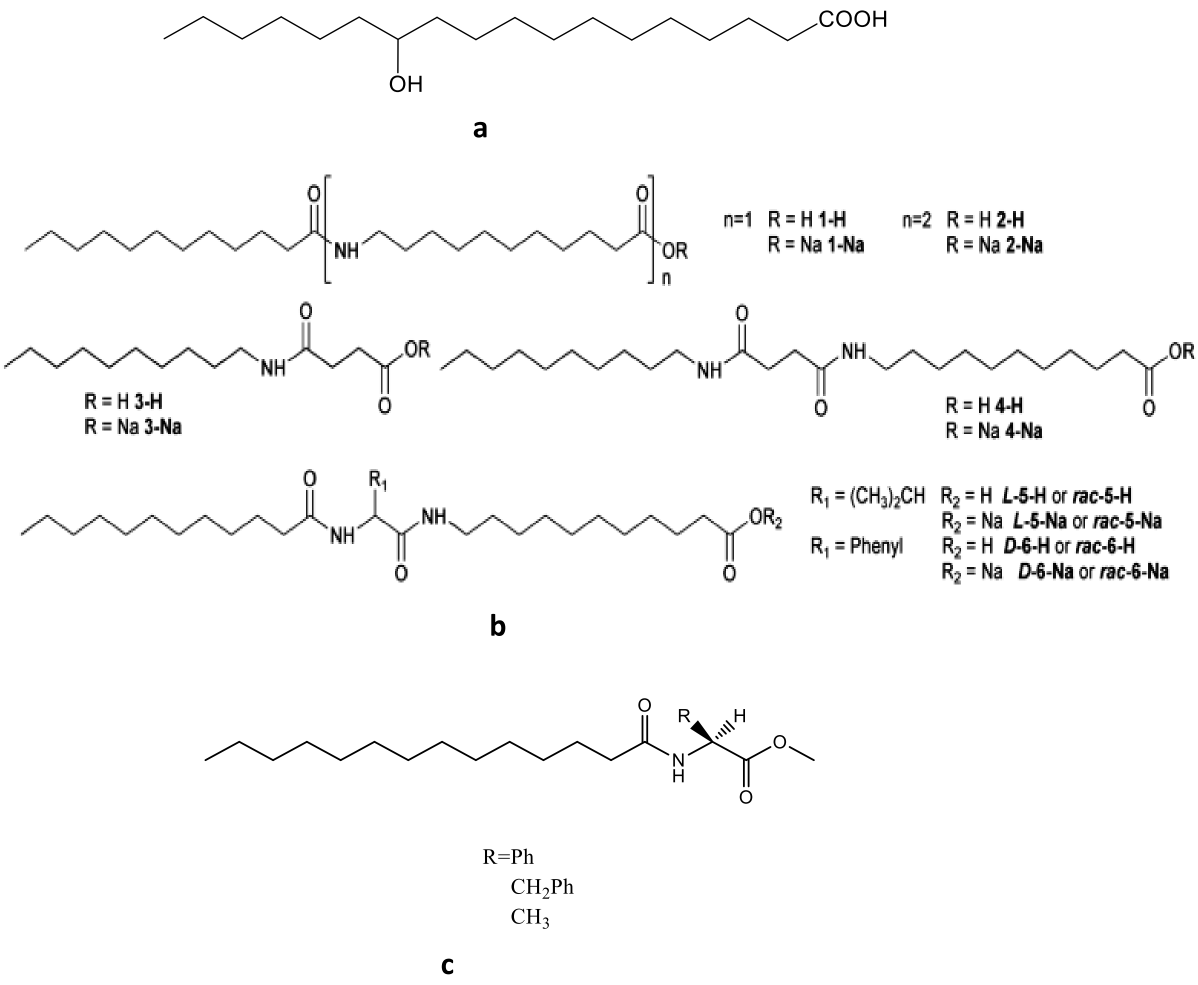
Last two decades have shown an exponential growth in the area of low molecular mass organic gelators (LMOGs). Numerous LMOGs have been found or created. However, designing LMOGs is still a difficult task; moreover, it is extremely hard to predict which solvent will be hardened by a particular LMOG. Although, LMOGs had been classified into various categories/groups based on their molecular structure or basic backbone by Terech and Weiss.[43]A detailed overview of LMOGs and its classification has already been discussed; however unremitting research in the field of LMOG is capable of adding a vast variety of novel LMOGs.

1.3.1.1 Fatty acid and aliphatic long chain based gelators

12-Hydroxyoctadecanoic acid and its related salts **(Scheme 1.7a)** are one of the earliest known examples of fatty acids based LMOG, reported to hardened organic liquids.[46] The gel synthesized by dispersions of these compounds in oils has been used in the lubrication industry since long.[47-48] The 3D networks of aggregated fatty acid molecules act as a “sponge,” maintaining the oil component in lubricating greases close to the friction regions of metallic surfaces in various mechanical systems.[49]

D’Aléo et al.[50] have demonstrated the use of 11-aminoundecanoic acid **(Scheme 1.7b)** as a synthetic building block which allows the systematic preparation of (oligo) amide organogelators which display remarkable gelation properties in organic solvents and water. In addition, they also demonstrated that gelation properties can be tuned by (a) simply adjusting the ionization state of the terminal carboxylic acid functionality, (b) introducing additional amide hydrogen bonding sites and (c) incorporating a chiral amino acid fragment. Phase selective gelation[51-55] of organic solvents (oil) from oil–water mixtures can be an excellent way for oil spill recovery.

Recently, Basak et al. [56] have reported an aromatic amino acid (phenylglycine) based amphiphile with amide and ester groups and a long fatty acyl chain**(Scheme 1.7c)** , which found to form organogels selectively in the fuel hydrocarbon solvents, including hexane, heptane, cyclohexane, diesel, kerosene and pump-oil at room temperature. They revealed that the simple gelator molecule could selectively, efficiently and instantly immobilize the fuel oils from the oil–water mixture. The gelator was acting as a phase selective, thermo-reversible organogelator, which selectively gelate the oil phase in the oil–water mixture and were promising for oil spill treatment.

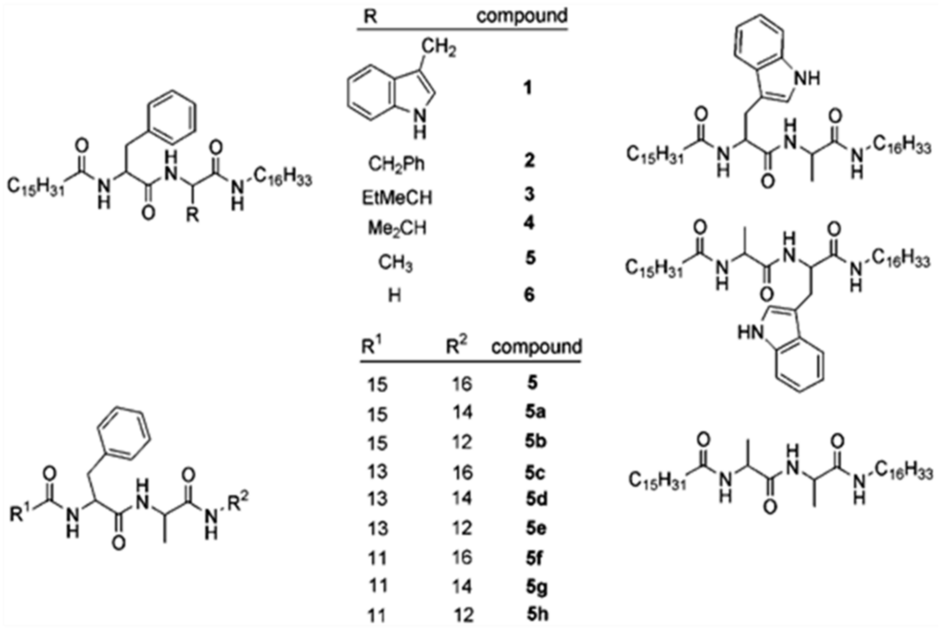


Scheme 1.7 Representative example of fatty acid and aliphatic long chain based gelator synthesized by (a)Polishuk et al.[46](b) D'Aléo et al.[50](c) Basak et al.[56]

1.3.1.2 Amino acid /peptide based gelators

Amide and urea derivatives of α–amino acids represent an important class of LMOGs. Large number of gelator systems capable of hardening organic solvents,[57-63] water[64-68] and both organic and aqueous solvents [69-70] (ambidextrous gelators) are well-known in the literature. The use of amino acid containing compounds as gelators (LMOGs) is very important due to their inherent biocompatibility and easy functionalization for tuning the properties. These qualities make LMOGs containing amino acids as excellent candidates for the application in biomedicinal area.[71-72]

Debnath et al. [73] have discussed organogelators which were synthesized using different l-amino acids with nonpolar aliphatic/aromatic residues and by varying alkyl-chain length **(Scheme 1.8)**. They have carried out a systematic investigation on the influence of different structural components of the dipeptide organogelators on their gelation efficiency. They systematically analyzed the organogelation properties of a series of dipeptide amphiphiles, specialy emphasising on the structural aspects. They described how minute changes in the chemical structure influence the self-assembling behavior.



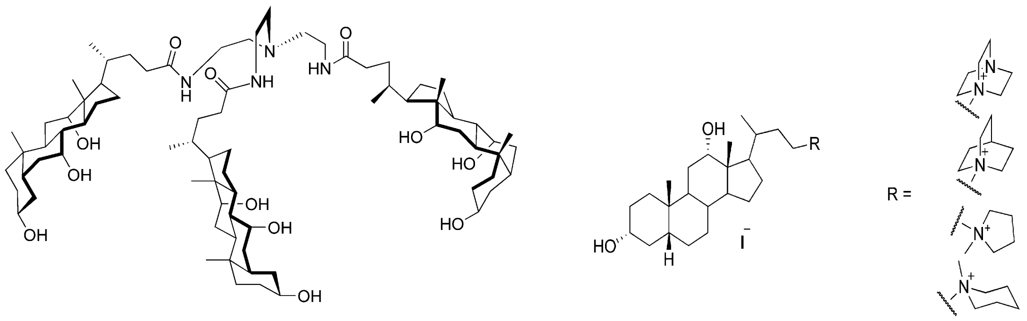
Scheme 1.8 Chemical structures of the gelator/non gelator compounds synthesized by Debnath et al.[73]

1.3.1.3 Bile acid/Steroid based gelators

Steroids are natural products comprised of a tetracyclic ring system, to which derivetizable functional groups are attached leading to an adjustable polarity profile, which makes them attractive building blocks when designing novel low molecular weight gelators.[74] Sievanen and co-workers[75-77] have carried out extensive studies on Bile acid/Steroid based gelators. Owing to the unique properties, steroid-based supramolecular gels could find applications in various fields ranging from material science and nano electronics to their application as reaction media or as sensing and responsive materials. Furthermore, steroidal gels may also find use in biomedicine, drug delivery, regenerative medicine and tissue engineering.[78-79]

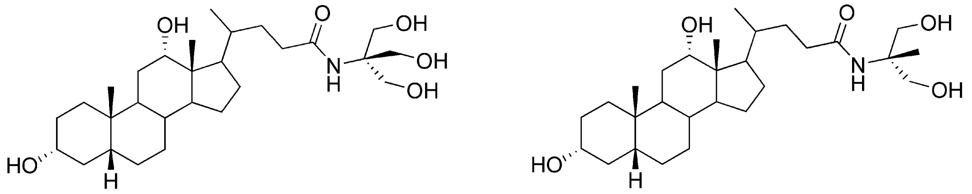
Bile salts are a class of molecules that belongs to the steroids family. An important characteristic of the bile salts is the formation of micelles in aqueous solutions. Bile salt possesses amphiphilic nature, as they have both hydrophobic surface and hydrophilic surface. The aggregates formed by the association of these molecules in solution are very different from those of the conventional surfactants which have well defined hydrophilic and hydrophobic parts.[80] Due to the unique structural features and versatile properties, bile acids and their derivatives have found numerous applications in the fields of pharmacology, supramolecular chemistry and material science.[81-83]

Svobodová et al.[74] have recently reported an article discussing recent advances in steroidal supramolecular gels. The article summarizes the most-recent advances in the field of steroidal supramolecular gels. Few examples are shown in **Scheme 1.9**. Furthermore, the potential applications of the systems were also discussed by them.



Structure of the tripodal cholamide

Structure of cationic bile salts



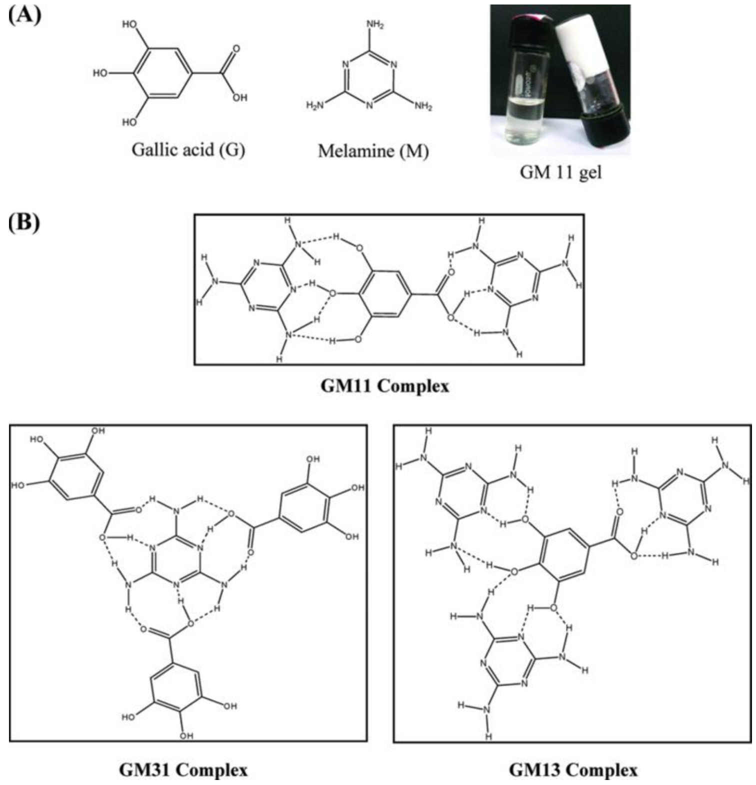
Structures of bile acid-based hydrogelators with neutral hydrophilic side chains

Scheme 1.9 Representative example of steroid/bile acid based gelator reported by Svobodová et al.[74]

1.3.1.4 Two-component gelators

One of most simple gelling system is two-component gelator such as an organic acid/amine salts, charge transfer complex and hydrogen bonded complex, which provide an opportunity to systematically vary one of the components and study structure–property correlation.Two-component gelators represent one of the most important classes of LMOGs as fine-tuning of physical gelation can be achieved by systematic variation of substitutions in any one of the two components. Recently, two-component systems producing hydrogels through supramolecular complex formation have attracted much interest for the potential use of it in biomedical applications.[84]

Nandi and co-workers [85-89]discovered many two-component hydrogelators systems using melamine as one of the components. In one of their articles, a new two-component hydrogel of melamine and gallic acid was reported for three different compositions of the components **(Scheme 1.10)**.[90]

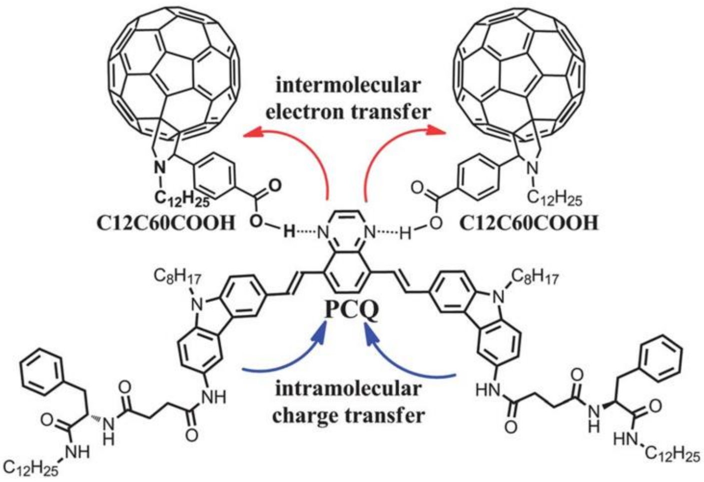


Scheme 1.10 Schematic illustration of two components Gelator based on Gallic acid and Melamine as shown by Nandi et al.[90]

One of the early known examples of such hydrogen bond based two-component gelator was reported by Hanabusa et al.[91] They synthesized a organogelator made up of 5-alkyl-2, 4,6-triaminopyrimidine and 5,5-dialkylbarbituric acid derivatives.

Recently, Xue et al.[92] have reported two-component gel composed of carbazole derivative and fullerene derivative. A carbazole derivative, N^1,N$^{1'}$-(6,6'-((1E,1'E)-quinoxaline-5,8-diylbis(ethene-2,1-diyl))bis(9-octyl-9H-carbazole-6,3-diyl))bis(N^4-

dodecylsuccinamide)(PCQ) with a quinoxaline moiety was designed**(scheme 1.11).** PCQ was reported as a highly efficient gelator toward various apolar and polar organic solvents. In addition, PCQ could construct two-component gel with fullerene derivative driven by intermolecular hydrogen bonds. Moreover, the two-component gel film could generate photocurrent under light irradiation, indicating photo-induced electron transfer from the PCQ aggregate to the fullerene derivative.



Scheme 1.11 Chemical structures of $N^1,N^{1'}$-(6,6'-((1E,1'E)-quinoxaline-5,8-diylbis(ethene-2,1-diyl)) bis (9-octyl-9H-carbazole-6,3-diyl))bis(N^4-dodecylsuccinamide)(PCQ) and $C_{12}C_{60}COOH$ synthesized by Xue et al.[92]

1.3.1.5 Metallogel

A new class of hybrid inorganic-organic gel popularly known as Metallogel, created by extending metal-ligand coordination interactions, have been less explored in terms of the design and construction of gel materials [93-96] despite their application such as gas storage, molecular sieves, ion exchange, sensing, magnetism, and catalysis.[97-99] There is no obvious difference between the conventional organic gelators and the metallogel, containing a strongly bound metal ion within the organic molecule. However, the introductions of a metal into the framework of gelator molecules can affect self-aggregation and thus it possibly can add advantage of tuning gel properties.[100-103]

Zhang et al.[104] have designed and synthesized a new family of platinum complexes, in which the iptycene groups were introduced into the platinum acetylide frameworks, followed by the attachment of long alkyl chains on two sides of the molecules **(Figure 1.4)**. All the designed complexes reported to have efficient gel formation properties in most nonpolar alkyl solvents and some polar solvents.

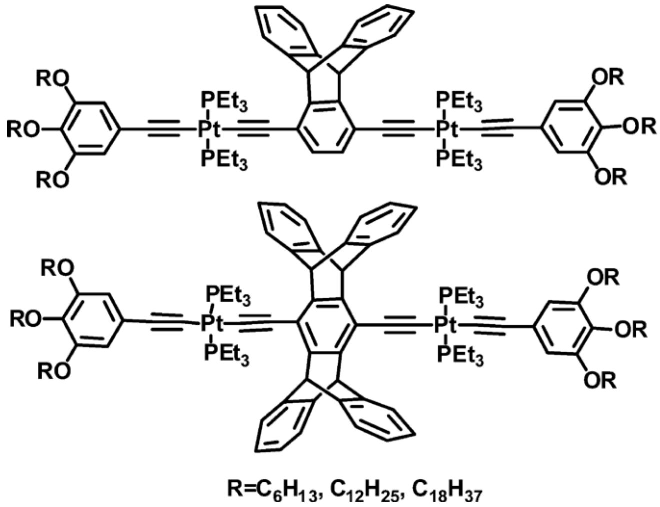
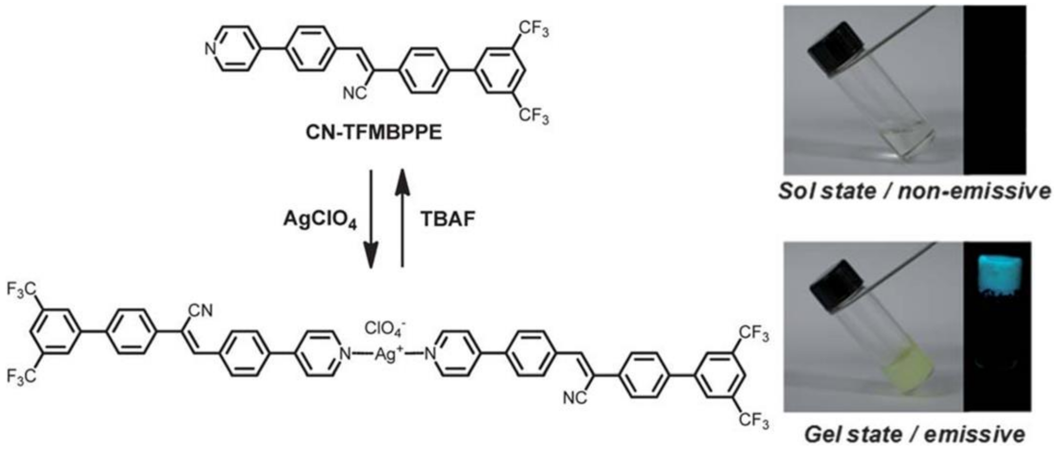


Figure 1.4 Chemical structures of the iptycene containing platinum acetylide organogelators synthesized by Zhang et al.[104]

The introduction of a metal center into the skeletons of gelator molecules can affect self-aggregation process; as a result it allows additional scope for tuning gel properties.[105] For example, Kishimura et al.[106] have synthesized class of trinuclear Au (I)pyrazolate metallacyclic gels which upon doping or dedoping of Ag(I) ions, the gel to sol phase transition showed a reversible switching of red-green-blue luminescence.

Recently, Seo et al.[107] have reported simultaneous supramolecular gelation and fluorescence turn-on triggered by coordination of silver ion. By using the ligand 2-(3-bistrifluoromethyl biphenyl -4- yl)-3- (4-pyridin-4-yl-phenyl) acrylonitrile(CN-TFMBPPE) they presented a ‘‘turn-on’’ fluorescent supramolecular gel triggered by coordination of a silver ion, which exhibits the emission enhancement via the combined events of silver ion-complexation with two CN-TFMBPPE molecules and their simultaneous self-assembly **(Scheme1.12)**. The silver ion-coordinated supramolecular gel formation was found to be reversible by chemical ion-stimulated gel-to-sol reverse transformation.



Scheme 1.12 Schematic representation of the silver ion-coordinated complex. Photo images of CN-TFMBPPE solution (upper) and silver-complex gel (bottom) under daylight with the corresponding fluorescence images under a UV radiation presented by Seo et al.[107]

1.3.2 Characterization of supramolecular gels

Supramolecular gels are an intriguing class of soft materials. Gels derived from low molecular mass compounds which stick together through a combination of non-covalent interactions like H-bonding, π-π stacking, donor–acceptor interactions, metal coordination, solvophobic forces (hydrophobic forces for gels in water) and van der Waals interactions. As these networks involve weak interactions; they are generally thermally reversible. However, the dynamic nature of supramolecular gels, which endows them with unique properties, makes their characterization diversified at the same time. Yu et al.[108] recently reported a review summarizing various methods for characterizing supramolecular gels. Some of the important characterization techniques are discussed in the present report.

1.3.2.1 ^{1}HNMR spectroscopy

Nuclear magnetic resonance (NMR) spectroscopic investigation of supramolecular gels can provide information about the structural properties of the components. Hydrogen nuclei within the molecules of a substance can be examined by ^{1}HNMR to determine the structure and the interactions of its molecules. Chemical shift changes can be monitored, accompanied by the formation of gels. These shifts can be attributed to various noncovalent interactions, which ultimately might drive to supramolecular gel.

Yang et al.[109] reported 9, 10-bis (1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (ex-TTF) based organogelator with L-glutamide-derived lipid unit. They found that the synthesized compound could gel several organic solvents. The inter-molecular π-π and S···S interactions due to the ex-TTF unit and the hydrophobic and hydrogen-bonding interactions due to the L-glutamide-derived lipid unit was considered to be the driving force for the gelation, which were established by applying the ^{1}H-NMR spectroscopy.The^{1}H-NMR spectra for the gel formed in d_6-DMSO at different temperature and the corresponding solution at 373 K were measured **(Figure 1.5)**.The signals due to the protons of the amide units were reported to upfield shifted by increasing the temperature, implies that hydrogen bonding owing to the amide units exists in the gel phase, and it becomes weak after heating. Moreover, upfield shifts for the signals due to the protons of the dithiol ring of ex-TTF unit by increasing the temperature have been attributed to the intermolecular π-π and S···S interactions due to the ex-TTF unit in the gel phase.

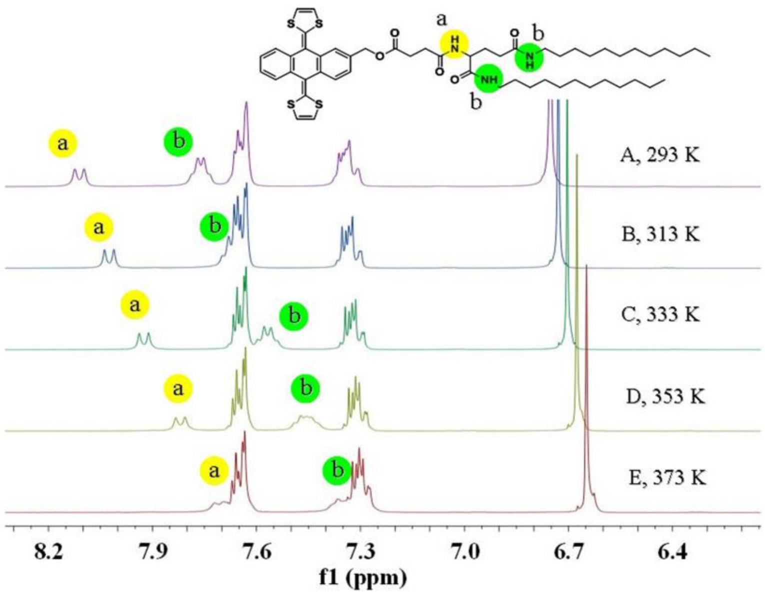


Figure 1.5 ^{1}HNMR spectra for the gel at different temperatures Reported by Yang et al. [109]

Escuder et al.[110] reported the NMR study of supramolecular gels formed by two organogelators derived from valine **(Figure 1.6, 1 and 2)**, particularly to study the capabilities of functional self-assembled fibers to interact selectively with guest molecules.

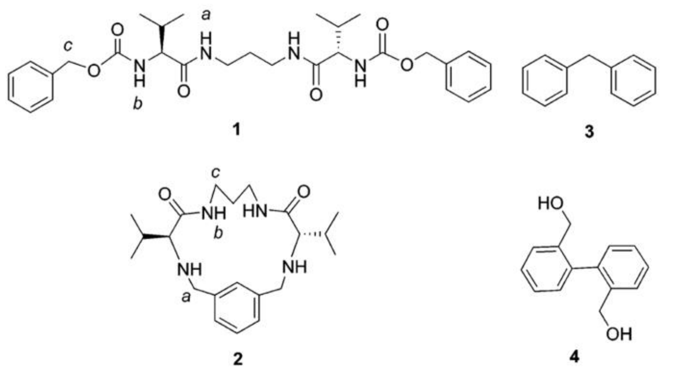


Figure 1.6 Chemical structures of organogelators (1 and 2) and diphenylmethane (3), and 2, 2’ bishydroxymethylbiphenyl (4) used by Escuder et al.[110]

They have shown that molecules, apart from the gelator can interact with the gel network **(Figure 1.7)** and this process can be monitored easily by measurement of relaxation times. As a proof, the selective interaction of 2, 2’ bis(hydroxyl- methyl) biphenyl **(Figure 1.6,3)** over diphenylmethane **(Figure 1.6, 4)** with the self-assembled fibers formed by one of the gelator was demonstrated.

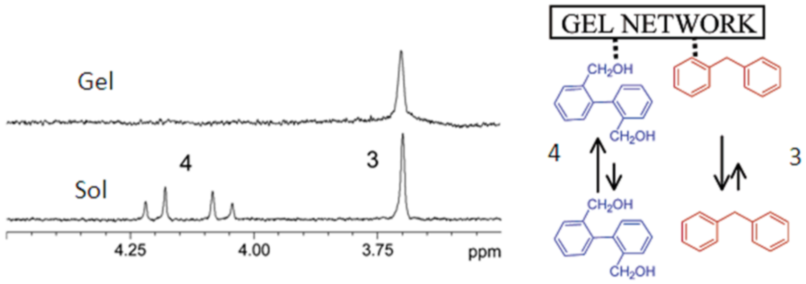
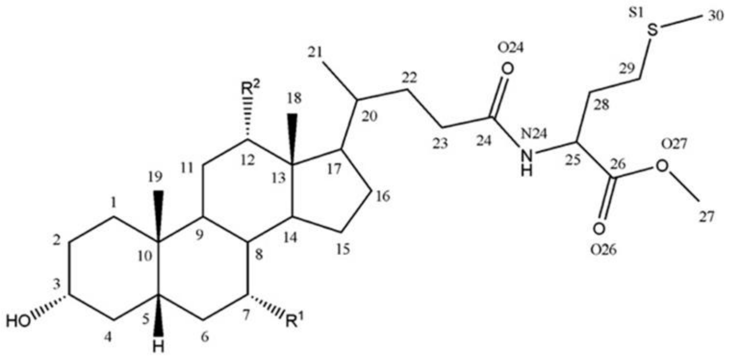


Figure 1.7 Section of the T_2 filtered ^{1}HNMR spectra of mixtures of organogelator 1, compound-3 and 4 presented by Escuder et al.[110]

1.3.2.2 X-Ray techniques

1.3.2.2.1 Powder X-Ray diffraction analysis - X-ray powder diffraction finds frequent use in materials science because sample preparation is relatively easy, and the test itself is often rapid and non-destructive. The materials which are crystalline and even amorphous material yield some useful information in diffraction experiments. The pattern of powder diffraction peaks can be used to quickly identify materials and changes in peak width or position can be used to determine crystal size, purity and texture. X-ray powder diffraction (XPRD) is also important to extract valuable information in the field of supramolecular gel.

How packing of molecules in the crystalline state is with packing in metastable gel state is a fundamental question. Weiss and co-workers[111] developed an indirect method to probe the packing of gelator molecule in gel, xerogel (dried gel) and bulk state by comparing powder X-ray diffractogram (XRD) of gelator molecule with simulated single crystal of gelling agent, if any. This method suffers from inherent drawbacks namely growth of single crystal of gelator molecule is mostly unsuccessful especially in its gelling solvent. Secondly, packing of gelator molecules in bulk crystalline state is mostly different from xerogel or gel state,[112] thirdly, PXRD of gel is masked by strong scattering from solvents making the diffractogram unreliable. Even though, the method suffers from some shortcomings, it is frequently being used for elucidating the mechanism and probable packing of gelator molecules in the gel state. Noponen et al.[113] have reported three novel biocompatible bile acid– L-methionine methyl ester conjugates **(Figure 1.8)**.



1 $R^1 = R^2 = H$
2 $R^1 = H, R^2 = OH$
3 $R^1 = R^2 = OH$

Figure 1.8 Chemical structures of compounds synthesized by Noponen et al.[113]

Two of the conjugates have been shown to undergo self-assembly leading to organogelation. In order to investigate the molecular packing of compound 1 in the xerogel state they employed Powder X-ray diffraction analysis. The X-ray diffraction patterns (XRD) of xerogel resembled the pattern simulated from the structure determined by single crystal diffraction **(Figure 1.9)**.

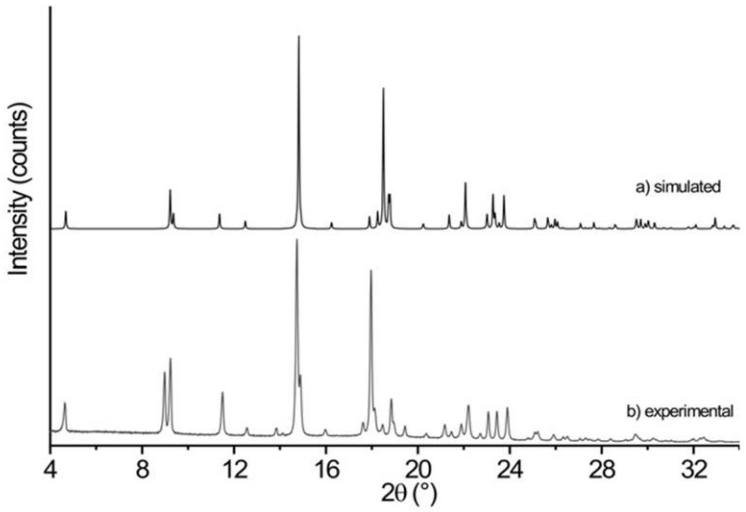


Figure 1.9 Simulated (a) and experimental (b) Powder XRD diffraction patterns of compound 1.

Moreover, powder X-ray diffraction studies employed to reveal that compound 1 undergoes a dynamic and reversible conformational change in the solid state when cooling from ambient temperature to -150°C **(Figure 1.10)**.

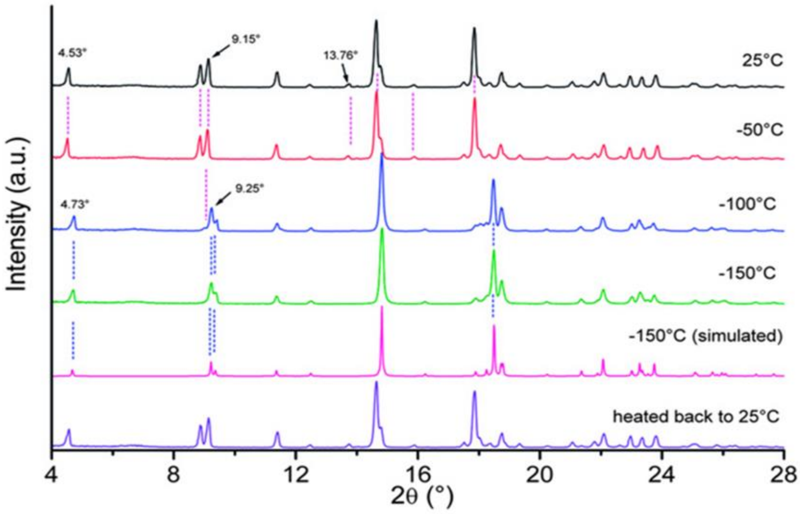


Figure 1.10 Temperature-dependent diffraction patterns of xerogel of compound1

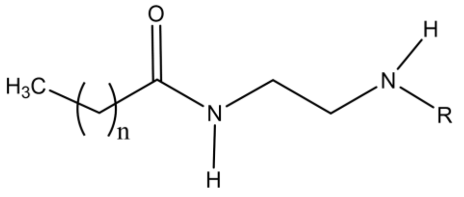
The XRD pattern measured at -150 ^{0}C found to be perfectly identical to the simulated pattern corresponding to the single crystal structure determined at the same temperature. In addition, when the sample is heated back to +25 ^{o} C the diffraction pattern returns equivalent to that obtained before cooling.

1.3.2.2.2 Single crystal XRD analysis – single crystal XRD is emerged as a significant tool in the field of supramolecular gelation. In supramolecular synthesis, the target molecule is a supermolecule i.e. crystal structure in present case. The crystal structure chart can be designed by using the crystal engineering approach.[114] Desiraju has introduced a new term “supramolecular synthons” in conext of crystal engineearing[115] and are spatial arrangements of intermolecular interactions and play the same focusing role in supramolecular synthesis that conventional synthons do in molecular synthesis.” However, designing a gelator molecule is still a daunting task; nevertheless, Dastidar and group have demonstrated that the 1D network promoted organo gelation, whereas 2D and 3D networks either produced weak gel or no gelation through a large number of organic salt based compounds.[116-122] Thus, it is worth identifying a supramolecular synthon that would promote the 1D network and consequently, results in the gelling agent.

1.3.2. 3 FT-IR spectroscopic studies

Infrared spectroscopy (IR) deals with the infrared region of the electromagnetic spectrum; it is a simple and reliable technique widely used in both organic and inorganic chemistry for the purpose of characterization as well as monitoring applications. Consequently, IR can readily be utilized to characterize the formation process of supramolecular gels, as it is well-known that hydrogen bonding is one of the driving forces for the self-assembly of gelator in appropriate solvents. As a powerful tool for investigating noncovalent interaction responsible for gelation, FTIR spectroscopy can be performed.[123-124]

A family of low molecular weight organogelators (LMOG) based on monochain derivatives of ethylenediamine were investigated by Luo et al.[125]**(Scheme 1.13)**. The monochain derivatives of ethylenediamine showed strong gelation ability in a number of organic solvents. They observed that the IR spectrum of compound-4 in gel state was similar to that of the of in powder state, **(Figure 1.11**) suggesting that the pattern of hydrogen bonding in the gel is close to that in the crystal. Furthermore, the peak shifts of $\gamma_s NH_2$ and $\gamma C=O$ in gel state compare to powder state, implies intermolecular hydrogen bonding between the neighbouring molecules and thus they form a hydrogen bond network.



1: n=6 R=H **2**: n=8 R=H
3: n=10 R=H **4**: n=12 R=H
5: n=14 R=H **6**: n=16 R=H
7: n=12 R=C (=O) $(CH_2)_6CH_3$

Scheme 1.13 Molecular structures of monochain derivatives synthesized by Luo et al.[125]

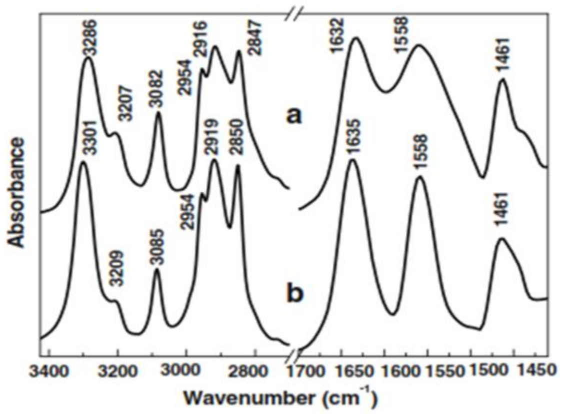
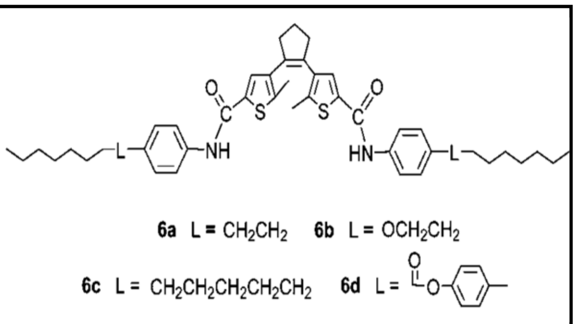


Figure 1.11 FT-IR spectra of compound-4 in gel (a) and the powder (b) state.

Rameshbabu et al.[126] has also performed FT-IR experiments to analyze the intermolecular hydrogen bonding motif. FT-IR spectra of the xerogel 6c **(Scheme 1.14)** showed strong absorption bands corresponding to N–H and C=O stretching vibrations, whereas its corresponding organogel in toluene, exhibited observable shifts in the absorption bands **(Figure 1.12)** .This indicates the existence of the intermolecular hydrogen bonding through two amide moieties in the gel state.



Scheme 1.14 Structures of compounds synthesized by Rameshbabu et al.[126]

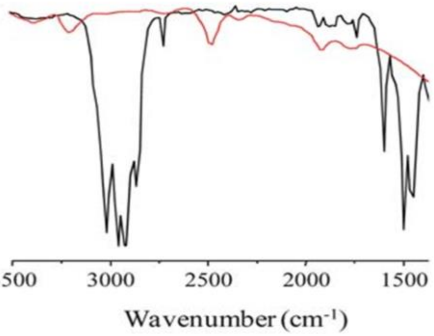
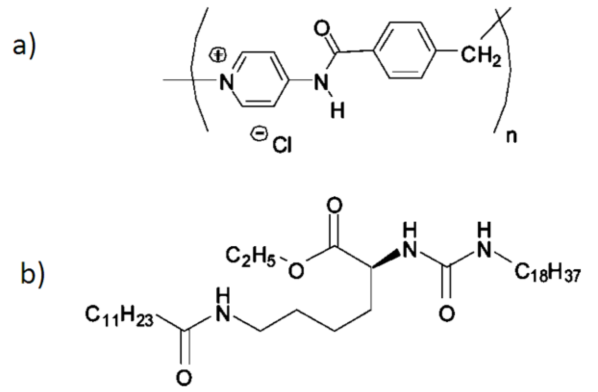


Figure 1.12 IR spectra of 6c in xerogel (black line) and toluene organogel state (red line)

1.3.2.4 Rheology

Rheology is the study of flow and deformation of materials under applied forces. The measurement of rheological properties is applicable to materials ranging from fluids such as dilute solutions of polymers and surfactants to concentrated protein formulations, semi-solids, molten or solid polymers and so on. Rheological properties can be measured from bulk sample deformation using a mechanical Rheometer.Rheology is basically the science of deformation and flow behaviour caused by external forces and provides information about the type of network that is responsible for the observed gelation, about their dynamics, and even about their self-assembly mechanisms.

Kundu et al.[127] had discussed the sol-gel transitions and hysteresis behaviors of an ionic gelator, a low-molecular weight organogelator, and a polymeric hydrogelator by rheological methods.



Scheme 1.15 Chemical Structures of organogelators a) 1-Cl and b) LEE synthesized by Kundu et al.[127]

They have also discussed the gel recovery process after mechanical agitation with a high shear rate. Comparison of gel-recovery processes of a novel ionic gelator, poly [pyridinium1,4-diyl-iminocarbonyl-1,4-phenylene-methylene chloride] (**1Cl**) **Scheme 1.15a)** with those of other gelators, i.e., a low-molecular weight organogelator (LEE) **(Scheme 1.15b)** and a high-molecular weight hydrogelator (gelatin) was studied. They demonstrated that **1-Cl** exclusively undergoes self-recovering **(Figure 1.13)**.

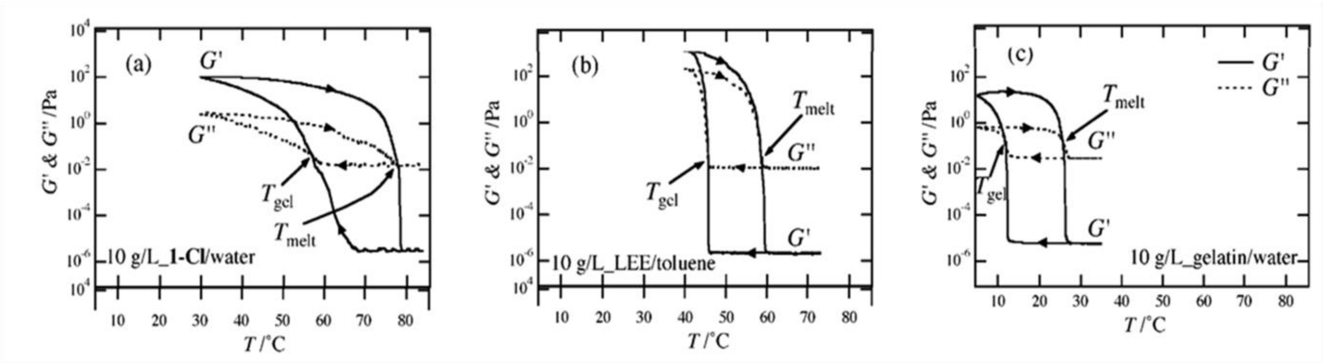


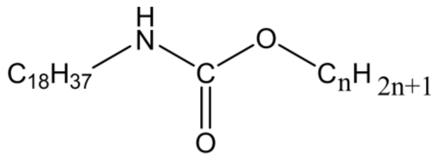
Figure 1.13 Hysteresis of the storage (*G*') and loss (*G*'') moduli for (a)**1-Cl**/water, (b)LEE/toluene, and (c) gelatin/ water on heating and cooling processes.

1.3.2.5 Scanning electron microscopy

Scanning electron microscopy (SEM) is a type of electron microscopy that produces images of a sample by scanning over it with a focused beam of electrons. These electrons interact with the electrons in the sample, producing various signals that can be detected and that contain information about the sample's surface composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image.

SEM is a versatile technique in the field of supramolecular chemistry and materials chemistry to elucidate their mophology.[128-131] Supramolecular gels can be regarded as a solid-like material mainly composed of liquid phase and small concentration of solid phase.The solid-like appearance of the gel can be attributed to the immobilization of the solvent molecules in the three-dimensional (3D) network formed by the gelator molecules. The fibers formed by the self-assembly of molecular blocks with the size ranging from several nanometers to a few tens of micrometers. The sizes of these fibers are appropriate for SEM; consequently, SEM can be regarded as an ideal method for observing their mophology.

Moniruzzaman et al.[132] have reported thermoreversible organogels prepared from carbamates with alkyl side chains of different lengths **(Scheme 1.16).** Gelation was possible up to an alkyl side chain length of 12 carbons, beyond which crystallization occurs. Morphology of these xerogels was studied by SEM Analysis.



n=4,7,8,10,12,16,18

Scheme 1.16 Chemical Structures of carbamates with various alkyl side chains synthesized by Moniruzzaman et al.[132]

Figure 1.14 Shows the SEM images of the xerogels of C_7, C_8, C_{10}, C_{12}, and C_{16}. They proposed that the thickness of the fibers is affected by the gel formation procedure.

By these observations from SEM images they suggested the competing roles of hydrogen bonding and the crystallization of the alkyl segment promoted by van der Waals interaction.

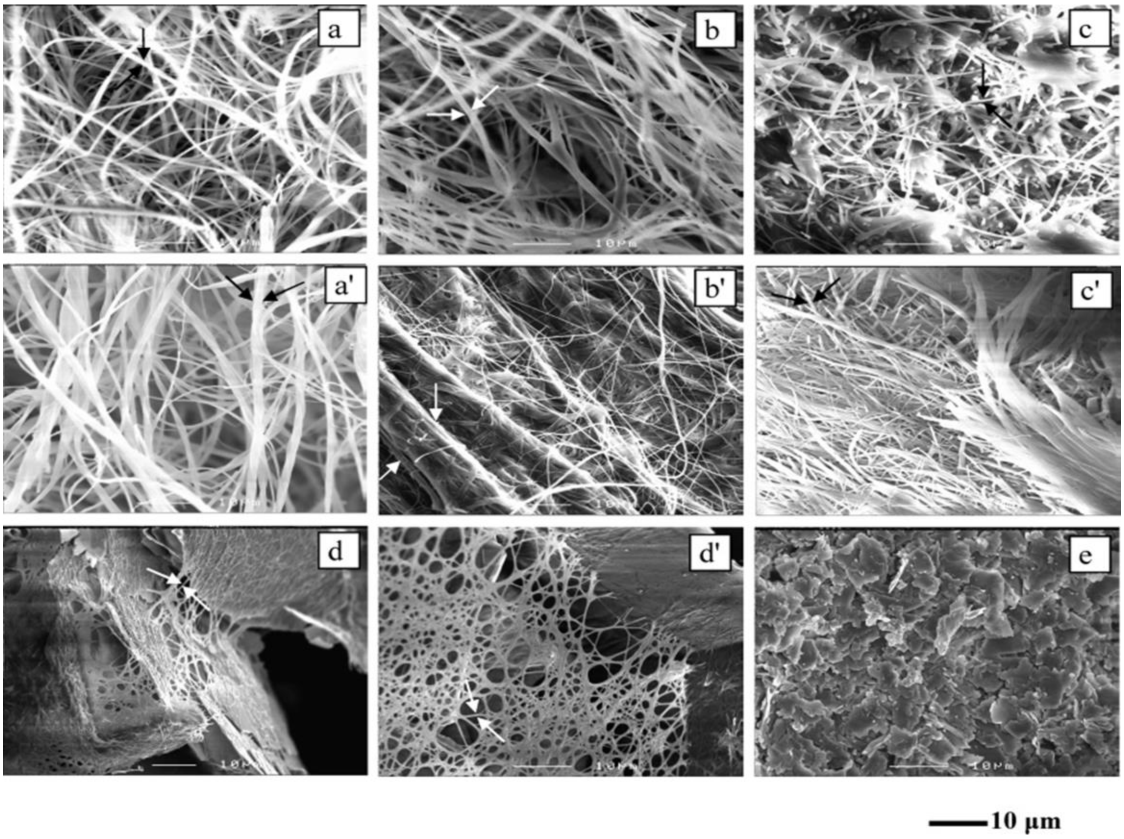


Figure 1.14 SEM images of the xerogels obtained from different carbamate/ benzonitrile gels: from quenched gels (a-e) and from slow-cooled gels (a’-d’).

1.4 Applications of LMOGs

In recent years, self-assembled low molecular weight organogelators have grabbed significant attention obviously due to its intriguing property and plentiful applications in various fields ranging from chemical science to physical science to biological science. Gels have found numerous applications in cosmetics,[133]plastic surgery,[134-135] contact lenses,[136-137]experimental solar cells,[138-141] electrochemical cells,[142-144] sensors,[145-149] drugs delivery systems,[150-153] as well as many other products and areas.[154-157] Some of the important applications are discussed in this report briefly.

1.4.1 Supramolecular gels as templates for the synthesis of inorganic nano-structures

One of the most fascinating applications of LMOGs is their use as organic templates for the fabrication of nonmaterial. Organogelators are preferable choice for nano-materials synthesis due to well-defined supramolecular assembly of gelator molecules in a solvent such as fibres, rods, tubes etc.[158]

Gao et al.[159] have reported the synthesis of double and multiwall silver nanotubes by using the uniform low-molecular-mass organogel nanotubes self-assembled from a L-glutamic-acid-based bolaamphiphile, N, N-eicosanedioyl-di-L-glutamic acid (EDGA) **(Figure 1.15)**.The EDGA could gel mixed water/ethanol solvent and form helical nanotubes.

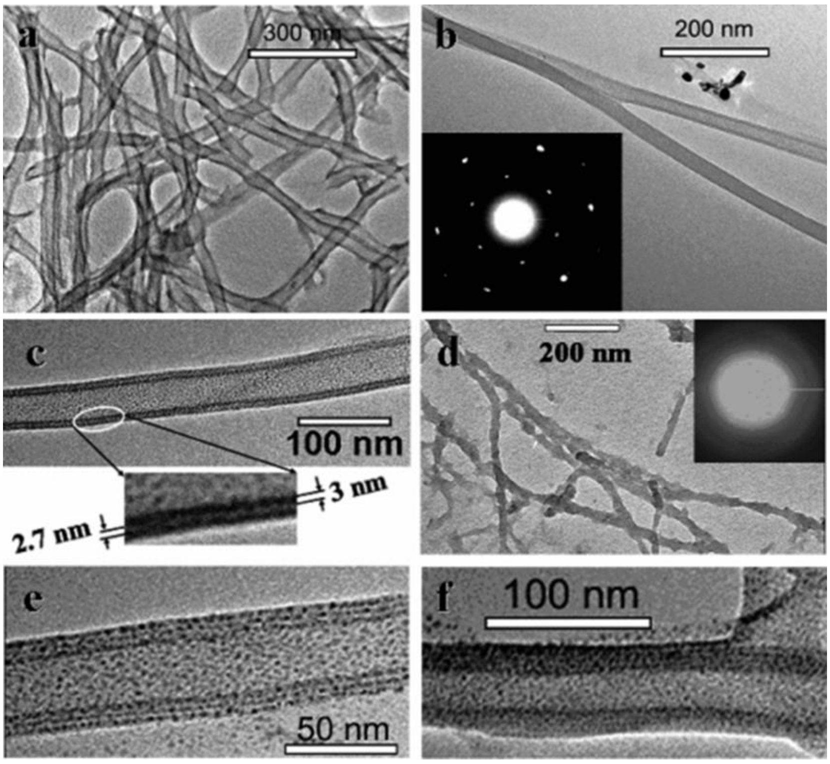


Figure 1.15 TEM images of the Silver nano tubes synthesized by Gao et al.[159]

The gel thus formed, on mixing with $AgNO_3$ followed by reducing the silver cation under the photoirradiation yielded double-wall silver nanotubes. Increasing the reduction time of the mixed gels and $AgNO_3$ in the solution led to the formation of three, four, and five-wall silver nanotubes. They proposed a possible mechanism of the template synthesis of the double walled, and Multi walled silver nanotubes under photoirradiation**(Figure 1.16)**.

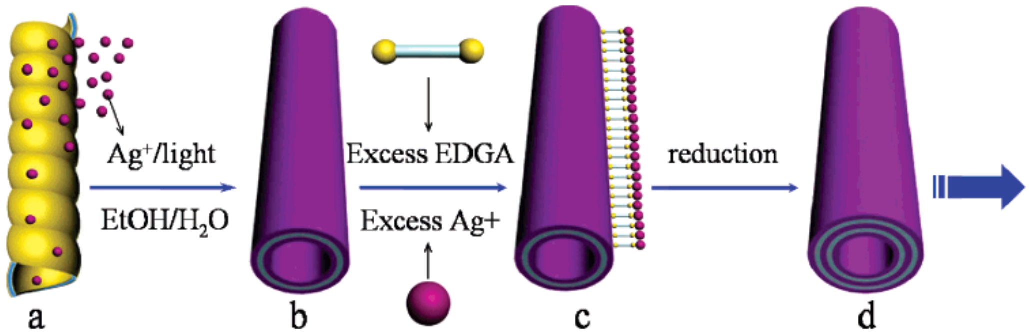
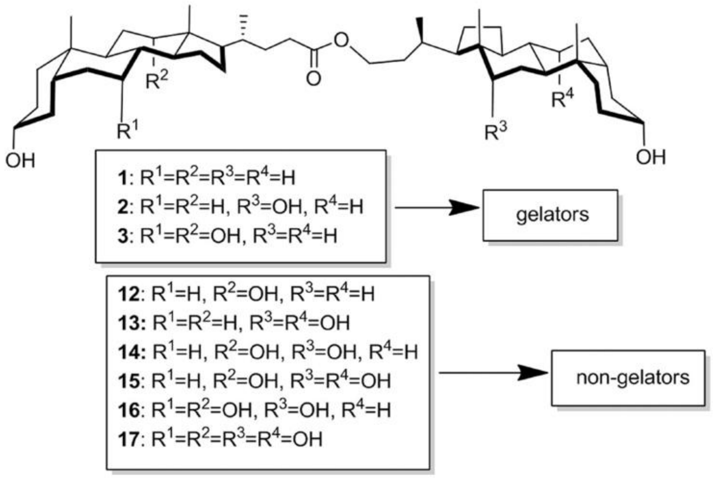


Figure 1.16 Probable mechanism of synthesis of silver nanotubes.[159]

Recently, Chakrabarty et al.[160] reported in Situ formation of Gold Nanoparticles by means of organogels from dimeric bile acid esters **(Scheme 1.17).** They synthesised a new class of steroid dimers (bile acid derivatives) linked through ester functionalities, which gelled various aromatic solvents.



Scheme 1.17 Bile-Acid-Derived Dimeric Ester Organogelators synthesized by Chakrabarty et al.[160]

The nanofibers in the organogel were employed to synthesize gold nano-particles of different sizes and shapes. They designed an in situ synthesis of gold nanoparticles on the fibers of organogel. Organogel was prepared in the desired solvent containing a gold precursor followed by addition of a reducing agent such as tetrabutylammonium borohydride at the top of the gel layer to reduce Au (III) to Au (I). This approach, lead to purple/blue colored gel-nanoparticle hybrid material obtained **(Figure 1.17)**.

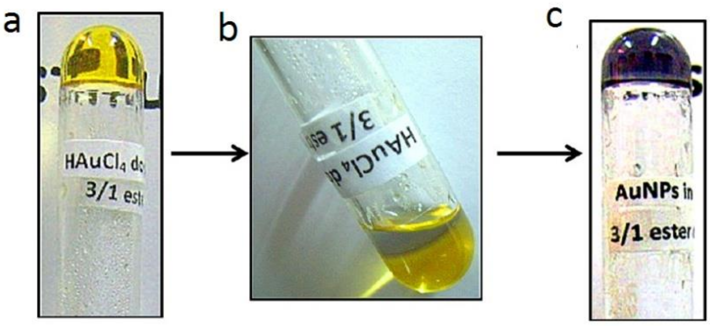
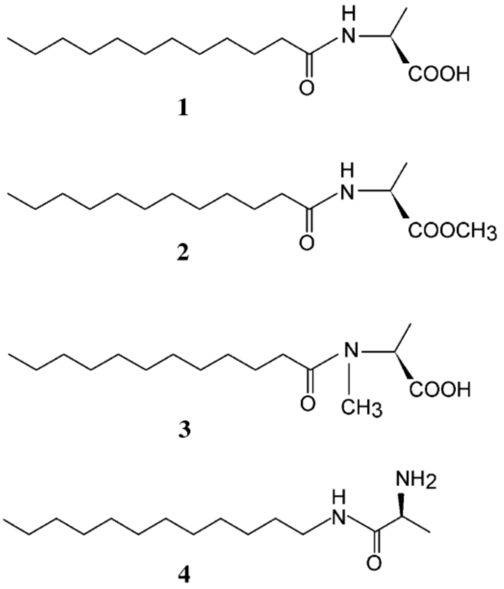


Figure 1.17 Preparation of Au Nanoparticles embedded in organogel fibers.[160]

1.4.2 Phase selective gelation for oil spill recovery

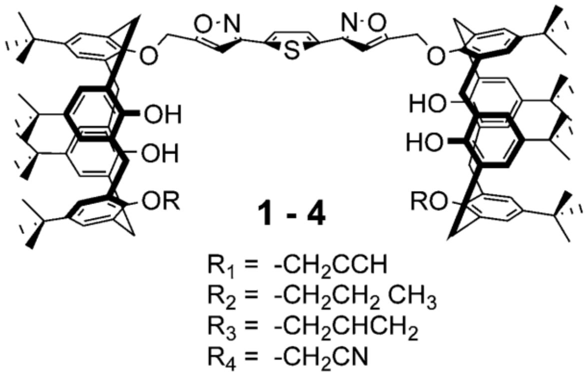
An oil spill is the release of a liquid petroleum hydrocarbon into the environment, especially in marine areas, due to human activity, and is a form of pollution. Oil spills affect animals, plants and environment adversely in several ways. An oil spill represents an immediate fire hazard, spilled oil can also contaminate drinking water supplies; it can also blind an animal; leaving it defenceless, animals can be poisoned, and may die from oil entering into their lungs or liver etc. Cleanup and recovery from an oil spill is difficult and depends upon many factors, including the type of oil spilled, the temperature of the water, etc. Current methods for cleaning up include bioremediation, skimming, vacuum and centrifuge, use of dispersants and others. As an alternative method oil can be solidified by using gelator. The oil can also be recovered from the gelled phase by heating and distillation.

Bhattacharya et al. [161] made the first report of phase selective gelation of oil from oil/water mixtures. From a two-phase mixture of water and oil (either commercial fuel or pure organic solvent), a simple amino acid derivative, *N*-lauroyl L-alanine **1(Scheme 1.18)** was shown to be capable of geling the oil phase selectively which may find application in containing oil-spill problem. After this report, many more examples of LMOGs for selective gelation of various organic fluids, including petrol have been added in the list.[162-164]



Scheme 1.18 Chemical structure of fatty acid derived amino acid synthesized by Bhattacharya et al.[161]

Recently, Tsai et al.[165] have also reported a biscalixarene framework, without long alkyl chains **(Scheme1.19)**. The Biscalix [4]arene **1** was able to form organogels in various alcoholic solvents. It also exhibited an excellent phase selective gelation oil/water mixtures that is potentially useful in oil spill recovery.



Scheme 1.19 chemical structure of biscalix[4]arenes synthesized by Tsai et al.[165]

When solution of biscalixarene **1** dissolved in ethyl acetate and then added it to several commercially available gasoline fuels, they formed organogels **(Figure 1.18)**. The solution of **1** in ethyl acetate could form organogels with almost all commercially available gasoline fuels (diesel, pump oil, silicone oil, etc.).

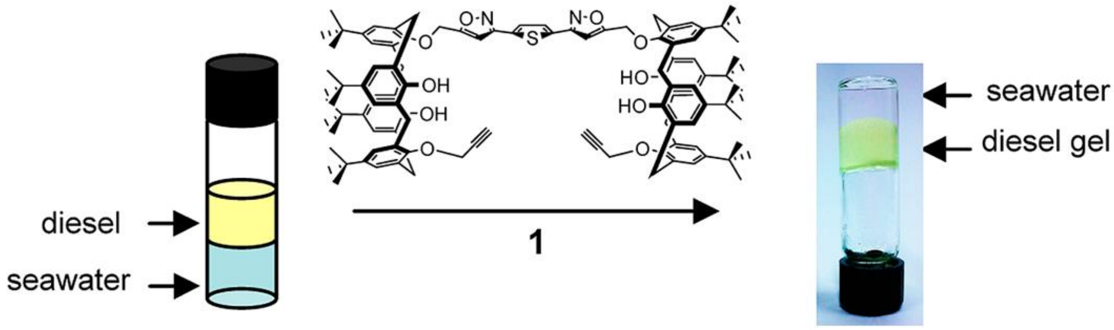


Figure 1.18 Photographic representation of phase selective gelation of diesel from diesel/sea water mixtures.[165]

1.4.3 Organogel as a Template for the synthesis of porous polymer

The porous polymers finds useful applications in various fields such as mesoporous catalysts, membranes and stationary phases for chromatography and chemical sensors.[166-168]Synthesis of porous polymer, using "template" techniques, is comparatively new method, has been investigated for the past decade.[169-171]The template can efficiently be used as structure-directing agent. The polymerisation can be carried out in presence of templates. The nanoscale templates can directly be mixed with the initiators and monomers, followed by conventional polymerization method i.e thermal or photopolymerization. This method found to be capable of resulting nano structured, solid polymers including templates. The exclusion of template can lead to porous polymer. Usually, low molecular weight organogelator, colloids and micelles are employed as templating agents due to their ease of extraction by the solvents.[172]

Organogels are thermoreveversible and viscoelastic materials, consisting of low molecular weight gelators and organic solvents. They have a unique structural feature in that the nanosized fibers formed by the self-assembly of the gelator molecules, are finely distributed in a gel composed mainly of solvent molecules. A highly controlled and entirely dispersed morphology of the fibrils makes them a potential candidate of template for the synthesis of porous/imprinted polymer.

Tan et al.[173] have used the concept of reverse templating of an organogel to form imprinted porous divinylbenzene polymer films. The organogel comprising a 1:1 molar ratio of two organogelators, that is, bis (2-ethylhexyl) sodium sulfosuccinate (AOT) and 4-chlorophenol, **(Figure 1.19)** was formed in divinylbenzene.

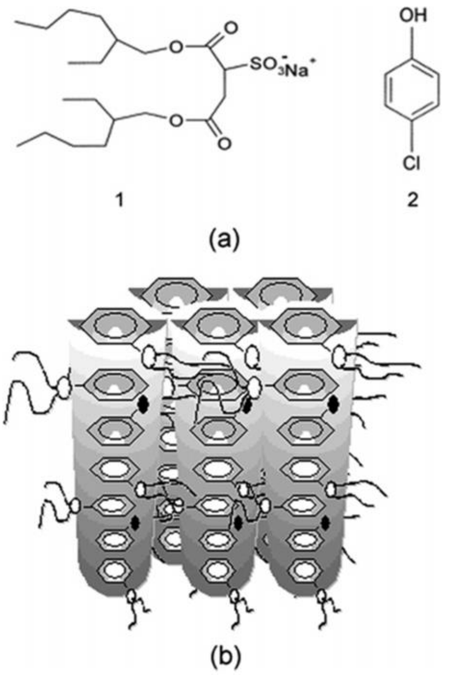


Figure 1.19 (a) Chemical structures AOT (**1**) and 4-chlorophenol (**2**). (b) Illustration of thehexagonal packing of gel strands to form a gel fiber presented by Tan et al.[173]

The gel was cast as a thin film before UV polymerization of the solvent, and the organogelators were later removed. The integrity of the fiber bundles of the organogel was preserved during polymerization, and an exact hollow replica was obtained on removing the organogelators. Additionally with the incorporation of functional nano particles in AOT inverse micelles and hence the organogel, nanoparticle-containing porous polymer films exhibiting luminescence or magnetic properties were demonstrated.

Li et al.[174] have reported the synthesis of dendritic polyaniline nanofibers with diameters between 60 and 90 nm by chemical oxidative polymerization of aniline in a special surfactant gel, which was formed by a mixture of hexadecyltrimethylammonium chloride (CTMA), acetic acid, aniline, and water at -7 °C. The morphologies of polyaniline nanofibers were characterized by scanning electron microscopy (**Figure 1.20**). The polyaniline nanofibers were interconnected to form dendritic or network structures, rather than isolated nanofibers or bundles. A few polyaniline nanoparticles absorded onto the nanofibers were also found.

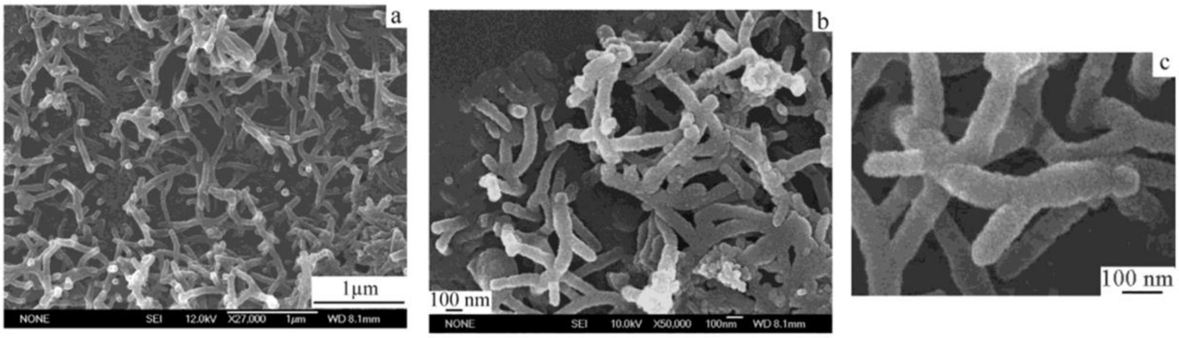


Figure 1.20 SEM images of dendritic polyaniline nanofibers (a, b) at low magnification and (c) at high magnification as presented by Li et al.[174]

1.4.4 Stimuli responsive organogel

A variety of noncovalent interactions, suchas multiple hydrogen bonding, π-π stacking, hydrophobic interactions, metal–ligand coordination, and integrated noncovalent interactions, are responsible for bringing the building blocks together to prepare supramolecular assemblies. Hence, the nature of noncovalent interactions and the structures of building blocks employed in supramolecular gelator determine the responsiveness of the resultant supramolecular gels to surrounding environments. Therefore, stimuli-responsive supramolecular gel can be fabricated sophisticatedly. Smart gels grabbed a good amount of attention owing to its potential applications in various areas, such as delivery systems, sensors, actuators, chemical valves and switches, industrial separators etc. Stimuli-responsive supramolecular gel is reported to respond various triggers, for example, pH [175-176] magnetic fields [177-178] addition of salts,[179] electric fields,[180] addition of sugars, [181-182] IR,[183] UV light,[184] etc. Yang et al. [185] have recently published a detailed review on the Stimuli responsive gels based on low molecular weight gelators.

Zhang et al.[186] have reported Fluoride-responsive gelator and colorimetric sensor. They designed a new fluoride responsive gelator based on cyano-substituted amide which lacks steroidal units and long alkyl chains **(Figure 1.21)**.

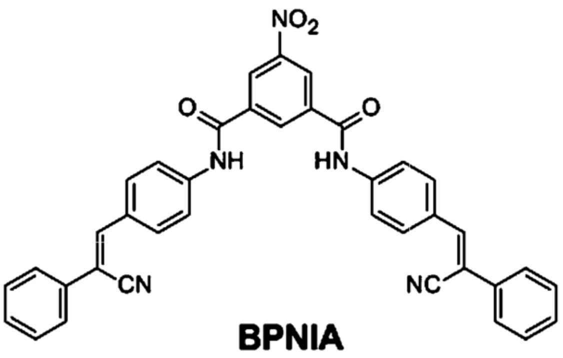


Figure 1.21 Chemical structure of stimuli responsive gelator BPNIA synthesized by Zhang et al.[186]

The compound not only acts as a smart gel that shows reversible gel–sol transition and a visibly noticeable colour change controlled by using fluoride stimuli, but also exhibits a highly selective sensing activity against fluoride in DMSO solution. The photographs of the gel-to-sol conversion of BPNIA in the presence of fluoride are shown in **Figure 1.22**.On addition of solid TBAF onto the top of the DMSO gel, a thin layer of red solution immediately appeared at the upper part. As time passed, the pale yellow gel gradually vanished, and more and more red-colored solution appeared until all the gel transferred into solution.

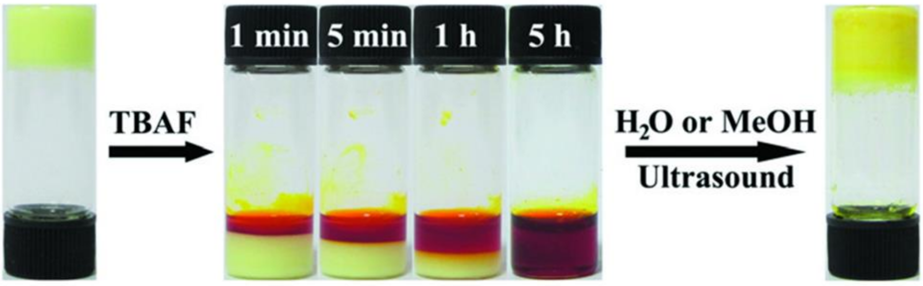


Figure 1.22 Photographic representations of the changes in the DMSO gel after addition of solid TBAF

Eastoe et al.[187] have reported a new photo-responsive organogel, which displays a UV-induced gel-to sol transition. The gel is formed by stilbene-containing Gemini photo-surfactant **(Figure 1.23)**, toluene and trace amounts of dimethyl dodecylamine.

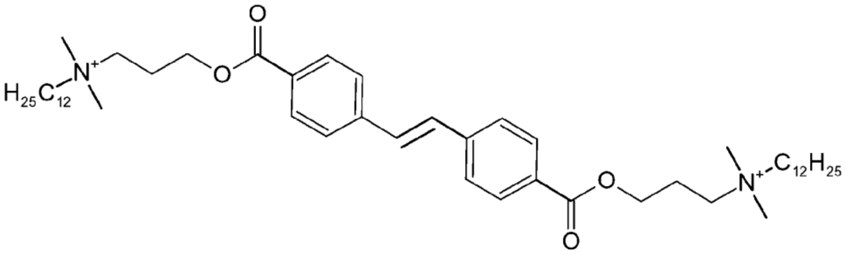


Figure 1.23 Stilbene-containing gemini photo-surfactant synthesized by Eastoe et al.[187]

They demonstrated the gel-to-sol transition for this system after irradiation with UV light. Initially, it was the opaque gel, and after irradiation a transparent low viscosity solution was formed from the gel. When the system was irradiated through a mask, only the illuminated areas were converted to the sol (**Figure 1.24).**

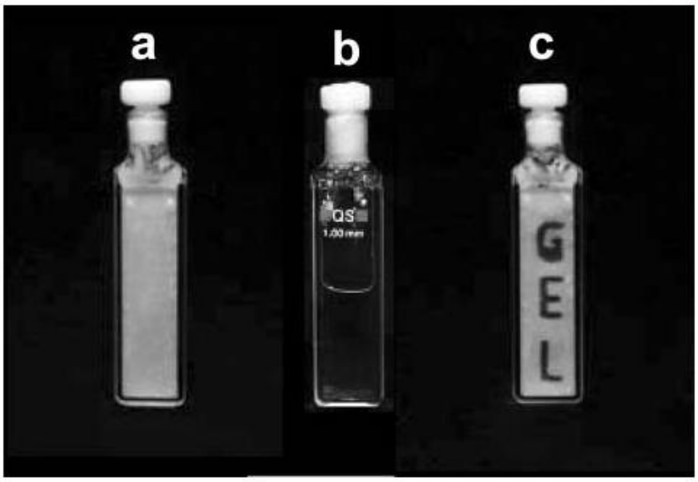


Figure1.24 Photo-induced gel-to-sol transition: initial gel state (a); after irradiation (b) and after irradiation through a mask (c).

1.4.5 Low molecular mass organogelator based gel electrolyte

Solid electrolytes, which are electrically conductive solids with ionic carriers, have received special attention, because of their significant utilization in the fields of solid state batteries, fuel cells, energy storage, and chemical sensors.[188-190] Because of high-efficiency and potential low-cost, dye-sensitized solar cells (DSC), which may be an alternative to conventional inorganic photovoltaic devices,[191] are currently attracting widely to both academic and commercial interests. Largely efforts have focused on manufacturing high efficiency DSCs. Furthermore, high-efficiency DSCs usually employs liquid electrolytes. But liquid environments often leak or degrade photochemically, causing poor long-term stability. Therefore, polymer solid electrolytes are of special interest for applications owing to their excellent characteristics, such as high reliability, non-leakage of electrolyte solution, thin film formation, and flexibility.[192-194]

Tao et al.[195] have fabricated Stable quasi-solid-state dye-sensitized solar cells (DSCs) by using room-temperature molten salts (1-methyl-3-hexyl-imidazolium iodide), and a series of diamine derivatives with different lengths of the alkyl chain as low molecular mass organogelators (LMOGs). They systematically studied how the molecular structures of the gelators influence the electrochemical properties of the gel electrolytes, the photovoltaic performances, and stabilities of the devices. The gel-to-solution transition temperature (T_{gel}) of the gel electrolytes, the electrochemical characteristics, photovoltaic performances, and long-term stabilities of quasi solid-state DSCs were changed regularly with variation of the even- and odd-numbered –CH_2– in the molecules of the LMOGs. Differential scanning calorimetry was used to study the gel phase to liquid phase transition (T_{gel}) of the gel. Generally, the high T_{gel} is useful for the application of DSCs to exhibit long-term stability. The T_{gel} values of the IGEs-based on the gelators containing even-numbered -CH_2-between the two amide carbonyl groups were reported higher than those of the IGEs containing odd numbered-CH_2- **(Figure 1.25)**.They demonstrated that the ionic liquid gel electrolyte-based DSCs could retain 93%-99% of their initial photoelectric conversion efficiencies (η) under heat at 60 °C, and 100% of their initial photoelectric conversion efficiencies under one sun light soaking with UV cut off filter at 50 °C for 1000 h.

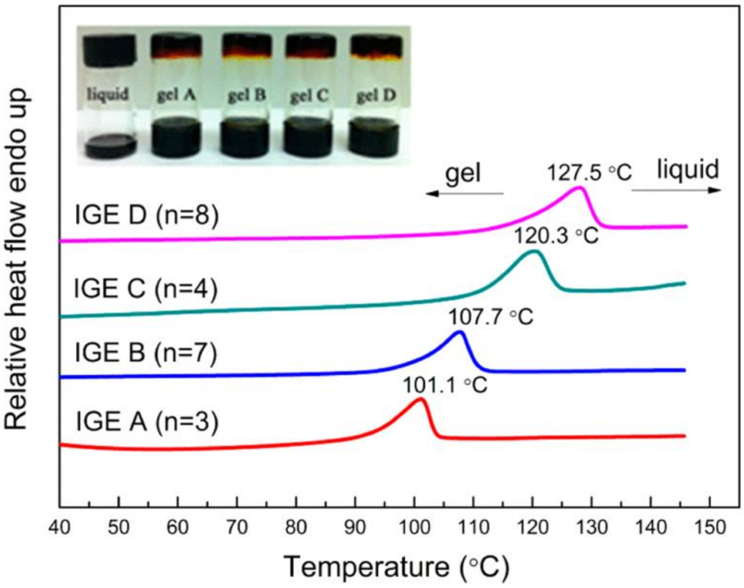
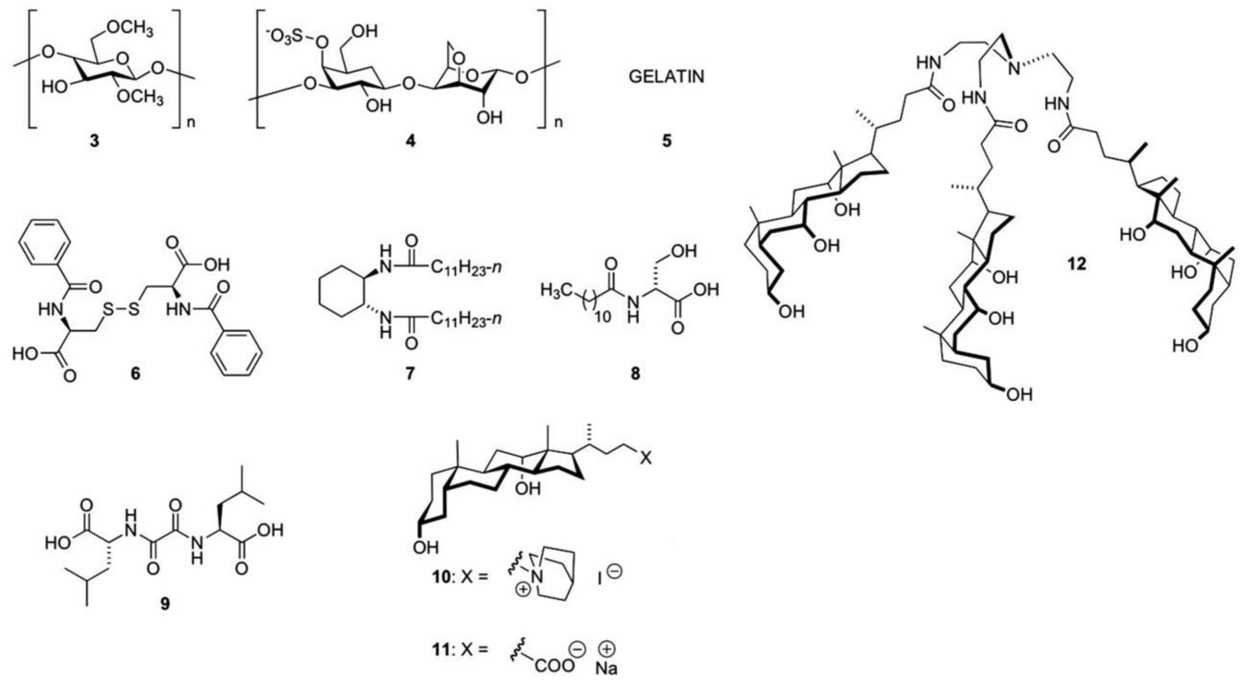


Figure1. 25 Differential scanning calorimetric thermograms of Ionic gel electrolytes (IGEs) with different LMOGs and the photographs of IGEs as presented by Tao et al.[195]

1.4.6 LMOGs as reaction media /catalytic systems

Gels made of low-molecular-weight compounds represent considerable potential as reaction media. The solid-like appearance of a gel is a result of the entrapment of the liquid in the interstices of a solid 3D-matrix of gelator molecules. The formation of the solid matrix is a consequence of the entanglement of 1D- supramolecular strands of gelator molecules. This can present a controlled environment for the reaction. Carrying out reactions in a constrained environment can provide the advantage of specific interactions between the reactants, leading to better selectivity.

Recently Bachl et al.[196] have investigated Riboflavin tetraacetate (RFT)-catalyzed aerobic photooxidation of 1-(4-methoxyphenyl) ethanol, as a model reaction under blue visible light in different soft gel materials, aiming to establish their potential as reaction vessels for photochemical transformations. They made use of Low molecular-weight and biopolymer-based gels **(Scheme 1.20)** as reaction vessel. Physical entrapment of both the catalyst and the substrate under optimized concentrations into several hydrogel matrices **(Figure 1.26)** allowed the photooxidation with conversions between 55 and 100%.



Scheme 1.20 Structures of various gelators used to study Riboflavin tetraacetate catalyzed photooxidation of 1-(4-methoxyphenyl) ethanol in gel media synthesized by Bachl et al.[196]

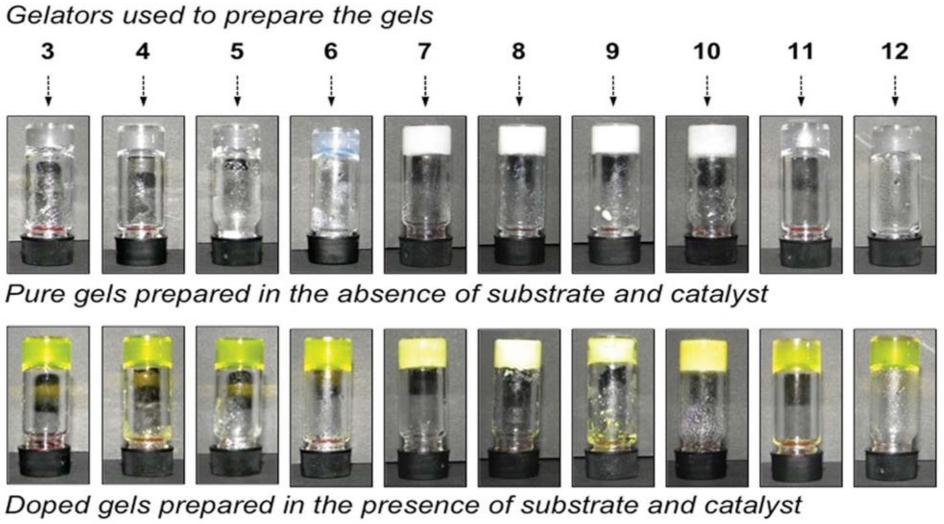


Figure 1.26 Photographs of vials containing stable gels prepared with each gelator (i.e., 3–12) in the absence and presence of substrate 1 and the Riboflavin tetracetate.[196]

1.4.7 Hydrogels in medicinal applications

Hydrophilic hydrogels have been of special interest due to their unique properties and potential applications in area of medicine such as cancer therapy,[197] protein delivery,[198]formulation of drugs[199]etc. In particular; localised and controlled release of drugs is important because of the risk of side effects if the drugs are released in a haphazard manner. Due to the reversible nature of the interactions holding the gel structure together, they can be designed to respond to various stimuli, like a change in pH, ionic strength, or the action of an enzyme to break the hydrogel structure and release the drug at specific targets.

Baral et al. [200] have just reported delivery systems capable of maintaining a sustained release of protein drugs at specific sites. They designed N-terminal protected long chain amino acid (11-aminoundecanoic acid) containing tripeptide, which formed a stable translucent hydrogel in phosphate buffer at physiological pH of 7.46 **(Figure 1.27)**.It possesses remarkable mechano-responsiveness (thixotropy) which leads to the injectability of the peptide hydrogel.

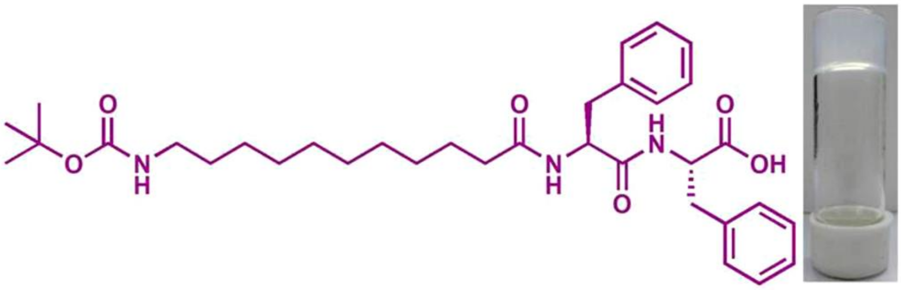


Figure 1.27 Structure of the gelator and the hydrogel in phosphate buffer of pH 7.46.[200]

They demonstrated the utility of hydrogel for entrapment and sustained release of an antibiotic vancomycin and vitamin B_{12} at physiological pH and temperature for about two days. The MTT assay of the gelator molecules showed almost 100% cell viability of the peptide gelator, indicating its noncytotoxicity. The thixotropic nature of the peptide hydrogel makes it injectable very convenient **(Figure 1.28)**.

Yu et al. [201]have demonstrated improvement in the oral bioavailability of curcumin using novel organogel based nanoemulsions. Curcumin has multiple health supporting properties, such as anticancer, anti-inflammatory and antioxidant activities. Additionaly it is also established that curcumin shows no toxicity in human.[202] However, curcumin bears low oral bioavailability, this limits its application.

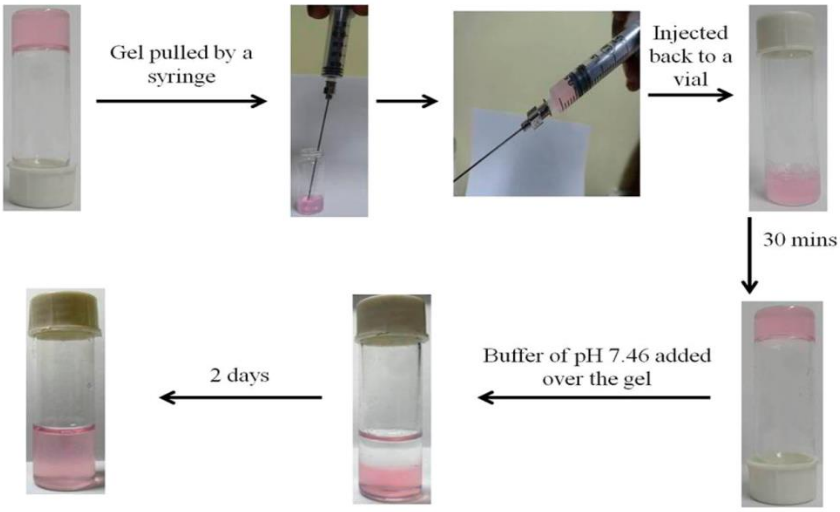


Figure 1.28 Photographic representation of the injectable nature of the hydrogel and its vitamin release phenomenon with vitamin B_{12} as shown by Baral et al.[200]

Hence they developed a novel organogel for curcumin encapsulation and oral delivery. High curcumin loading was achieved by the incorporation of Tween 20 in the medium chain triacylglycerols. Furthermore, monostearin was used as a GRAS (generally recognised as safe) organogelator to form the food-grade organogel. In vitro lipolysis profile revealed that the digestion of nanoemulsion was significantly faster and more complete than the organogel as shown in **Figure 1.29**.

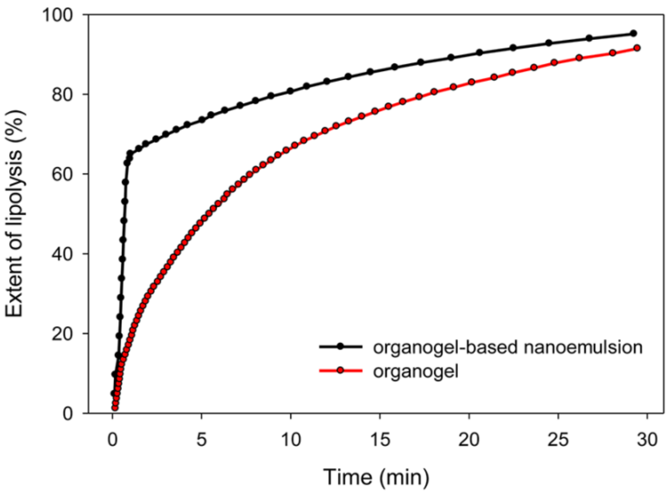


Figure 1.29 Comparison of the in vitro lipolysis of the organogel and organogel - based Tween 20 nanoemulsion presented by Yu et al. [201]

This organogel anticipated as the potential candidate to be used for oral delivery of curcuminoids as well as for incorporating in functional foods system.

1.4.8 Gels in conservation of Art

Gel systems have been widely used in several applications since the middle of the last century. Gels have proven their popularity in cosmetics, detergents, food, biomedical applications and so on; hence gels have grabbed a great deal of attention in the area of scientific research. However, they also registered their utility in the area of art. An interesting application of physical gels in the field of conservation science was proposed for the cleaning of oil paintings. The use of solvents in their gelated conditions would be a better option than using pure organic solvents to clean painted surfaces that deeply penetrate the painted layer, probably causing damage.[203] Wolbers proposed an innovative methodology for cleaning of painted surfaces using the liquid cleaning agents entrapped in gel matrices.[204] Cleaning artwork with gel has increased massively during the last decades. Aqueous, nonaqueous, and mixed gels have been utilised to remove varnish and over paint from paint surfaces, to remove stains from stone and stains from paper.[205]

Carretti et al. [206] have reported a new class of gels for the conservation of painted surfaces. They synthesized an isothermally rheoreversible organogels from polyamine-based gelators whose organic solvent solutions become gels when CO_2 is added by bubbling, which employed as the cleaning agents. The novelty of their approach was that the gel couid be applied directly onto the painted surface, and then removed easily by converting the gel to a low-viscosity fluid in situ by a mild chemical agitation. Thus, they demonstrated a convenient method which involves the application of a gel with an ammonium/carbamate gelator of polyethylenimine ($PEICO_2$) to a painted surface and subsequent addition of a drop of a weak acid at the moment that the gel is to be removed. The cleaning efficiency of the $PEICO_2$-based gel has been verified by applying it on the surface of not-aged easel painting **(Figure 1.30)**.

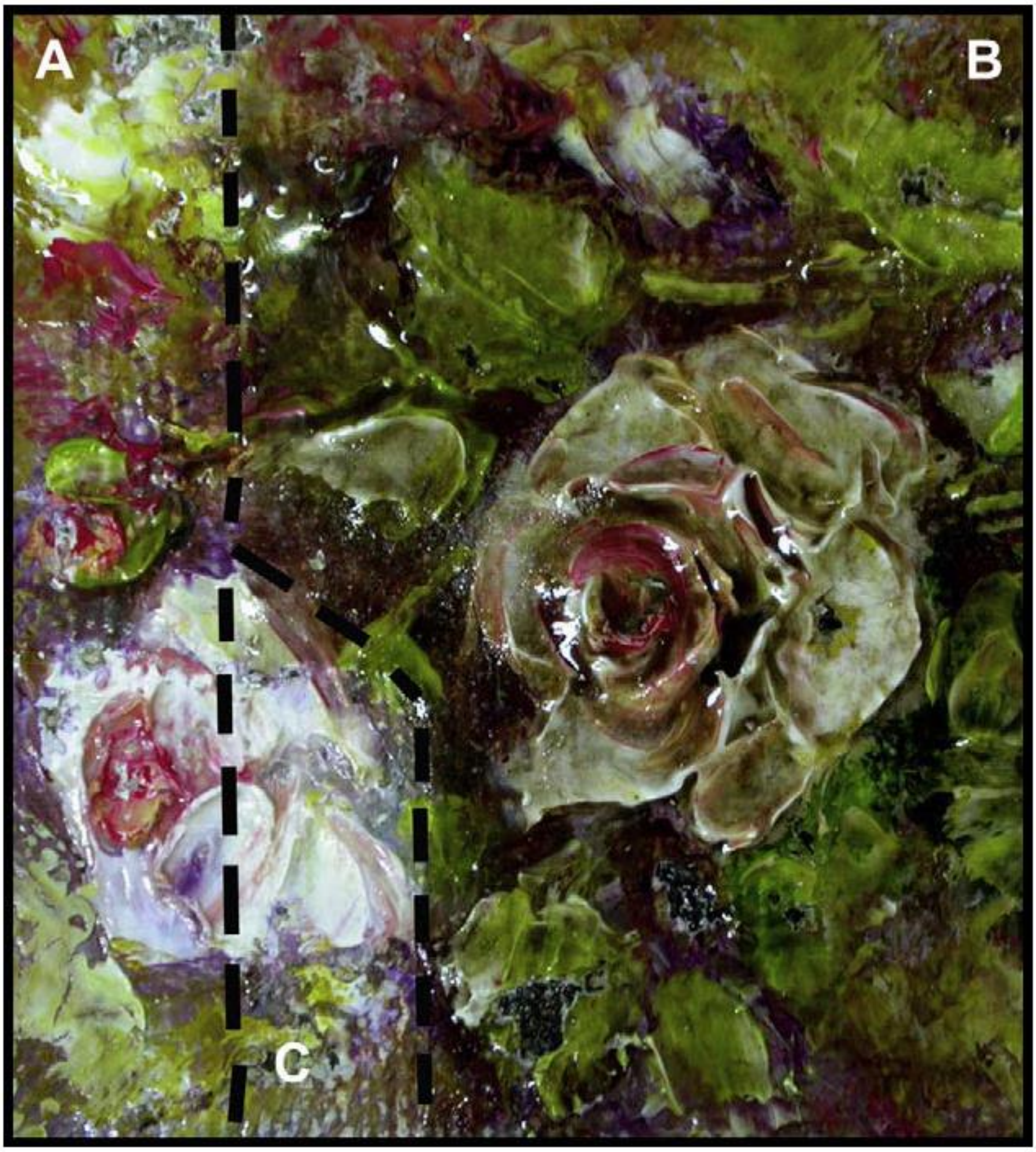


Figure 1.30 Not-aged easel painting used to verify the efficacy of the PEICO$_2$-based gels. (A) is the free paint surface used as reference, (B) is the portion of the paint coated by a surface layer of dammar varnish contaminated with a Siena's earth brown pigment, and (C) is the portion of the paint after being cleaned with the gel as presented by Carretti et al.[206]

Recently, Domingues et al.[207] have reported hydrogels based on semi-interpenetrating chemical poly (2-hydroxyethyl methacrylate)/poly (vinylpyrrolidone) networks with suitable hydrophilicity, water retention properties, and required mechanical strength to avoid residues after the cleaning treatment. An artificially soiled Thang-Ka mock-up artefact was considered to evaluate the efficiency of the chemical gel.

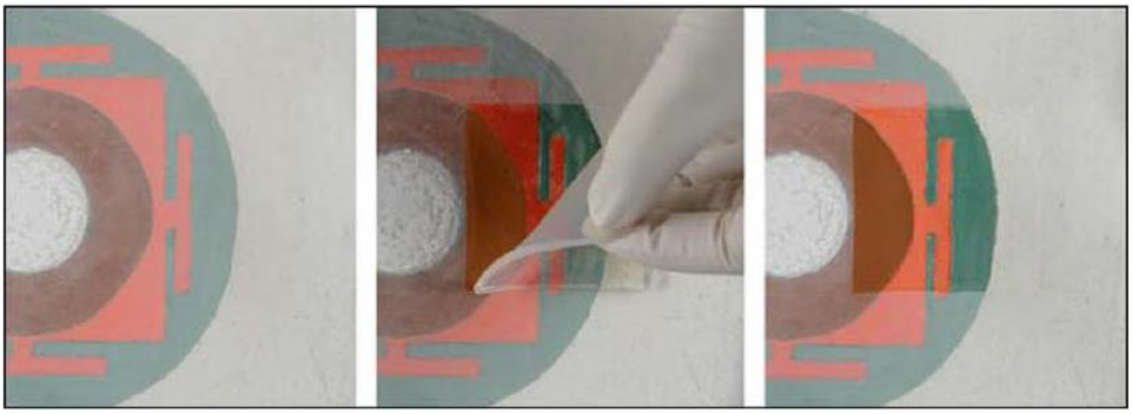


Figure 1.31 Stages of cleaning on Thang-Ka mock-up as presented by Domingues et al.[207]

1.5 Aim and outline

To exploit relatively weak and highly directional non-covalent interactions such as hydrogen bonding, and relatively strong and not-so-directional interactions such as electrostatic interactions to generate interesting and intriguing supramolecular architectures and also establish their role in supramolecular gelation/non gelation by determining the structure –property correlation; Moreover, to investigate the applications of supramolecular gel, if any.

Chapter 1 deals with the introduction of supramolecular chemistry, crystal engineering and Low molecular mass organogelator (LMOGs). The role of non-covalent interaction as designing tool in crystal engineering is discussed. Introduction, classifications, characterisation, applications and design of Low molecular mass organic gelators (LMOGs) is also emphasized.

Chapter 2 describes the syntheses and characterization of Melamine-based mono carboxylate salts of aliphatic dicarboxylic acids. All the salts are tested for gelation behaviour towards various solvents, including water. Two salts, melaminium hydrogen maleate and melaminium hydrogen adipate were found to be outstanding hydrogelators. The packing of gelator molecule melaminium hydrogen maleate in gel and dried state was probed by single crystal and powder x-ray diffraction studies. Single crystal X-ray study of gelator molecule with and without its gelling solvent suggested that supramolecular assemblies leading to a porous network may be one of the prerequisites for molecules to show immobilization of water. An application of two-component gelator melaminium hydrogen maleate as a template for silver nano-particle synthesis was demonstrated.

Chapter 3 discusses the syntheses of a new class of organic salt/co crystal. One of the salts namely 2-amino -1, 3-thiazolium hydrogen sebacate turn out to be non-polymeric hydrogelator. Single-crystal structures of the salts/cocrystal displayed a 2D hydrogen bonded network, irrespective of their gelling/nongelling properties. Moreover, the formation of porous hydrogen bonded network in structure of 2-amino 1, 3-thiazolium hydrogen sebacate seems to be one of the prerequisites for hydrogelation and this observation matches well with our observation made previously. So, we have proposed that molecules capable of forming three-dimensional supramolecular assembly with void may act as a potent hydrogelator.

Chapter 4(A) deals with the synthesis of a novel class of thiazole based organogelator [i.e. N-(thiazol-2-yl) tetradecanamide, N-(4-methylthiazol-2-yl) tetradecanamide and N-(5-methylthiazol-2-yl) tetradecanamide] and their characterization by various techniques such as VT-NMR, IR, single crystal and powder x-ray diffraction. Role of unusual H-bond interactions such as C-H...N and van der Waals interaction was probed as driving forces for physical gelation of various polar and non-polar solvents. A structure-property correlation between various derivatives of thiazole is explored for their gelation or non-gelation behaviour.

Chapter 4(B) discusses the synthesis and characterization of series of thiazole based amides namely, **(i)** [N-(thiazol-2-yl) decanamide] to [N-(thiazol-yl)stearamide], **(ii)** [N-(4-methylthiazol-yl)decamide] to [N-(4-methylthiazol-yl)stearamide] and **(iii)** [N-(5-methylthiazol-yl)decanamide] to (N-(5-methylthiazol-yl)stearamide].They were also investigated for their gelation properties. The thiazole amides which turned out to be good gelator for various organic solvents have also displayed odd-even effect towards organogelation with an additional increase in the methylene functional group. Template directed synthesis of silver and ZnO nanoparticles were carried out using various gelling agents and shape of nanoparticles of Ag and ZnO was found to be dependent upon the alkyl chain length of thiazole amides. Silver nanoparticles embedded in one of the gelling system i.e N-(5-methylthiazol-yl)hexadecanamide found to be good anti-bacterial agent towards gram positive and gram-negative bacteria.

Chapter 5 describes 2-aminothiazole and its derivatives, namely, 2-aminothiazole, 2-amino-4-methylthiazole and 2-amino-5-methylthiazole as ligands in metellogel formation. The coordination polymer of 2-amino-4-methylthiazole with Hg $(OAc)_2$ demonstrated room temperature gelation of water along with thixotropic behaviour. The role of the methyl functional group in controlling and enhancing the gelation behaviour has been demonstrated. Coordination polymer based metallogels of 2-amino-4-methylthiazole with Hg $(OAc)_2$ and 2-aminothiazole with Hg $(OAc)_2$ were found to be an ideal candidate for mercury ion detection (detection limits as low as 0.1 ppm with visual observation in a biphasic system of water/chloroform) and almost quantitative removal of Hg^{2+} ions from contaminated water.

Chapter 6 discusses the synthesis and characterization of thiazole amides having aromatic ring in its backbone. N-(thiazol-2-yl)benzamide and its derivatives are explored. Aromatic ring attached through amide linkage provides an opportunity to study weak non-covalent interaction such as (methyl) C-H... π, π- π, (methyl) C-H...N, (methyl)C-H...S, etc. in inducing supramolecular gelation. To study the effect of diamide functionality on gelation behaviour, Derivatives of thiazole based Pthalamide are also synthesized .All the synthesized compounds examined for gelation behaviour towards polar and non-polar solvents. Their Single crystal X-ray structures of were analyzed to establish structure property correlation.

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