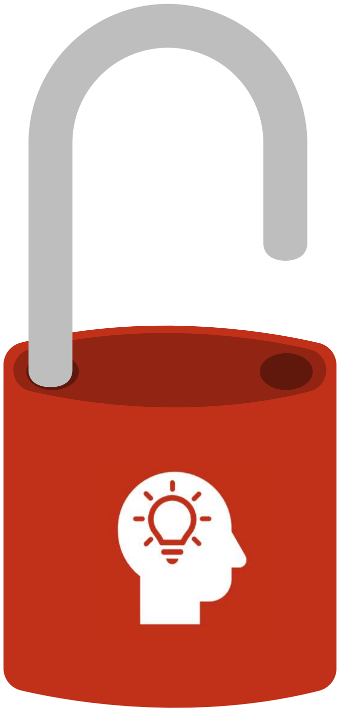
Chapter 1

Introduction



1.1 Supramolecular Chemistry

Supramolecular chemistry is "*chemistry beyond the molecule*" as define by Jean Marie Lehn[1] who was awarded with the Nobel prize in chemistry in 1987 for his contribution in development of molecule which can mimic important chemical function in the living organism. It is an active area of research mainly referring to understand the non-covalent interactions like H-bonding, π-π interactions, van der Waals Interactions and hydrophobic forces and using them to make supramolecules from molecules with potential applications. Non-bonded interactions between molecules form the basis of highly specific functions, reaction, transport in the living organisms such as substrate binding with receptor unit, enzymatic reactions, assembling of multiprotein complexes, and many more.

1.2 Self assembly

Self-assembly is the spontaneous and reversible self-organisation of the molecule to form a complex entity with the help of various non-covalent interactions[2–4]. Any self-assembly has three distinct features, that are

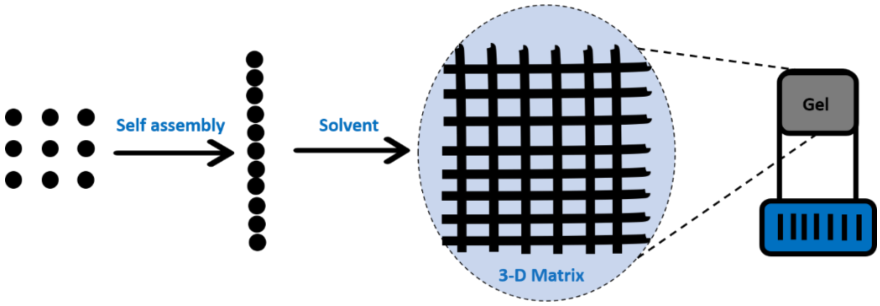
1) **Order:** It must consist of a high order than the isolated molecule.
2) **Interaction:** In this various non-covalent interaction like H-bonding, π-π interactions, van der Waals Interactions and hydrophobic forces important as they determine the physical state and solubility in the liquid, furthermore they provide direction and specificity in the self-assembly process.
3) **Building block:** They consist of an atom or molecule comprising of different shape and functional groups.

Generally, it implies that self-assembly is depends upon the three distinct features that building block must consist of a required functional group which self-assembled with the help of various interaction to form assembly of high order. One of the elegant examples of supramolecular assembly is supramolecular gels or physical gels.

1.3 Supramolecular gel

Supramolecular gels are defined by various researchers in diverse ways. In 1861 Graham define gel as "*The colloid possesses ENERGIA. It may be looked upon as the probable primary source of the force appearing in the phenomena of vitality*"[5] .

According to Jordan Llyod "*the colloid condition, the 'gel' is one which is easier to recognise than to define*"[6]. Herman had defined gels in more elaborate as, "*(a) . . . are coherent colloid disperse systems of at least two components, (b) . . . exhibit mechanical properties characteristic of the solid state. . .," and "(c) both the dispersed component and the dispersion medium extend themselves continuously throughout the whole system*"[7]. In Supramolecular gel, immobilization of solvents usually occurs due to low molecular weight gelators (LMWGs) typically having molecular weight less than ~3000 Daltons, self-assembled into fibre, ribbons, sheets and sphere utilizing various non-covalent interactions to form 3D network to confine the solvents in it. (Scheme 1.1)



Scheme 1.1 *Mechanism of gelation*

1.3.1 Classification of supramolecular gel

Supramolecular gel, a colloidal state, contain dispersion medium and dispersed phase. They can be classified based on the solvents gelled by LMWGs (Figure 1.1) or nature of non-covalent interactions generating the cross-linked 3D network immobilizing the solvent (Figure 1.2).

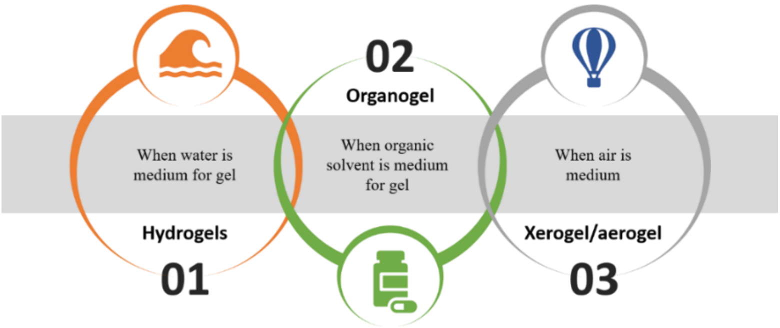


Figure 1.1 *Classification of gels on the basis of medium*

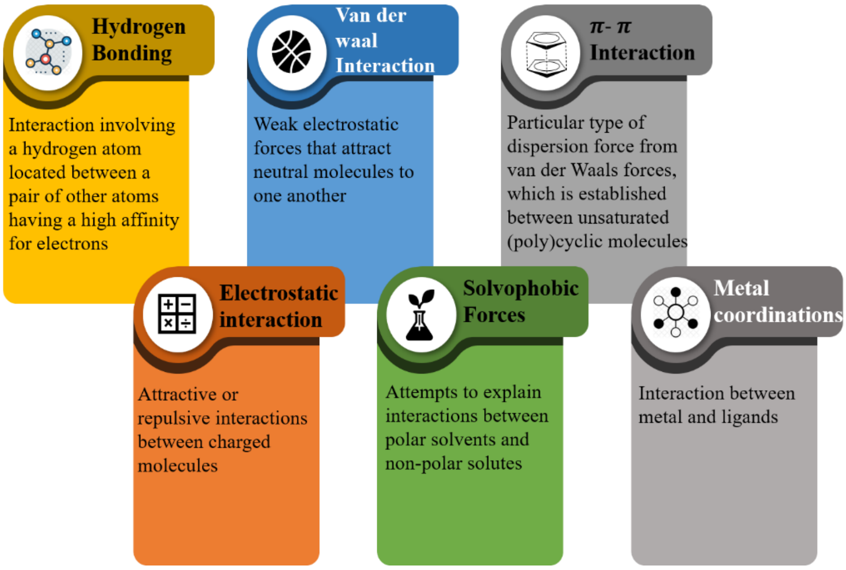


Figure 1.2 Classification based on cross linking.

1.3.2 Low Molecular weight gelators (LMWGs)

LMWGs are the molecule which are the building blocks consisting of different functional groups (urea, amide, thiourea nucleobases, etc.) and organic/inorganic backbone (anthryl, carbohydrates, amino acids, dendrimers, etc) (Figure 1.3). It is well understood that the gelation is a balance between solubilization and crystallization, therefore to the gel the given solvent molecule should provide this delegate balance of solubilization and crystallization. Therefore, in any gelator must contain the solvophobic groups to promote aggregation and solvophilic groups for solubility. Yet it is not possible to design the gelator definitely giving gel in selected solvent and the discoveries of gelator is still fluke.

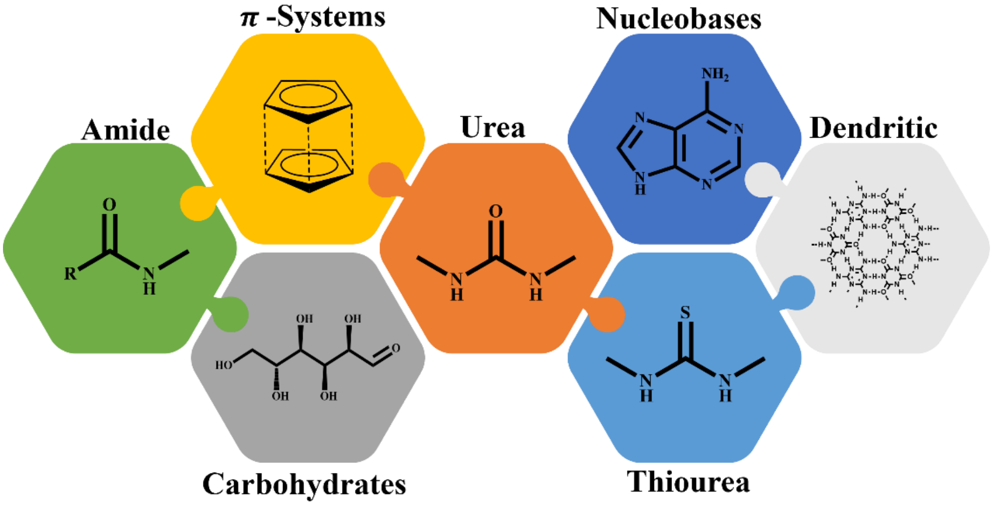


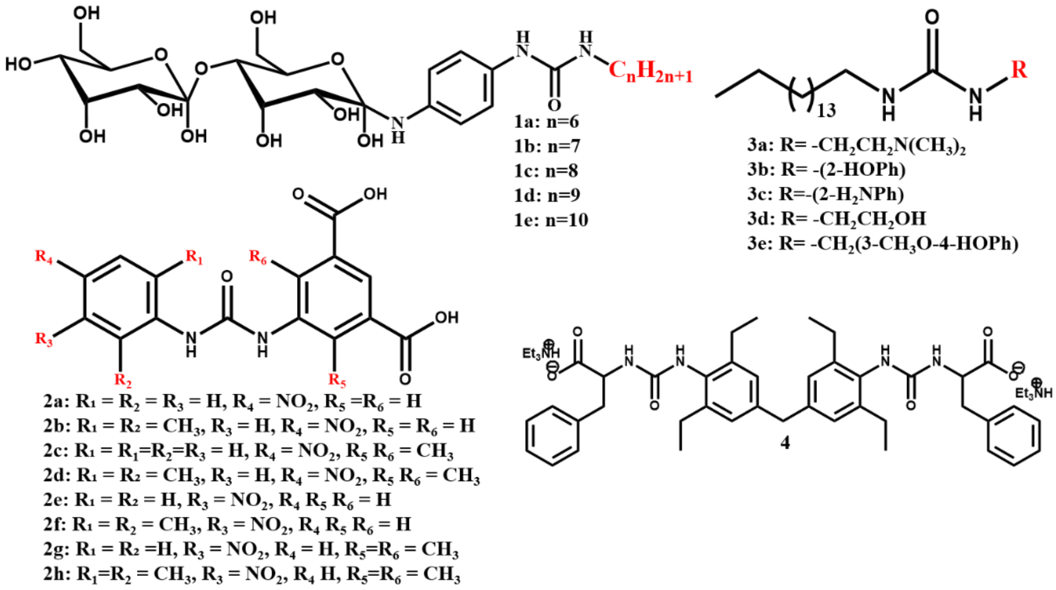
Figure 1.3 Various functional groups present in LMWGs

1.3.2.1 Urea based LMWGs

As fundamental strategy to design LMWGs is to incorporate the functional group which can induce the one dimensional self-assembly through non-covalent interactions. Urea is the prominent choice due to their ability to form directional assemblies. LMWGs containing urea functionality are summarized in the excellent reviews[8,9]. In the present literature review, we would like to discuss some of the potential applications of urea based gelators as follows:

Environmental remediation

Supramolecular gels have high porosity and solvent compatibility which makes them potential substances to solve the various environmental issue[10]. For instance **Yamanaka *et al*.** synthesized the amphiphilic lactose-based urea**(1a-1e)** with the alkyl chain ranging from hexyl to decyl group and was probed for their gelation capability[11](Scheme 1.2). It was found that length of alkyl chain significantly affects the gelation ability. **1c** Hydrogel so formed was able to entrap the cationic organic dyes like Rhodamine 6G which is stable even when submerged in water. Furthermore, hydrogel shows sol-gel transition in the presence of β-galactosidase enzyme (mainly present in small intestine) due to the hydrolysis of lactose group and slowly release the dye. Thus, this property can make hydrogel a carrier of the drug. In another work by **Hayes *et al.*** investigated eight pH sensitive hydrogelators (**2a-2h**) (Scheme 1.2) containing bis aromatic urea core containing carboxylic acid functional group on one aromatic core[12].

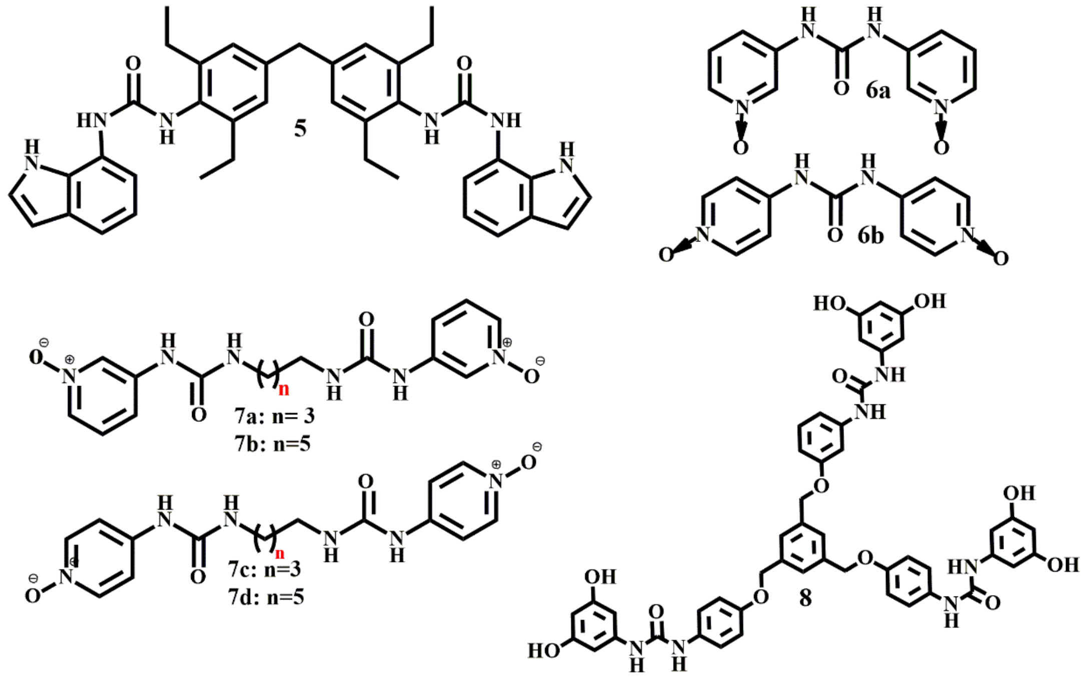


***Scheme 1.2** Chemical structure of gelators reported in the literature*

Gel is found to form at low pH by simply introducing the mineral acid in the system. Out of eight hydrogelators **2a, 2f** and **2h** were most efficient in the uptake of methylene blue from its solution which opens the new prospect for designing high efficiency water purification systems. Study presented by **Corea *et al.*** they synthesized ten compounds consisting of urea and carbamate functional group with the fixed hydrophobic part (Hexadecyl chain), while the hydrophilic part was varied to compare their ability to form supramolecular gels[13]. Urea derivative was found to be a better gelator than amide which is attributed to the additional N-H group in the molecule. Furthermore, removal efficiency of organic solvent from water is also tested using urea(**3d**) and amide derivatives (Scheme 1.2). **J.W. Steed and his co-workers** developed *L*-phenylalanine derived bis-urea supramolecular hydrogel consisting of the fluorescent hybrid quantum dots and enzymes like acetylcholinesterase (AChE) and choline oxidase (ChOx)[14]. The enzyme-functionalized gel (**4**) network so produced can detect insecticide dichlorvos with the detection limit of 2.61 X 10^{-8} M which outperformed biosensor available and provided a new scope for the development of environmental benign techniques (Scheme 1.2).

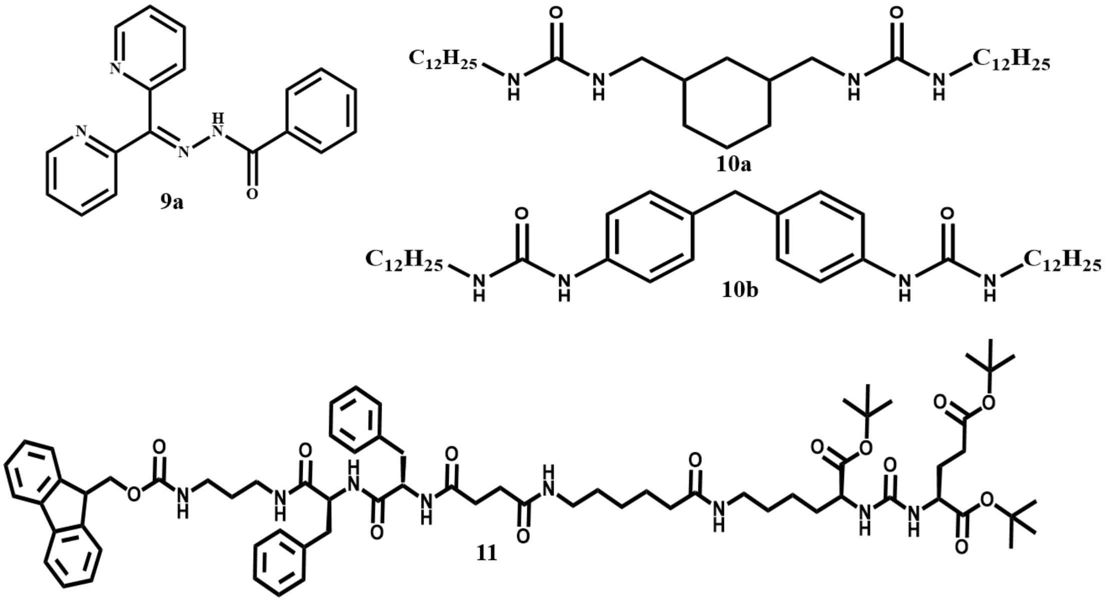
Stimuli responsiveness

The intrinsic property of supramolecular gel is their reversible gel to sol transition in response to the external stimuli like heat, pH, light, sound and chemicals. Smart stimuli responsive supramolecular gels can be synthesized by simply incorporating receptor units in LMWGs backbone. For instance, in the interesting work of **Steed *et al.*** three novel bis urea compounds containing tetraethyl diphenylmethane spacer has been synthesized. One of the gelator**(5)** (Scheme 1.3) was found to give gel in the mixture DMSO:Water[15]. Anion dependent study was done on the same gel system, and was found that anions like Fluoride, benzoate inhibit the gel formation, whereas dihydrogenphosphate ($H_2PO_4^-$) delay the gelation by 24 hours. Overall work opens new realm in the field of biomedical applications. **Damodaran *et al*.** had reported pioneer work of showing the role of non-covalent interactions by altering the functional groups in pre reported gelators[16]. In this pyridyl moieties of the two gelators (viz amide and urea based) are modified to Pyridyl N-oxide (**6a-6b**) (Scheme 1.3).



Scheme 1.3 Chemical structure of gelators reported in the literature

This modification of parent gelators enhanced thermal and mechanical stability and induced the gelation properties in solvents and mixture of solvents. Furthermore, stimuli responsive properties were studied, where **6a** shows better anion sensing than **6b** towards Iodide, acetate and cyanide salts. **Similar study** has been carried out by the **Damodaran *et al*.** where linkers are also modified and gelation and stimuli-responsive properties are compared with the parent molecules[17]. Additionally, it was demonstrated that most of the salt used in the study enhanced the mechanical stability of the hydrogel of **7a-7d** (Scheme 1.3) with the exception of aluminium chloride, cadmium chloride, zinc chloride, and copper chloride where degelation is observed. **Yamanaka *et al*.** designed tris-urea(**8**) (Scheme 1.3) compound containing resorcinol hydrophilic units which can gelate basic buffers whose pH ranges from 10-11[18]. This system is found to be responsive to the pH changes and gelation and de-gelation can easily be achieved by adding NaOH and Boric acid in appropriate amount.

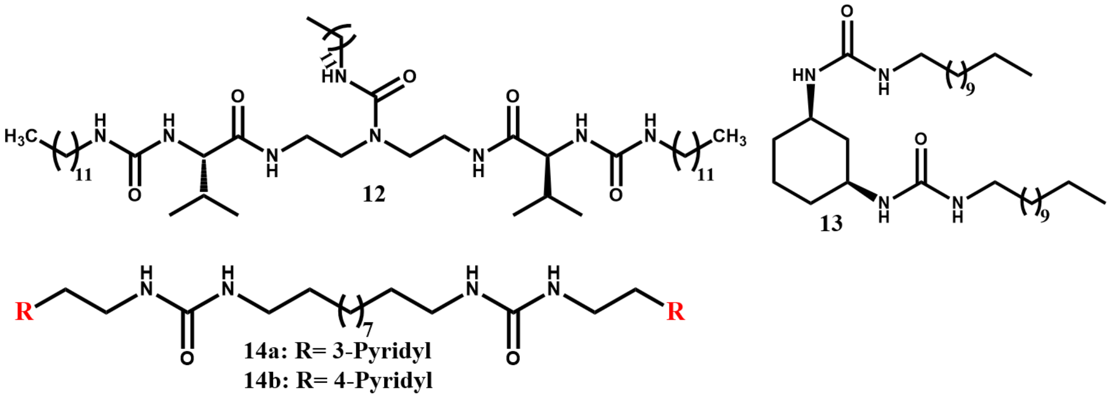


Scheme 1.4 Chemical structure of gelators reported in the literature

Damodaran *et al*. have developed the amide and urea like hydrazone (**9a**)(Scheme 1.4) and semicarbazone (**9b**)(Scheme 1.9) and their gelation properties were probed[19]. **10b** was found to be more fibrous and having better thermal and mechanical stability as compared to **9a**. Stimuli responsive studies includes the effect of metal salts and anion on the gels and suggests that metal disrupts the gel network to give sol whereas anion isn't able induce any gel-sol transition.

Cosmetic and biomedical application

Paderas *et al*. designed sixteen various molecules bearing cyclic and aromatic centre and their gelation capabilities and rheology modifier properties is probed in cosmetic solvents[20]. Aim of the study explore the organogels obtained and tuning its properties for efficient use in the commercial cosmetic formulations. Structure of some of the best gelators (**10a and 10b**) is provided in the scheme 1.4. **Beloglazkina *et al*.** synthesized urea and Fmoc containing diphenylalanine based hexaamide(**11**)(Scheme 1.4) and screen it in various solvents for its gelation properties[21]. Using various physicochemical techniques, authors obtained main driving force for the gelation and also demonstrated the effect of solvent on the morphology of the gel. An approach of attaching the alkyl Urea to the amino end of the different pseudopeptidic structure by **Luis *et al*** was found to show the excellent gelation capabilities in organic solvents of different nature[22].



Scheme 1.5 *Chemical structure of gelators reported in the literature*

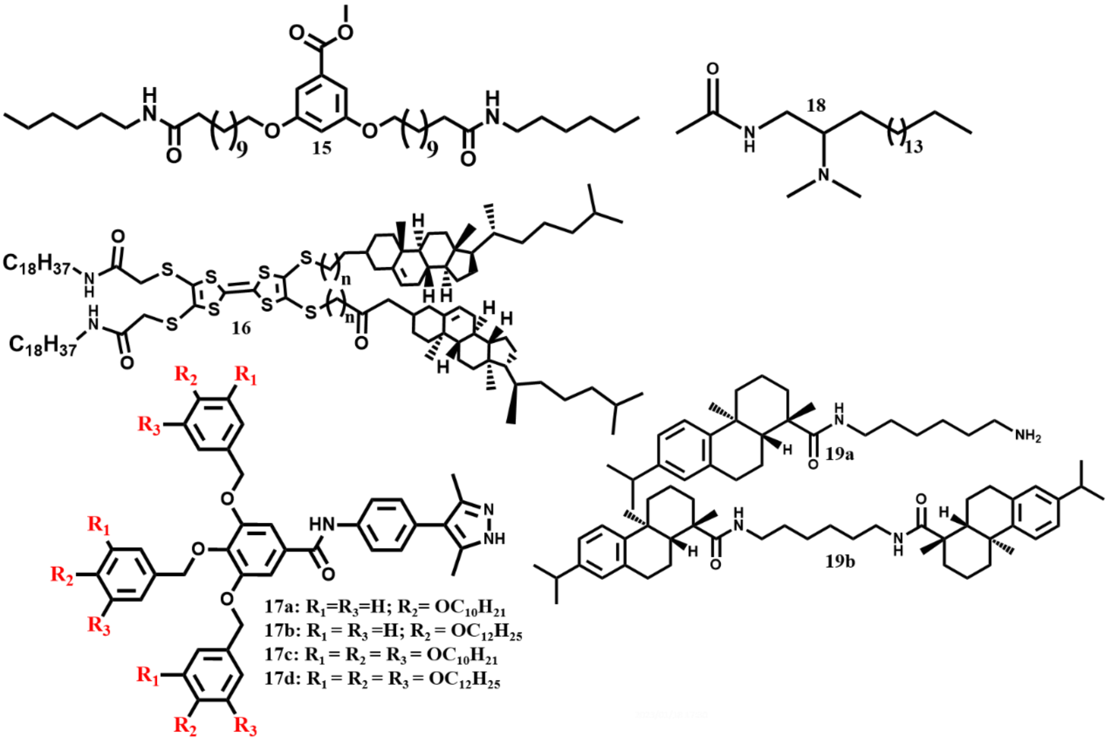
Study of three gelators indicates that simple addition of supramolecular guest like suberic acid with **12** (Scheme 1.5) can achieve the gelation of active substance like terpene natural oils and mixture of flavours and fragrances. This property could be useful to develop supramolecular systems for control release of active compounds. **Jung *et al.*** demonstrated the *in-situ* formation of mixing 1,3-diclohexaneamine and isocyanate derivative without any catalyst in various solvents[23], leading to the formation of urea moiety (**13**) and thermally reversible supramolecular gel through intermolecular hydrogen bonding (Scheme 1.5).

In a new approach by **Dawn *et al***., show that two pyridyl based bis-urea derivative (**14a** and **14b**) can be design to eliminate the other interactions which interfere in the gel formation and can gel the solvent even in the presence and absence of metal ions[24]. Moreover, **14b** and mixed ligand **14a** +**14b** can form hydrogels even in the absence of metal ions (Scheme 1.5). Such study is found to be beneficial for designing a new metallosupramolecular gels with potential functional applications.

1.3.2.2 Amide based LMWGs

Environment remediation applications

Castillo *et al.* designed bis-amide derivative containing hydroxybenzoic acid aromatic core **(15)** (Scheme 1.6) and tested in various solvents for its gelation capabilities[25]. Gelator was found to be useful for gelling fuels like gasoline and diesel. Furthermore, it is able to selectively immobilize gasoline from the water/gasoline mixture and may find application in remediation of oil spills in the water bodies.



Scheme 1.6 *Chemical structure of gelators reported in the literature*

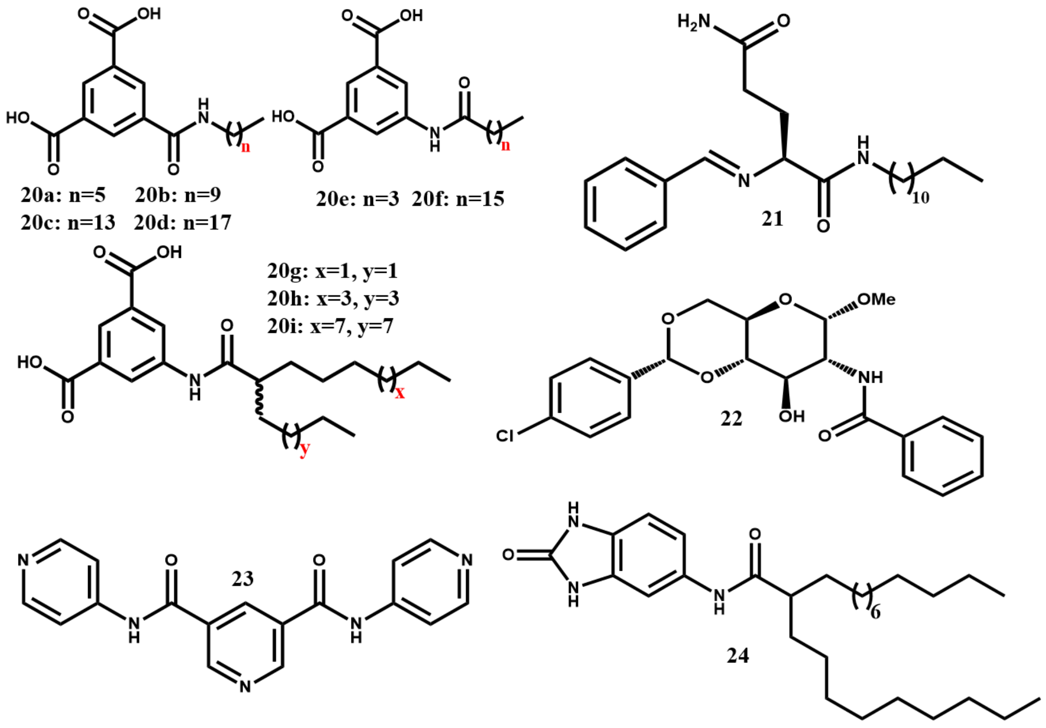
Hou *et al.* prepared the series of compounds consist of two cholesterol molecule and two hydrophobic chain via amide linker connected to tetrathiafulvalene core[26]. It was demonstrated that the gel of **16**(Scheme 1.6) in cyclohexane solvent had strong ability to absorb toxic dye Rhodamine B from its solution. Additionally, half of molecule from the series show liquid crystalline phase of type Smectic A. In another work by **Gimenez et al.** synthesized Pyrazole dendrons consist of two different linkers viz. amide(**17a-17d**) (Scheme 1.6) and ether are also investigated for its liquid crystalline (LC)/gel behaviour[27]. The study concludes that the series containing amide linkers produces super gel and also stabilizes the LC behaviour with the luminescence in the aggregated states. The work opens new window for development of stimuli responsive soft matter with the aggregation induced emission.

Akbulut *et al.* reported novel pH-responsive two component gel system consist of long chain amino-amide (**18**)(Scheme 1.6) and maleic acid[28]. The system demonstrated the sol-gel transition from pH 2 to 10. According to authors system demonstrated far better static viscosity, salt stability, enhanced oil recovery applications and pH responsiveness than traditional system like Cetyltrimethylammonium bromide or chloride (CTAB or CTAC).

Han *et al.* prepared two dehydroabietic-based mono-amide (**19a**) and diamide (**19b**) (Scheme 1.6) which can gel various mixed and single solvents[29]. Various physico-chemical techniques were employed and gelation mechanism was established. Additionally, carbon tetrachloride (CCl_4) gel of **19b** was found to effectively remove Congo red dye from the aqueous solutions. A work published by **Makeiff *et al.*** expands the design of supramolecular self-assembled networks (**20i**) for the purification of water and environmental remediation by selectively gelation of oil from oil-water mixture and removing the dye from water samples[30]. In this work novel 5-alkylamido isophthalic acid derivatives with linear (**20a-20f**) (Scheme 1.7) and branched alkyl chain with amide has been synthesized. Particularly, compounds with the branched alkyl chain (**20g-20i**) show ‘supergelator’ behaviour, forming gel stable upto months. Gelator ((**20a-20f**) displayed H-bonding and π-π stacking of aromatic groups as driving force of gelation and its application for removal of unwanted material was established.

Biomedical applications

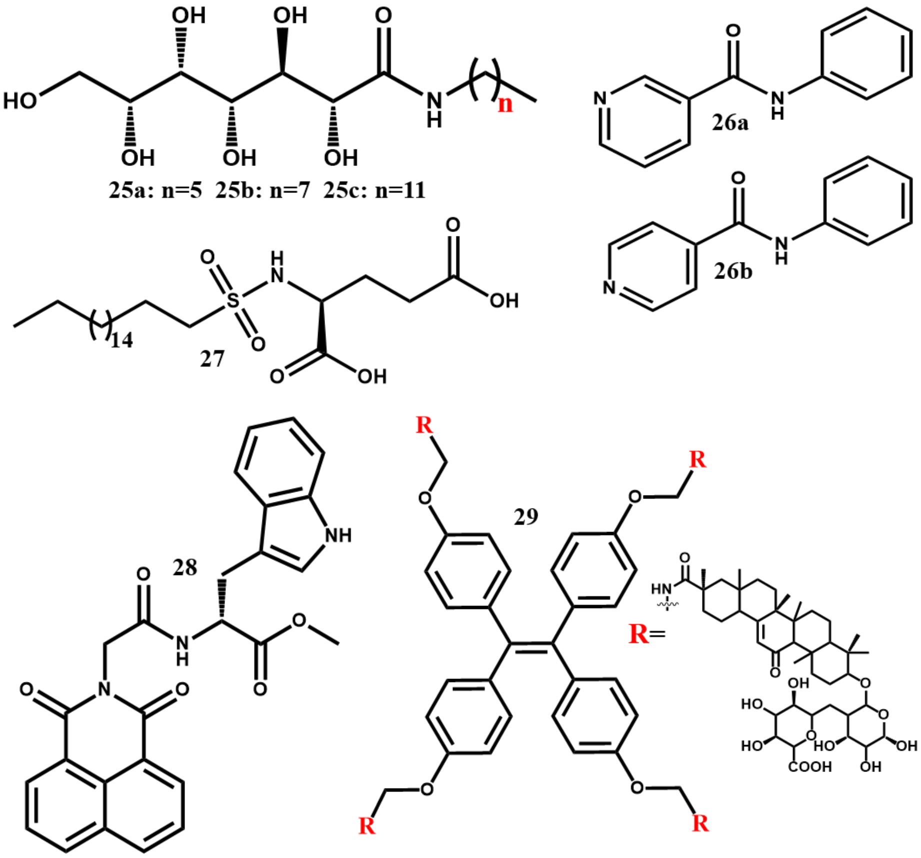
Jamal *et al.* synthesized gel of *L*-glutamine amide derivative and benzaldehyde(**21**) (Scheme 1.7) having self-healing characteristics for Nasal delivery of Parkinson’s disease drug L-DOPA[31]. This neurologically active drug loaded hydrogel can potentially avoid first pass liver metabolism and bypass the blood brain barrier, enhancing brain uptake of drug. Animal studies confirms and demonstrate that this drug-hydrogel system outperformed a simple intranasal *L*-DOPA solution. In the work by **Wang *et al***. include the synthesis of a series of para-chlorobenzylidene acetal protected D-glucosamine amide derivatives(15 derivatives) to explore the influence of halide substitution[32].



Scheme 1.7 Chemical structure of gelators reported in the literature

Few derivatives developed remarkably stable gels at concentrations below 0.1% in aqueous solutions, the majority of derivatives formed gels in multiple solvents at concentrations below 2%. The gel of **22**(Scheme 1.7) in water is used for encapsulation and control release of chloramphenicol and naproxen and gel of **22** in DMSO: water (1:1) is also used for removal of Toluidine blue dye from solution. In the research by **Hong *et al.*** ,low molecular weight gelator were constructed capable of gelling in mixed solvent of water and DMSO (or DMF) at only a fraction of 50% or more[33]. This behaviour indicates that gelation is efficiently modulated by the water content in the organic solvent. Furthermore, release of vitamin B12 from the gel of **23**(Scheme 1.7) in Water:DMSO(9:1) system was also evaluated following first order release mechanism. Additionally, xerogel shows good biocompatibility conclude by human unbilical venous endothelial cell culture studies which show that gel have potential of biological application in tissue engineering and control drug release. **Makeiff *et al.*** prepared the seven compounds consisting of different shape and size of alkyl chain connected to the benzimidazolone unit via amide(6 compounds) and urea(one compound) functional groups[34]. Gelation (**24**) behaviour was examined using Hansen Solubility parameters (Scheme 1.7) which established the role of amide functionality and branched chain backbone as designer element inducing better gelation property. Furthermore, cytotoxicity studies of all the compounds concludes its biocompatibility and some molecules possessed therapeutic properties. **Fitremann *et al*.** in their work designed thirteen(**25**)(Scheme 1.8) biocompatible molecules based on gluconamide, glucoheptonamide, galactonamide, glucamide, aliphatic chains and glycine[35]. These molecules are then tested for their applicability in wet spinning and 3D printing. Additionally, authors had also discussed the variation of microstructure with structural alterations.

Dastidar *et al.* design the new series of organic-inorganic-hybrid-systems (OIHS) consisting of eight non-steroidal anti-inflammatory drugs as ligand and N-phenyl-3-pyridylamide (**26a**) (Scheme 1.8) and N-phenyl-4-pyridylamide (**26b**), and $Zn(NO_3)_2$ as potential supramolecular metallogelators and can also act as a Drug Delivery systems(DDS)[36].Most of the synthesized compounds displayed hydrogelation and interestingly, crystal structure of all the compounds show the amide-amide 1D synthon. One of the compounds showed promising result of anti-cancer activity for human breast cancer cell line. The results showed the advantage of crystal engineering approach in designing and developing metallogel for bio-medical applications.

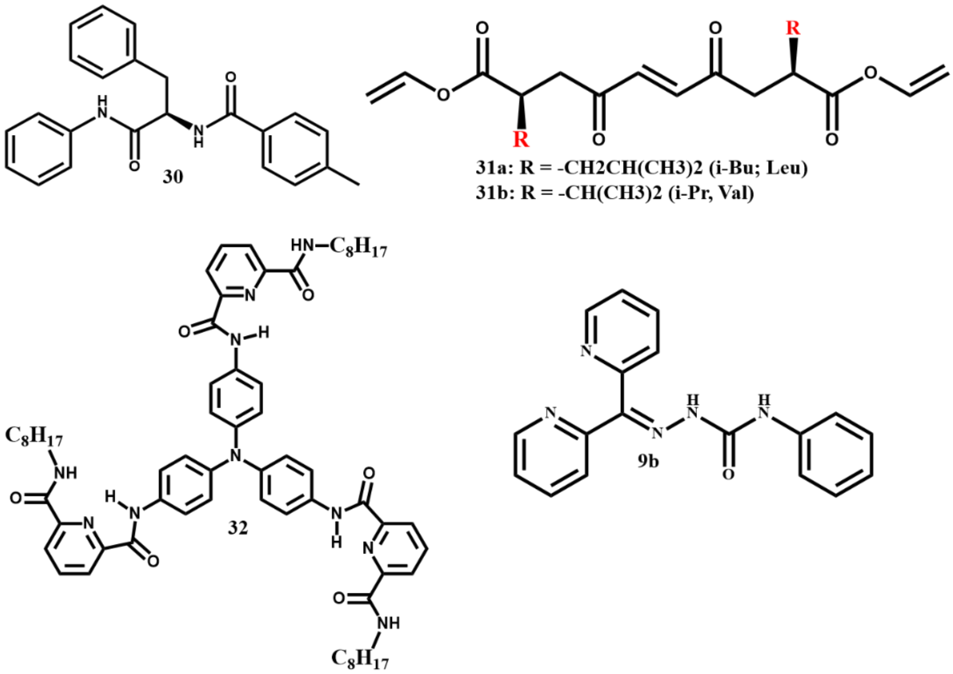


Scheme 1.8 Chemical structure of gelators reported in the literature

Herrera *et al*. presented the simply strategies to modify the pre-reported (*S*)-2-stearamidopentandioic acid(C8-Glu) into (*S*)-2-(octadecylsulphonamido)pentanedioic acid (**27**)[37](Scheme 1.8). The isosteric substitution of amide into Sulphonamide moiety provides enhanced thermal and mechanical properties at low concentration with pH-responsive properties. Furthermore, this modification amplifies the drug release ability of embedded antibiotic vancomycin leading to antibacterial *in vitro* against Staphylococcus aureu. **Nanda *et al*.** reported 1,8-Naphthalimide conjugate of dipeptide(**28**) (Scheme 1.8) which found to give J-aggregation in solid, liquid and gel state which is unique as compared to the properties generally show by unsubstituted Naphthalimide units[38]. The unsubstituted Naphthalimide units are highly fluorescent in solution, but in aggregation mode quenching is observed due to the face-to-face stacking of Naphthalimide units. This remarkable property of dipeptide conjugate of 1,8-Naphthalimide gives Aggregation induced emission (AIE) properties. Finally, this property was used for live cell imaging. **Hu *et al*.** design and synthesized a gelator(**29**) (Scheme 1.8) consist of Tetraphenylethene core and four Glycyrrhizic acids linked via amide bond showing aggregation-induced emission (AIE) feature[39]. Gelation is observed in DMSO/Water and Prop-1,2-diol/Water system. Additionally, effect of water content on fluorescence emission was also studied. The work provides straight forward way to obtain AIE featured gelator obtained from natural products.

Dastidar *et al*. synthesized five bis-amide based gelator decorated with 3-pyridine and *L*-phenylalanine groups along with the various substituted terminal benzoyl groups[40]. Gelation behaviour of all the compound is discussed, **30**(Scheme 1.9) is able to gelate methyl salicylate (MS) used as solvent for topical formulation for medical applications. Selected MS gel loaded with nano-molar iodine showed anti-bacterial properties. **Frkanec *et al*.** synthesized two bis(amido acid)formamide vinyl esters (**31a** and **31b**)(Scheme 1.9) molecules and tested for their gelation capabilities in various solvents[41]. Gelator molecule was found arrest the solvent via hydrogen bonding between amide and carboxyl group.

As this molecule contains reactive alkyl group, gel system was successfully used to carry out polymerization reaction initiated by Gamma or Ultraviolet radiations with the transcript of gel structure into polymers.

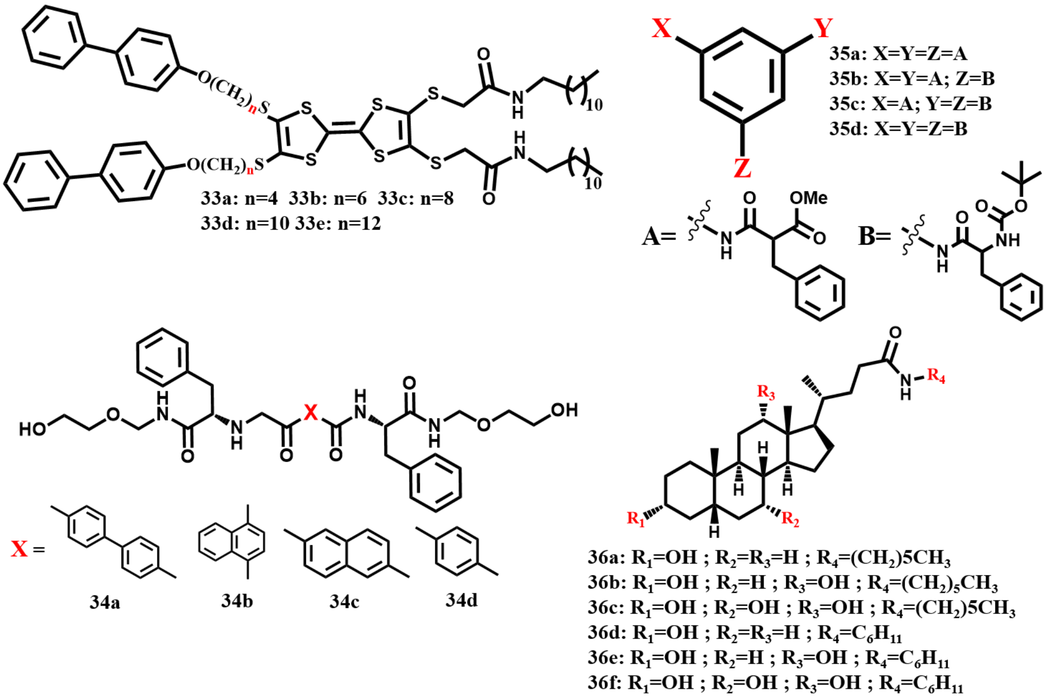


Scheme 1.9 Chemical structure of gelators reported in the literature

Anion and stimuli responsive

Damodaran *et al.* prepared semicarbazone with the urea like motif(**9b**). Gel (DMSO:water) of **9b** was prepared in the presence of sodium or potassium salt of various anions(1 equivalent) like fluoride, bromide, chloride, iodide, acetate and cyanide anions and no deformation of gel was observed. Same experiment with the higher concentration (5 equivalents) of anions was performed and interestingly, only cyanide ion was found to be capable of breaking the gel network. **Cao *et al.*** developed triphenylamine derivative (**32**)(Scheme 1.9) containing three pyridine group which can arrest toluene and o-dichlorobenzene to form yellow light emitting gel[42]. Additionally, this molecule is able to detect the methanol vapour with limit of detection (LOD) of 26.68 ppb. Detection mechanism includes transformation of enol form to amide type because of intermolecular hydrogen bonding interactions.

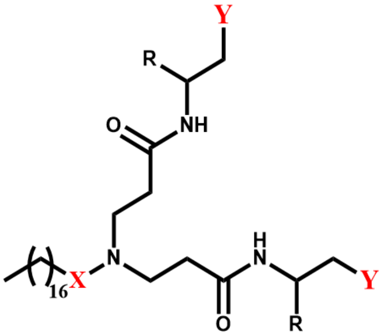
Ma *et al.* developed a series of compounds (**33a-33e**)(Scheme 1.10) containing Tetrathiafulavene and cyanobiphenyl linked by thiaoalkanoyloxy spacer with varying chain length and amide functionality with hydrophobic chain on the other side of the Tetrathiafulavene unit[43]. All the compound was screened for gelation, but **33a** compound with the shortest thiaoalkanoyloxy spacer able to gelate various organic solvents. Native gel displayed stimuli responsive property towards various external stimuli like Temperature, anions like Fluoride and chemical redox.



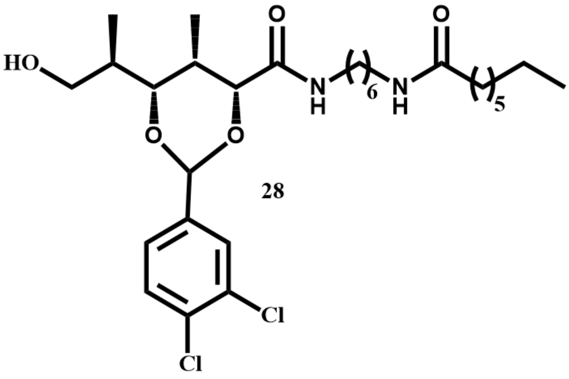
Scheme 1.10 Chemical structure of gelators reported in the literature

Structure correlation studies

Liu *et al.* in their work shows that how chirality and morphology can be altered through changing the core aromatic part in *L*-phenylalanine derived assemblies[44]. In the tuning of central core groups, right (**34a** and **34b**) (Scheme 1.10) and left-handed (**34c** and **34d**) fibrous structure was observed showing configurational regulated assembly behaviour. **Haldar *et al.*** had successfully demonstrated that how orientation of amide group can change the structure and self-assembly process of the compound[45]. In their work they had prepared the tripeptide (**35a-35d**) (Scheme 1.10) containing aromatic core and L-phenylalanine has been investigated and found that orientation of amide affects the intermolecular interactions which lead to the huge differences in the gelation properties. This result provides simple but important approach for fine tuning of futuristic functional materials. **Rissanen *et al.*** design six compounds (**36a-f**) (Scheme 1.10) consist of three different bile acid viz deoxycholic acid, cholic acid and lithocholic acid with hexyl or cyclohexyl amide side chain[46]. Gelation studies concludes the gelator with lithocholic acid derivatives (**36a,d**) was most effective and also gelator with hexyl chain (**36a-c**) are far better than its cyclohexyl conjugates (**36d-f**) providing scope for the design of the gelator for required purpose.



37a: X=CH_2 ; R=H ; Y=NH_2
37b: X= CH_2 ; R=H ; Y=OH
37c: X=$CONHCH_2CH_2$; R=H ; Y=NH_2
37d: X=-$(CH_2)_4$; R=H ; Y= NH_2
37e: X= CH_2; R=H ; Y=$NHCONH_2$
37f: X= CH_2 ; R= CH_3; Y=OH)



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Scheme 1.11 Chemical structure of gelators reported in the literature

Delbecq *et al*. in their work prepared the four new long chain amidoamine derivatives (**37c-f**) (Scheme 1.11) which are quite similar to the molecules earlier reported (**37a**,**b**) in the literature[47]. They successfully showed that Hansen parameters can be efficiently used to predict the gelation capability in the family of compounds. They also demonstrated the effect of position and their number of amide group on gelation behaviour. **Xue et al.** designed six D-gluconic-acetal based molecule with variable structural fragments[48]. One of the compounds (**38**) (Scheme 1.10) consist of amide in side chain and two chlorine atoms linked to benzene ring was found to be outstanding gelator forming gel in n-Butanol with high transparency, good mechanical strength, self-supporting behaviour, and great self-healing ability from mechanical damage. Authors proposed that combine effect of hydrogen bonding and halogen effect promoted the self-healing property. Additionally, solvents parameters like Hansen solubility parameters and plots are also employed for efficient structure property correlation in solvents.

1.3.3 Characterization of Supramolecular gel

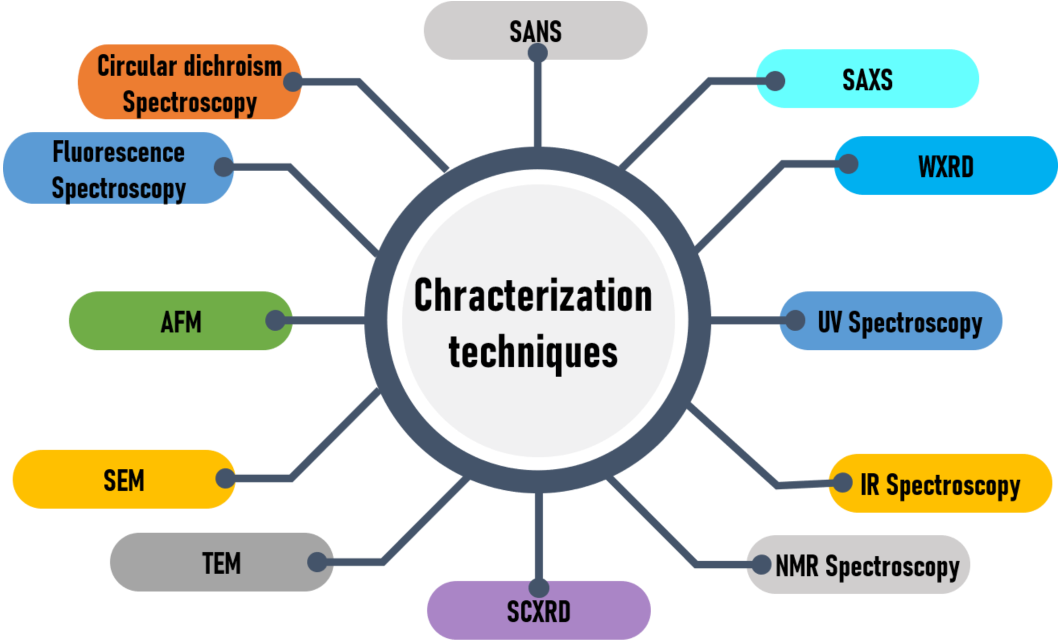

Figure 1.4 *Characterization technique for Supramolecular gels*

1.3.3.1 ^{1}H-NMR Spectroscopy

^{1}H NMR technique is widely used for the characterization of supramolecular gel and lots of information can be extracted from it[49]. Proton NMR probes the hydrogen nuclei in the molecule which is used to determine its structure and also helps to validate intra and inter molecular interactions. ^{1}H NMR generally provides the chemical shift values which can be monitored during the process of aggregation, thus gives the knowledge of moieties taking part in the aggregation process driven by non-covalent interactions. Commonly, temperature and concentration variation ^{1}H NMR studies is carried out to investigate the molecular interaction. In concentration variation studies, if signal is found to be shifting upfield, it represents the formation of hydrogen bonding. In case of temperature variation studies, signal from gelators' molecule was found to shift downfield with increase in the temperature, supporting the breaking of gel system, as gel is very sensitive to the temperature[50]. Additionally, sol-gel transition temperature can also be determined by temperature variation studies[51]. In this at very low temperature, the signal from the gelators' molecule in gel phase almost vanished, suggesting strong intermolecular interactions, and gelators' peaks will appear at specific temperature corresponding to the T_{gel}. Furthermore, it was also successfully used to determine the effective molar ratio in the two component gel system using integration approach[52]. Here advanced techniques like

High resolution magic angle spinning (HRMAS), Diffusion ordered NMR spectroscopy (DOSY), Nuclear Overhauser effect spectroscopy (NOESY) and Rotating frame nuclear Overhauser effect spectroscopy (ROESY) also used to determine the aggregation behaviour of gel system[3,53].

1.3.3.2 Infrared spectroscopy

Infrared spectroscopy is the technique in which the sample is subjected to the light of infrared region (λ=2.5 to 25 μm), and the corresponding absorbance of the light of specific wavelength is measured. FT-IR spectroscopy is a reliable technique widely used for the characterization of organic and inorganic molecule. Of course, this technique is broadly used for characterization of LMWGs having characteristics of self-assembly. The non-covalent interactions responsible for aggregation/gelation behaviour can be effortlessly determine by using FT-IR as characterization tool. Generally by analysing and comparing the FT-IR spectra of gel and solution, the driving forces behind the aggregation can be inferred[54,55]. Furthermore, temperature variation study on gel phase, can be successfully applied to reveals the probable hydrogen bonding interaction[56].

1.3.3.3 Ultraviolet-Visible Spectroscopy

UV-Visible spectroscopy, works on the similar principle as Infrared spectroscopy, but here instead of IR light, UV light is used. This technique is widely used as it can detect the change in the surrounding of particular group of gelator, hence helps to reveal the aggregation mechanism[57–61]. In this, different band corresponding to the gelator molecule is monitored with function of temperature, as decreasing band are favoured by gel network, whereas the increasing band favoured by the monomeric units of gelator[62]. So, by this simple analysis can leads to the understanding of participation of specific group in the gelation process.

1.3.3.4 Fluorescence Spectroscopy

Fluorescence spectroscopy, is the complementary technique to UV-Visible spectroscopy, since UV-Visible monitors transition from ground state to excited states, fluorescence deals with transition from excited state to ground state. Generally, the gelators containing photoisomerizable unit show unique property to react to the external stimuli like light. Das et. al. and Tian et. al. successfully describe the aggregation path of the gelators using florescence spectroscopy[63,64].

1.3.3.5 Circular dichroism spectroscopy

Circular dichroism (CD) spectroscopy is powerful technique to probe the conformational and configurational changes in the system. As many supramolecular systems consists of chiral centre in its structure, and chirality of the molecule may play importance in mediating and directing the self-assembly, thus it is the best accordant method to explore the aggregation steps throughout the gelation process[65–67]. Conformational information obtained by simple regulated heating and cooling cycle can tell about the aggregation process briefly[68].

1.3.3.6 Single crystal diffraction

X-ray diffraction is non-destructive technique, relies on the phenomenon of X-ray scattering provides the better understanding of various bond and covalent interactions. In this angles and intensity of diffracted beam are monitored and from this using the suitable tool[69,70] crystallographer can create 3-dimensional arrangement of electron density, which is helpful to provide the arrangements of atoms in the crystal lattice. X-ray crystal structure so obtained provides the insights of inter and intra molecular interactions, which are primary forces for the self-assembly process, and thus one easily utilized it for the prediction of gelation mechanism[71–73].

1.3.3.7 Wide-angle X-ray scattering

In this technique, X-ray beam are allowed to incident on the sample and the results are observed as function of incident angle, polarization and the wavelength of diffracted beam. In this, scattering intensity was measured from the scattering angle of 2ϴ values larger than 5°. The pattern so obtained was used to determine the crystallinity, chemical composition, phase of the sample. Every crystalline solid consist of the imaginary planes made up of atoms of the molecule define as d-spacing and the intensity is directly proportional to the number of atoms present in the plane. Thus, every solid will have unique pattern of d-spacing. Therefore, WAXS is important method to know the composition and texture of the sample. As WAXS is carried out on the xerogel and packing of molecule in gel differs from that of solid state. Therefore, various studies have been carried out to relate single crystal data with the WAXS data in different phase without losing the correlation between them[74]. So by simply analysing data from xerogel, crystal structure one can proposed the mechanism of aggregation in the gel state[71,75].

1.3.3.8 Small angle X-ray scattering

Small angle X-ray scattering is similar to that of WAXS, the only difference is distance between sample and detector is larger than WAXS and thus diffraction spectra is analysed with the scattering angle closed to 0-5°. Generally, this technique employed to get the data like average particle size, distribution, Molecular weight (M_w), radius of gyration (R_g) and maximum interplanar distance (D_{max}).As supramolecular gel consists of fibers which are interconnected with the non-covalent interactions, the shape, size and distribution of this fibers can be extracted from the SAXS results.[76–78].

1.3.3.9 Small angle neutron scattering

Small angle neutron scattering (SANS) is the technique, very similar to the SAXS. In SANS the beam of neutron is directed on the sample and these neutrons are elastically scattered by interaction of nuclei of the atoms. This technique is widely used to investigate the mesoscopic structures ranging from 1 nm to 100 nm[79]. The scattering raw data collected is corrected with the background and the scattering from the empty cell. Then the final data so obtained was analysed using model-dependent and model-independent analysis to extract the useful information. Usually the analysis is done at 25°C but, depending upon the requirement the variables like temperature and concentration are changed accordingly[80].

1.3.3.10 Scanning electron microscopy

Surface morphology can be easily probed using the scanning electron microscopy (SEM). It uses the beam of electron which are projected on the surface of the sample and their detailed surface topography and composition is obtained. In this incident beam of electron interact with the electron of sample detected by the detector to create an image. As gel is colloidal system, mainly consist of the liquid phase which immobilised by the small amount of LMWGs by the formation of 3D-network. The fibers from in the 3D-network have a size varies from few nanometers to micrometer, SEM is the useful technique to observe the morphology. From this image, length and width of fibers can be extracted.

1.3.3.11 Transmission electron microscopy

Transmission electron microscopy (TEM) is another microscopy technique in which the electron beam is transmitted through the sample and the image of high resolution as compared to SEM is obtained. Images are form by the interaction of electron beam and electron cloud present in the sample. Currently, TEM is widely used to elucidate the surface morphology of supramolecular gels as gelators are self-assembled into the micelles, fibers and tubes like microstructures to form gel[67,81–89].

1.3.3.12 Atomic force Microscopy

Unique from SEM and TEM techniques, Atomic force microscopy (AFM), consist of a mechanical probe that can move on the surface of the any type of sample (viz Solid, liquid and gaseous phase) and form the 3-Dimensional image to provide true morphological information. Apart from other technique AFM doesn't requires the special treatment before analysis, thus conserves the real topology of the system. AFM is used in the various studies to elucidate the surface morphology of the supramolecular gels and holds promise for the in depth studies of aggregation microstructure[90–96].

Apart from SEM, TEM and AFM the techniques like Confocal laser scanning microscopy(CLSM), polarized optical microscopy(POM) and fluorescence confocal microscopy are also used to study morphologies of the gel sample[3,53].

1.3.3.13 Dynamic Light Scattering

Dynamic Light Scattering is non-destructive technique to investigate size and size distribution of the particle in the solution. Generally, laser light is used which is scattered by the Brownian motion of the particle at different angles and intensity. Analysis of this scattered lights gives the velocity of the Brownian motion thus describing the particle size using Stokes-Einstein relationship. Periodic DLS analysis, are used to identify the process of aggregation over a time. Investigation of gel network by DLS is widely used to support the hypothesis of gelation mechanism[97–103].

1.3.3.14 Isothermal titration calorimetry

Generally Isothermal titration calorimetry (ITC) is a technique use to determine the molecular interactions between two species by simply measuring the heat exchange during the binding process. It is ultrasensitive technique to determine the binding constant(K), Stoichiometry(n) and enthalpy changes in the system. From this primary measurement the Gibbs Free energy(ΔG) and entropy changes(ΔS) can also be calculated using the equation 1.

$$\Delta G = -RT\ln K_a = \Delta H - T.\Delta S$$

Self-assembly is depends on the interactions within the molecule, thus ITC is widely used to probe the molecular interaction[104–109].

1.3.3.15 Differential scanning calorimetry

Differential scanning calorimetry (DSC) is destructive technique based on the principle of heat absorption/ evolution by the sample while undergoing going to phase transformations. In this sample is subjected to controlled temperature program and then heat flow in and out of the sample is measured as function of temperature and time. Using the DSC data one can calculate the enthalpy of sol-gel transitions. Detailed DSC studies are used to gain further insight of the thermal stability of the gel[16,110–116].

1.3.3.16 Rheology

Oscillatory rheology simultaneously measures viscous and elastic properties and is therefore a valuable technique in the characterization of gels. In this deformation or flow of the sample is measured under the influence of the applied stress. Here, two terms viz storage modulus(G’) and loss modulus(G”) are important. In general, gels that have G’ > G’’ are interpreted as solid-like materials, whereas gels with G’’ > G’ are considered liquid-like. In these two experiments are used to determine the formation of gel (1) Fixed amplitude with varying stress known as Frequency sweep experiment (2) Fixed frequency with varying stress known as amplitude sweep experiment. Rheology can yield the size, structure and in some case mechanism also and perhaps the most important analysis of gel[117–126].

1.3.4 Applications of supramolecular gels

Molecular gels can be formed by diverse range of building blocks. The fact that one can easily fabricate the desired molecule and furthermore, it can be modified to introduce the diversity in the molecule scaffold, additionally requisite additives in the gel network can give the supramolecular gels an extraordinary applications industrial use and provide time ahead high-tech applications of wide range. This section will focus on the supramolecular gel as material of wide applications.

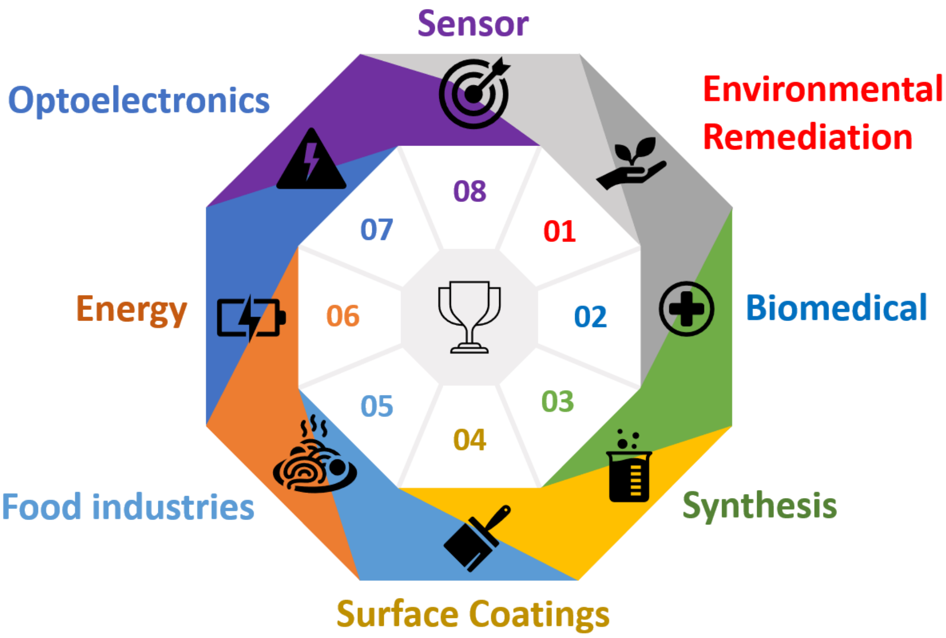

Figure 1.5 Applications of LMWGs

1.3.4.1 Environmental remediation

Rapid pace of industrialization, had seriously impacted the environment by release of toxic waste like heavy metals, dyes, petrochemical products, pesticides and accidental oil spills in water bodies. As supramolecular gel has nano/micro level of solid network in the liquid medium makes it highly solvated and have high surface area which produce high absorption level, hence make it fine filtration agents. Additionally, the reversibility of the gel offers recovery of the pollutants and recyclability to the gel for reuse. Furthermore, as describe above the modification of the gelator scaffold can maximise the interaction of gel to the target molecules. Various reports has been of the reports for phase selective gelation[125–131] ,dye adsorptions[134–138], heavy metal uptake from water[130,139–142], detection and remediation of anions[143–147].

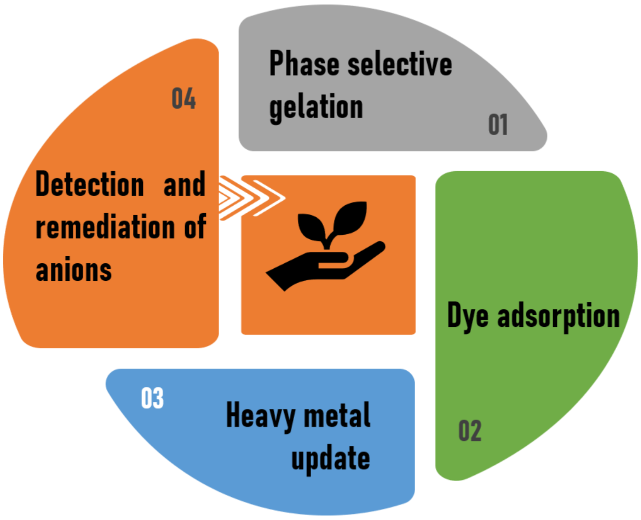

Figure 1.6 Applications of LMWGs in environmental remediation

1.3.4.2 Biomedical applications

As discussed above gels can be used to remove unwanted materials from the aqueous medium, analogous to this it can also use to release the desired species into the water environment makes the gel system desire candidate for control drug release applications. Additionally, they can be self-assembled in the body to provide the required bioactivity which can revolutionize tissue engineering. Generally, peptide based LMOGs which can form hydrogel are studied due to their inherent bioactivity[148].

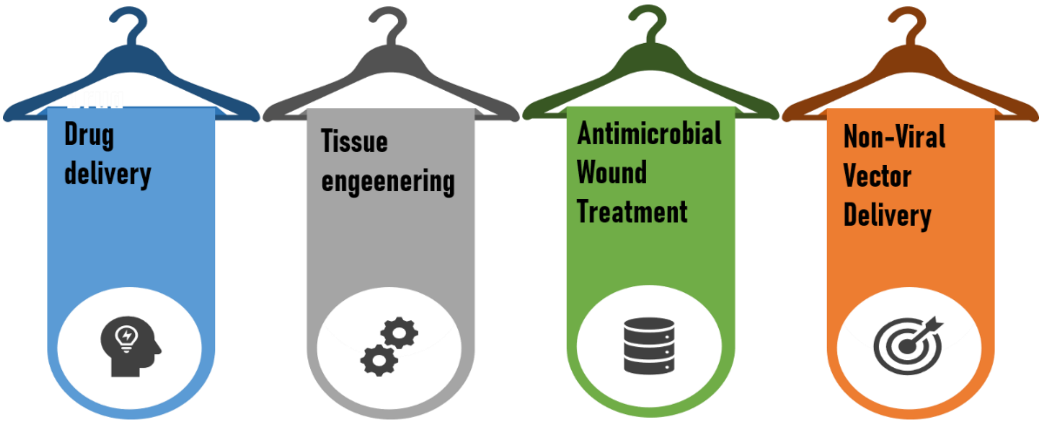

Figure 1.7 Applications of supramolecular gels in biomedicals.

Another unique advantage of supramolecular gels was their ability to repair bone which was done without any surgery[149,150]. Silver is widely accepted as antimicrobial agents, hence introduction of silver in the fibrous network can be used for wound dressing with the prevention of growth of bacteria[151–153]. Supramolecular gels consists of an fibrous network with the dimension of the order of extracellular matrix which has a tunable biomedical and mechanical properties, often use to store cells[154–157]. In biological field separation of DNA, RNA and protein is extensively used by gel electrophoresis which is carried out by traditional sodium dodecyl sulphate polyacrylamide. Here supramolecular gels are used instead of polymers gels because of advantage of tunable properties of it[158,159]. Supramolecular gel shows gel-sol transition in the presence of specific biological compounds providing effortless detection of this biological compounds without special needs of expensive instruments. Various reports has been done which detects the same[160–162].

1.3.4.3 Synthesis Applications

Supramolecular gels have been used as catalyst as it is a combination of properties of “solid like” thus can easily remove from the reaction mass and is also “Liquid like” makes it solvent compatible and makes reagent access and product release easy. Different approaches have been used to make the catalytic gels, as one can introduce catalytic unit in LMWGs, forming catalytic network in gel phase. Another method is to embed the catalytic units like nanoparticle or enzymes within the gel. Some of the examples of catalytic gels are reported earlier[163–166].

Figure 1.8 *Applications of supramolecular gels in synthesis*

In addition to using the gel for catalytic applications, they can also be used for templating crystal growth has it provide the high-quality crystal with the minimum defects than the crystal grown from traditional gel templates. In past decades there are various reports of using of organogels as a crystallisation media[167–170].

1.3.4.4 Surface coatings

Lubricants (Oils and semi-solid greases) are commonly used to overcome the problem of friction that led to the damage to mechanical equipment and unnecessary energy consumptions. As oils are subjected to the risk of leakage and semi-solid greases has poor lubrications as they consist of a thickener. Therefore supramolecular gel are often used as intermediate of oil and grease to overcome the problems of leakage and poor lubrications[171–174]. Along with the lubrications, in various reports various supramolecular gels are used for anti-corrosion applications[175,176].

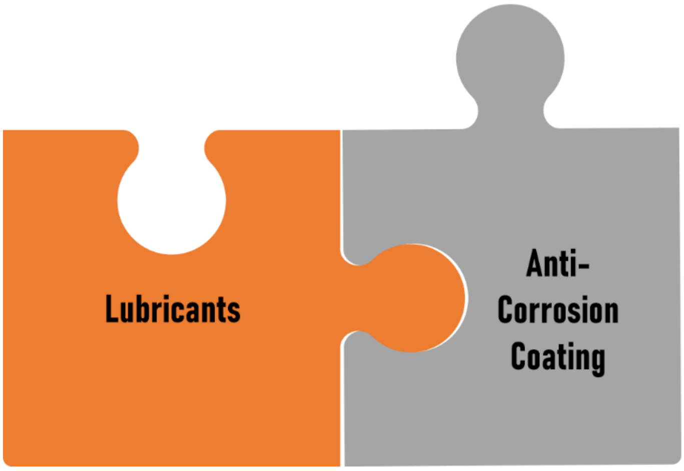

Figure 1.9 *Applications of supramolecular gels in surface coatings*

1.3.4.5 Food industry

Saturated and trans-fat present in the various food products is responsible for numerous global epidemics related to metabolic syndrome and cardiovascular diseases. Organogels with the suitable ingredient can efficiently replace the use of saturated and trans-fat from the food industry as they are food grade, cost effective, no adverse effects on health and can be modify according to the need[177]. Multiple reports highlighted that supramolecular gel can replace the fat sources with benefit of consumer health[178–181].

1.3.4.6 Energy applications

Tunable Electrical and optical properties of supramolecular gels can make them good candidates for fabrications of solar cells used in energy generation sectors. In one of the reports Bairi *et al*. showed the rectification of photocurrent under the exposure of white light with the use of xerogel[182]. In another works supramolecular gel are used in dye -sensitized solar cell technology replacing traditional liquid electrolyte[183–185].

Along with the energy generations, supramolecular gels found significant uses in the energy storage applications like Li-ion batteries[186–189], supercapacitors[190–192] and fuel cells[193–195].

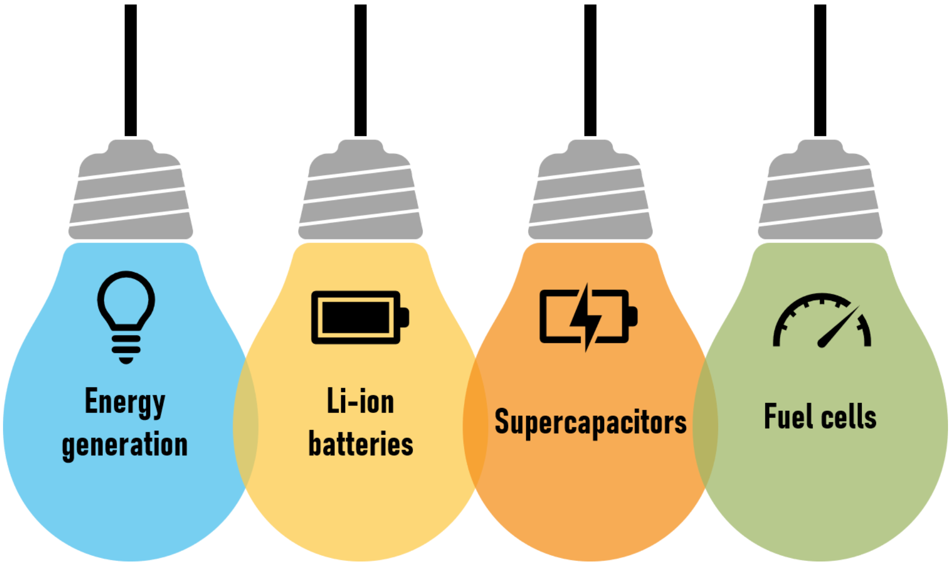

Figure 1.10 Applications of supramolecular gels in energy sector

1.3.4.7 Optoelectronic Applications

Unique property of supramolecular gels has overcome the difficulty of flexibility and processibility of traditional conductive polymers. Replacing the traditional conductive polymers with supramolecular conductive gels has beneficial aspect of conductions with the improved flexibility, processibility and self-healing properties[148]. Other than the electrical conduction, supramolecular gels are widely used photonic applications due their ability to interact with the light. Designing of the LMWGs with the ideal group can induce the suited functions like luminescence[196–198], scattering[199–201], refraction[202] and absorption of light[203].

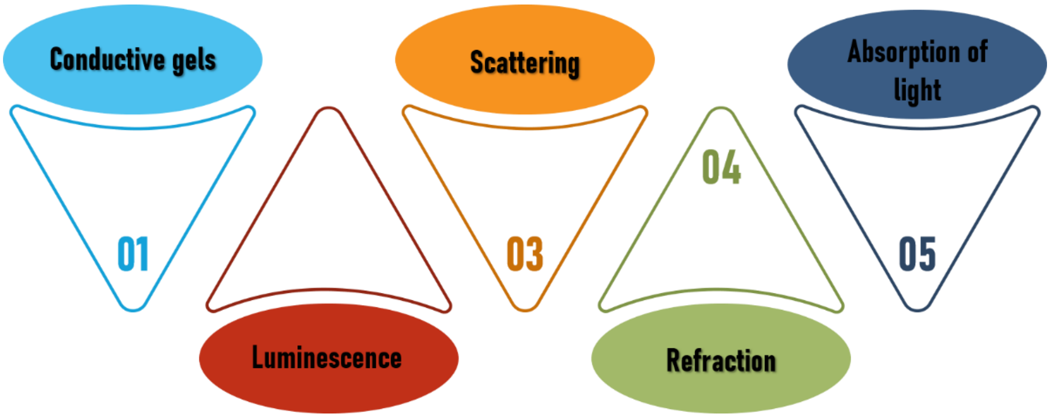

Figure 1.11 Applications of supramolecular gels in optoelectronics

1.3.4.8 Sensing applications

Gels can easily undergo reversible gel to sol transitions in presence of external stimuli, therefore can act as a visualized sensor technology. In the interesting report by Xu *et. al.* β-Lactam based hydrogelator was able to from gel only in the presence of enzyme β-Lactamase(enzyme present in the bacteria which are resistant to penicillin-class antibiotics)[204]. Therefore, this system can be used clinically to find out whether the bacteria is resistant to penicillin-class antibiotics. There are also various examples of supramolecular gels used to detect ionic and small molecules[15,205]. In another gelator reported by Gale *et al.* gel in cyclohexane was found to go under gel to sol transition in the presence of chemical weapon agents (CWAs) Soman[206].

1.4 Aim and Outline

These thesis compromise of four chapters, which demonstrate the simple strategy to design thiazole and benzimidazole based amide and urea derivatives LMWGs and their applications in removal and detection of harmful ions. Additionally, non-covalent interactions such as hydrogen bonding, van der waal interactions are exploited for their role in gelation/non-gelation for establishment of structure-property correlation.

Chapter 1 deals with the introduction of supramolecular chemistry, self-assembly and LMWGs and their classification with the various applications. LMWGs based on urea and amide is discussed briefly and the chapter focuses on the recent advancements of amide and urea based LMWGs in last 3 years.

Chapter 2 discusses the synthesis of a new and known thiazole based aliphatic amides to understand the hierarchal assembly of molecules in the solid-state to metastable gel state. Our effort was directed to establish the relationship between packing in solid-state (SANS, Powder and single crystal X-ray study) and supramolecular assembly in gel state (variable temperature SANS study). Moreover, the gelator was tested for selectivity and sensitivity towards fluoride ion.

Chapter 3 demonstrates the synthesis of a series of compounds having thiazole moiety, hydrogen bonding site (urea functional group), and long alkyl chain. The systematic increase in the aliphatic long chain from decyl to heptadecyl was carried out to explore the role of van der Waals interaction (or hydrophobic effect) on gelation process along with reliable 1D hydrogen bonding urea functional group. All the compounds were well characterized using various physico-chemical techniques and lastly compounds are screened for anion sensitivity.

Chapter 4 presents molecules based on benzimidazole consisting of varying alkyl chain functionalized with amide and urea groups to provide strong hydrogen bond interaction. Also, this study will provide the effect of presence of amide and urea in the same organic scaffold. Moreover, the anion sensing capability of this compounds was explored.

References

1. Lehn, J. M. *Supramolecular Chemistry*. (Wiley-VCH, 1995).
2. Abdallah, D. J. & Weiss, R. G. Organogels and low molecular mass organic gelators. *Adv. Mater.* **12**, 1237–1247 (2000).
3. Yu, G., Yan, X., Han, C. & Huang, F. Characterization of supramolecular gels. *Chem. Soc. Rev.* **42**, 6697–6722 (2013).
4. Sangeetha, N. M. & Maitra, U. Supramolecular gels: Functions and uses. *Chem. Soc. Rev.* **34**, 821–836 (2005).
5. Thomas Graham. Liquid Diffusion Applied to Analysis. *Philos. Trans. R. Soc. London* **151**, 183–224 (1861).
6. Lloyd, D. J. *Colloid Chemistry*. (New York: The Chemical Catalog Co., 1926).
7. Hermans, P. H. *Colloid science*. (Amsterdam: Elsevier, 1949).
8. Yokoya, M., Kimura, S. & Yamanaka, M. Urea Derivatives as Functional Molecules: Supramolecular Capsules, Supramolecular Polymers, Supramolecular Gels, Artificial Hosts, and Catalysts. *Chem. - A Eur. J.* **27**, 5601–5614 (2021).
9. Yamanaka, M. Urea derivatives as low-molecular-weight gelators. *J. Incl. Phenom. Macrocycl. Chem.* **77**, 33–48 (2013).
10. Okesola, B. O. & Smith, D. K. Applying low-molecular weight supramolecular gelators in an environmental setting-self-assembled gels as smart materials for pollutant removal. *Chem. Soc. Rev.* **45**, 4226–4251 (2016).
11. Maki, T., Yoshisaki, R., Akama, S. & Yamanaka, M. Enzyme responsive properties of amphiphilic urea supramolecular hydrogels. *Polym. J.* **52**, 931–938 (2020).
12. O’Donnell, A. D. *et al.* Conformational control of bis-urea self-assembled supramolecular pH switchable low-molecular-weight hydrogelators. *Arkivoc* **2021**, 222–241 (2021).
13. Corea, M. & Jim, R. New Carbamates and Ureas : Comparative Ability to Gel Organic Solvents. *Gels* **8**, 440 (2022).
14. Sahub, C. *et al.* Enhancement of sensitivity for dichlorvos detection by a low-weight gelator based on bolaamphiphile amino acid derivatives decorated with a hybrid graphene quantum dot/enzyme/hydrogel. *Mater. Chem. Front.* **5**, 6850 (2021).
15. Picci, G. *et al.* Anion-Responsive Fluorescent Supramolecular Gels. (2022).
16. Ghosh, D., Bjornsson, R. & Damodaran, K. K. Role of N–oxide moieties in tuning supramolecular gel-state properties. *Gels* **6**, 1–17 (2020).
17. Jayabhavan, S. S., Ghosh, D. & Damodaran, K. K. Making and breaking of gels: Stimuli-responsive properties of bis(pyridyl-n-oxide urea) gelators. *Molecules* **26**, (2021).
18. Kimura, S. *et al.* Formation of pH-responsive supramolecular hydrogels in basic buffers: Self-assembly of amphiphilic tris-urea. *Chem. Pharm. Bull.* **69**, 1131–1135 (2021).
19. Tómasson, D. A., Ghosh, D., Kurup, M. R. P., Mulvee, M. T. & Damodaran, K. K. Evaluating the role of a urea-like motif in enhancing the thermal and mechanical strength of supramolecular gels. *CrystEngComm* **23**, 617–628 (2020).
20. Genio, F. A. F. & Paderes, M. C. Functional Supramolecular Gels Comprised of Bis-Urea Compounds and Cosmetic Solvents. *ChemistrySelect* **6**, 7906–7911

(2021).

21. Petrov, S. A. *et al.* Synthesis and organogelating behaviour of urea- and Fmoc-containing diphenylalanine based hexaamide. *J. Mol. Struct.* **1234**, (2021).
22. Valls, A. *et al.* Urea-Based Low-Molecular-Weight Pseudopeptidic Organogelators for the Encapsulation and Slow Release of (R)-Limonene. *J. Agric. Food Chem.* **68**, 7051–7061 (2020).
23. Park, J., Kim, M., Seo, M. & Lee, J. In Situ Supramolecular Gel Formed by Cyclohexane Diamine with Aldehyde Derivative. *Communications* **14**, 400 (2022).
24. Kumari, H. Manipulating Assemblies in Metallosupramolecular Gels, Driven by Isomeric Ligands, Metal Coordination, and Adaptive Binary Gelator Systems. *Langmuir* **38**, 1705–1715 (2022).
25. Zapién-Castillo, S. *et al.* Recovery of Fuels Using the Supramolecular Gelation Ability of a Hydroxybenzoic Acid Bisamide Derivative. *Water. Air. Soil Pollut.* **232**, (2021).
26. Xu, C., Wang, L., Xia, Y. & Hou, R. A novel tetrathiafulvalene based liquid crystalline organogelator: synthesis, self-assembly properties and potential utilization. *New J. Chem* **46**, 22663–22671 (2022).
27. Iguarbe, V., Romero, P., Barberá, J., Elduque, A. & Giménez, R. Dual liquid Crystalline/Gel behavior with AIE effect promoted by Self-assembly of pyrazole dendrons. *J. Mol. Liq.* **365**, (2022).
28. Liu, S. *et al.* Dynamic , hollow nanotubular networks with superadjustable pH-responsive and temperature resistant rheological characteristics. *Chem. Eng. J.* **452**, 139364 (2023).
29. Zhang, J. *et al.* Molecular Design, Supramolecular Assembly, and Excellent Dye Adsorption Capacity of Natural Rigid Dehydroabietic Acid-Tailored Amide Organogelators. *Lamgmuir* **38**, 8918−8927 (2022).
30. Makeiff, D. A., Cho, J. Y., Smith, B., Carlini, R. & Godbert, N. Self-Assembly of Alkylamido Isophthalic Acids toward the Design of a Supergelator: Phase-Selective Gelation and Dye Adsorption. *Gels* **8**, (2022).
31. Wang, J. T. *et al.* Enhanced Delivery of Neuroactive Drugs via Nasal Delivery with a Self-Healing Supramolecular Gel. *Adv. Sci* 2101058 (2021).
32. Bietsch, J., Olson, M. & Wang, G. Fine-Tuning of Molecular Structures to Generate Carbohydrate Based Super Gelators and Their Applications for Drug Delivery and Dye Absorption. *gels* 134 (2021).
33. Liao, L. *et al.* Supramolecular gel formation regulated by water content in organic solvents: self-assembly mechanism and biomedical applications. *RSC Adv.* **11**, 11519–11528 (2021).
34. Makeiff, D. A. *et al.* Supramolecular gels from alkylated benzimidazolone derivatives. *J. Mol. Liq.* **339**, 116723 (2021).
35. Bordignon, D. *et al.* Wet spinning of a library of carbohydrate low molecular weight gels. *J. Colloid Interface Sci.* **603**, 333–343 (2021).
36. Mondal, S. & Dastidar, P. Designing Metallogelators Derived from NSAID-based Zn (II) Coordination Complexes for Drug-Delivery Applications. *Chem asian J.* **15**, 1–11 (2020).
37. Alegre-Requena, J. V. *et al.* Sulfonamide as amide isostere for fine-tuning the gelation properties of physical gels. *RSC Adv.* **10**, 11481–11492 (2020).
38. Souvik Misraa, Pijush Singhb, Ankita Dasc, Paula Brandãod, Pathik Sahooe, Nayim Sepaif, G. & Bhattacharjeeg, Pallab Dattac , Ajit K. Mahapatraa, B. S. and J. N. Supramolecular assemblies of a 1,8-Naphthalimide conjugate and its

aggregation-induced emission property. *Mater. Adv.* **1**, 3532–3538 (2020).

39. Zhang, B. *et al.* Four-armed biobase d glycyrrhizic acid-tailore d AIE fluorescent gelator. *J. Mol. Struct.* **1258**, 132684 (2022).
40. Manna, U., Roy, R., Datta, H. K. & Dastidar, P. Supramolecular Gels from Bis-amides of L -Phenylalanine : Synthesis , Structure and Material Applications. *Chem asian J.* **17**, e202200660 (2022).
41. Gregoric, T., Makarevic, J., Štefanic, Z., Žinic, M. & Frkanec, L. Gamma Radiation- and Ultraviolet-Induced Polymerization of Bis(amino acid)fumaramide Gel Assemblies. *Polymers (Basel).* **14**, (2022).
42. Gao, A. *et al.* Triphenylamine derivative-based supramolecular self-assembly system for selective sensing methanol via hydrogen bonding. *Dye. Pigment.* **195**, 109689 (2021).
43. Ma, L. *et al.* Synthesis and properties of supramolecular gels based on tetrathiafulvalene and cyanobiphenyl units. *Soft Mater.* **19**, 243–253 (2021).
44. Makeiff, D. A. *et al.* Effect of aromatic core on the supramolecular chirality of L-phenylalanine derived assemblies. *Colloids Surfaces A Physicochem. Eng. Asp.* **339**, 1–9 (2021).
45. Kumar, S., Bera, S., Nandi, S. K. & Haldar, D. The effect of amide bond orientation and symmetry on the self-assembly and gelation of discotic tripeptides. *Soft Matter* **17**, 113–119 (2021).
46. Kuosmanen, R. T., Truong, K., Rissanen, K. T. & Sievänen, E. I. The Effect of the Side Chain on Gelation Properties of Bile Acid Alkyl Amides. *Chem. open* **10**, 1150–1157 (2021).
47. Delbecq, F., Adenier, G., Ogue, Y. & Kawai, T. Gelation properties of various long chain amidoamines: Prediction of solvent gelation via machine learning using Hansen solubility parameters. *J. Mol. Liq.* **303**, 112587 (2020).
48. Chen, S., Fan, Y., Song, J. & Xue, B. The remarkable role of hydrogen bond , halogen , and solvent effect on self-healing supramolecular gel. *Mater. Today Chem.* **23**, 100719 (2022).
49. Brown, S. P. Advanced solid-state NMR methods for characterising structure and self-assembly in supramolecular chemistry, polymers and hydrogels. *Current Opinion in Colloid and Interface Science* vol. 33 86–98 at (2018).
50. Dong, S. *et al.* A crown ether appended super gelator with multiple stimulus responsiveness. *Adv. Mater.* **24**, 3191–3195 (2012).
51. Yan, X. *et al.* A multiresponsive, shape-persistent, and elastic supramolecular polymer network gel constructed by orthogonal self-assembly. *Adv. Mater.* **24**, 362–369 (2012).
52. Hirst, A. R. *et al.* Self-Assembly of Two-Component Gels : Stoichiometric Control and Component Selection. *Chem. Eur. J.* **15**, 372–379 (2009).
53. Denzer, B. R., Kulchar, R. J., Huang, R. B. & Patterson, J. Advanced methods for the characterization of supramolecular hydrogels. *Gels* vol. 7 158 at (2021).
54. Wu, W. *et al.* Calcium ion coordinated dexamethasone supramolecular hydrogel as therapeutic alternative for control of non-infectious uveitis. *Acta Biomater.* **61**, 157–168 (2017).
55. Song, Q., Zhang, R., Lei, L. & Li, X. Self-Assembly of Succinated Paclitaxel into Supramolecular Hydrogel for Local Cancer Chemotherapy. *J. Biomed. Nanotechnol.* **14**, 1471–1476 (2018).
56. Nebot, V. J. *et al.* Molecular Hydrogels from Bolaform Amino Acid Derivatives : A Structure – Properties Study Based on the Thermodynamics of Gel Solubilization. *Chem. Eur. J.* **18**, 4063–4072 (2012).

57. Strassert, C. A. *et al.* Light from Thin Assemblies Switching On Luminescence by the Self-Assembly of a Platinum (II) Complex into Gelating Nanofibers and Electroluminescent Films **. *Angew. Chem. Int. Ed.* **50**, 946–950 (2011).
58. Osakada, K. Metallohydrogel Formed from Amphiphilic Pd Complex and ¡-Cyclodextrin: Control of its Sol-Gel Transistion. *Chem. Lett.* **42**, 1062–1064 (2013).
59. Ogawa, Y., Yoshiyama, C. & Kitaoka, T. Helical Assembly of Azobenzene-Conjugated Carbohydrate Hydrogelators with Specific Affinity for Lectins. *Langmuir* **28**, 4404–4412 (2012).
60. Sugimoto, T., Suzuki, T., Shinkai, S. & Sada, K. A Double-Stranded Helix by Complexation of Two Polymer Chains with a Helical Supramolecular Assembly. *J. AM. CHEM. SOC* **129**, 270–271 (2007).
61. Bhattacharya, S. & Samanta, S. K. Unusual Salt-Induced Color Modulation through Aggregation-Induced Emission Switching of a Bis-cationic Phenylenedivinylene-Based p. *Chem. Eur. J.* **18**, 16632–16641 (2012).
62. Hisaki, I. *et al.* Ester Groups Prevent Crystallization and Promote Gelation **. *Angew. Chem. Int. Ed.* **48**, 5465–5469 (2009).
63. Kumar, N. S. S., Varghese, S., Narayan, G. & Das, S. Hierarchical self-assembly of donor-acceptor-substituted butadiene amphiphiles into photoresponsive vesicles and gels. *Angew. Chemie - Int. Ed.* **45**, 6317–6321 (2006).
64. Wang, S., Shen, W., Feng, Y. & Tian, H. A multiple switching bisthienylethene and its photochromic fluorescent organogelator. *Chem. Commun.* **2**, 1497–1499 (2006).
65. Smith, D. K. Lost in translation? Chirality effects in the self-assembly of nanostructured gel-phase materials. *Chem. Soc. Rev.* **38**, 684–694 (2009).
66. Suzuki, M. & Hanabusa, K. L-Lysine-based low-molecular-weight gelators. *Chem. Soc. Rev.* **38**, 967–975 (2009).
67. Yang, Z., Gu, H., Zhang, Y., Wang, L. & Xu, B. Small molecule hydrogels based on a class of antiinflammatory agents. *Chem. Commun.* **4**, 208–209 (2004).
68. Rodríguez-Llansola, F., Miravet, J. F. & Escuder, B. Supramolecular gel formation and self-correction induced by aggregation-driven conformational changes. *Chem. Commun.* 209–211 (2009).
69. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **42**, 339–441 (2009).
70. Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr. Sect. C Struct. Chem.* **71**, 3–8 (2015).
71. Patel, A. M., Ray, D., Aswal, V. K. & Ballabh, A. Probing the mechanism of gelation and anion sensing capability of a thiazole based amide gelator: A case study. *Colloids Surfaces A Physicochem. Eng. Asp.* **607**, 125430 (2020).
72. Yadav, P. & Ballabh, A. Odd-even effect in a thiazole based organogelator: Understanding the interplay of non-covalent interactions on property and applications. *New J. Chem.* **39**, 721–730 (2015).
73. Yadav, P. & Ballabh, A. N-(thiazol-2-yl)benzamide derivatives as a new series of supramolecular gelators: Role of methyl functionality and S⋯O interaction. *J. Solid State Chem.* **281**, 2–8 (2020).
74. Proeerjliw, E., Anthraquinone--carboxylate, C., Ostuni, E., Kamaras, P. & Weiss, R. G. Novel X-ray Method for In Situ Determination of Gelator Strand

Structure: Polymorphism of Cholesteryl. *Angew. Chem. Int. Ed.* **35**, 1324–1326 (1996).

75. Patel, A. M., Ray, D., Aswal, V. K. & Ballabh, A. Probing the supramolecular assembly in solid , solution and gel phase in uriede based thiazole derivatives and its potential application as iodide ion sensor. *J. Mol. Liq.* **362**, 119763 (2022).
76. Sutton, M. A review of X-ray intensity fluctuation spectroscopy. *Comptes Rendus Phys.* **9**, 657–667 (2008).
77. Hirst, A. R., Smith, D. K., Feiters, M. C. & Geurts, H. P. M. Two-component dendritic gel: Effect of stereochemistry on the supramolecular chiral assembly. *Chem. - A Eur. J.* **10**, 5901–5910 (2004).
78. Cosgrove, T., Newby, F. N. & Sabadini, E. Formation of a Supramolecular Gel between r-Cyclodextrin and Free and Adsorbed PEO on the Surface of Colloidal Silica: Effect of Temperature, Solvent, and Particle Size. *Langmuir* **20**, 9124–9129 (2004).
79. Yu, G., Yan, X., Han, C. & Huang, F. Characterization of supramolecular gels. *Chem. Soc. Rev.* **42**, 6697–6722 (2013).
80. Kumari, H. & States, U. *Small-Angle Neutron Scattering in Supramolecular Complexes*. *Comprehensive Supramolecular Chemistry II* vol. 2 (Elsevier, 2017).
81. Patil, S. P., Jeong, H. S. & Kim, B. H. A low-molecular-weight supramolecular hydrogel of riboflavin bolaamphiphile for VEGF-siRNA delivery. *Chem. Commun.* **48**, 8901–8903 (2012).
82. Gunnar Buhler, Martinus C. Feiters, Roeland J. M. Nolte, and K. H. D. A Metal Carbene Carbohydrate Amphiphile as a Low-Molecular-Mass Organometallic Gelator. *Angew. Chem. Int. Ed.* **42**, (2003).
83. Wang, L. *et al.* A multifunctional supramolecular hydrogel: Preparation, properties and molecular assembly. *Soft Matter* **14**, 566–573 (2018).
84. Breiel, R. w. Solid behaviour of unsheared sickle haemoglobin and the effects of shear. *Nature* **288**, 622 (1980).
85. Qin, Z. *et al.* Nonswellable and Tough Supramolecular Hydrogel Based on Strong Micelle Cross-Linkings. *Biomacromolecules* **20**, 3399–3407 (2019).
86. Brizard, A. *et al.* Preparation of nanostructures by orthogonal self-assembly of hydrogelators and surfactants. *Angew. Chemie - Int. Ed.* **47**, 2063–2066 (2008).
87. Mukhopadhyay, S. *et al.* Structure and dynamics of a molecular hydrogel derived from a tripodal cholamide. *J. Am. Chem. Soc.* **126**, 15905–15914 (2004).
88. Yao, S., Beginn, U., Gress, T., Lysetska, M. & Würthner, F. Supramolecular polymerization and gel formation of bis(merocyanine) dyes driven by dipolar aggregation. *J. Am. Chem. Soc.* **126**, 8336–8348 (2004).
89. Parisi, E., Garcia, A. M., Marson, D., Posocco, P. & Marchesan, S. Supramolecular tripeptide hydrogel assembly with 5-fluorouracil. *Gels* **5**, 5 (2019).
90. EzEldeen, M. *et al.* Chlorite oxidized oxyamylose differentially influences the microstructure of fibrin and self assembling peptide hydrogels as well as dental pulp stem cell behavior. *Sci. Rep.* **11**, 1–12 (2021).
91. Fukui, T. *et al.* Direct Observation and Manipulation of Supramolecular Polymerization by High-Speed Atomic Force Microscopy. *Angew. Chemie - Int. Ed.* **57**, 15465–15470 (2018).
92. Roy, S. *et al.* Dramatic specific-ion effect in supramolecular hydrogels. *Chem.*

- *A Eur. J.* **18**, 11723–11731 (2012).

93. Norman, M. D. A., Ferreira, S. A., Jowett, G. M., Bozec, L. & Gentleman, E. Measuring the elastic modulus of soft culture surfaces and three-dimensional hydrogels using atomic force microscopy. *Nat. Protoc.* **16**, 2418–2449 (2021).
94. Nalam, P. C., Gosvami, N. N., Caporizzo, M. A., Composto, R. J. & Carpick, R. W. Nano-rheology of hydrogels using direct drive force modulation atomic force microscopy. *Soft Matter* **11**, 8165–8178 (2015).
95. Rao, K. V., Jayaramulu, K., Maji, T. K. & George, S. J. Supramolecular hydrogels and high-aspect-ratio nanofibers through charge-transfer-induced alternate coassembly. *Angew. Chemie - Int. Ed.* **49**, 4218–4222 (2010).
96. Alakpa, E. V. *et al.* Tunable Supramolecular Hydrogels for Selection of Lineage-Guiding Metabolites in Stem Cell Cultures. *Chem* **1**, 298–319 (2016).
97. Liao, X. *et al.* Photoresponsive pseudopolyrotaxane hydrogels based on competition of host-guest interactions. *Angew. Chemie - Int. Ed.* **49**, 4409–4413 (2010).
98. Samanta, K., Ehlers, M. & Schmuck, C. Two-Component Self-Assembly: Hierarchical Formation of pH-Switchable Supramolecular Networks by π–π Induced Aggregation of Ion Pairs. *Chem. - A Eur. J.* **22**, 15242–15247 (2016).
99. Felip-León, C., Cejudo-Marín, R., Peris, M., Galindo, F. & Miravet, J. F. Sizing Down a Supramolecular Gel into Micro- and Nanoparticles. *Langmuir* **33**, 10322–10328 (2017).
100. Gao, Y. & Dong, C. M. Triple redox/temperature responsive diselenide-containing homopolypeptide micelles and supramolecular hydrogels thereof. *J. Polym. Sci. Part A Polym. Chem.* **56**, 1067–1077 (2018).
101. Razavi, B., Abbaszadeh, R., Salami-Kalajahi, M. & Roghani-Mamaqani, H. Multi-responsive poly(amidoamine)-initiated dendritic-star supramolecular structures containing UV cross-linkable coumarin groups for smart drug delivery. *J. Mol. Liq.* **319**, 114138 (2020).
102. Croitoriu, A. *et al.* New Fmoc-Amino Acids/Peptides-Based Supramolecular Gels Obtained through Co-Assembly Process: Preparation and Characterization. *Polymers (Basel).* **14**, (2022).
103. Croitoriu, A., Nita, L. E., Chiriac, A. P., Rusu, A. G. & Bercea, M. New physical hydrogels based on co-assembling of fmoc–amino acids. *Gels* **7**, (2021).
104. Pradhan, M. K. *et al.* Anion-responsive self-assembled hydrogels of a phenylalanine–TREN conjugate allow sequential release of propranolol and doxorubicin. *Nanoscale* **14**, 15079–15090 (2022).
105. Kim, K. *et al.* Functionalized cucurbiturils and their applications. *Chem. Soc. Rev.* **36**, 267–279 (2007).
106. Solvent Switchable Nanostructure and Function of a π-Amphiphile.pdf.
107. Aparicio, F., García, F. & Sánchez, L. Supramolecular polymerization of C3-symmetric organogelators: Cooperativity, solvent, and gelation relationship. *Chem. - A Eur. J.* **19**, 3239–3248 (2013).
108. Denadai, Â. M. L. *et al.* Supramolecular self-assembly of β-cyclodextrin: an effective carrier of the antimicrobial agent chlorhexidine. *Carbohydr. Res.* **342**, 2286–2296 (2007).
109. Desmarchelier, A. *et al.* Tuning the nature and stability of self-assemblies formed by ester benzene 1,3,5-tricarboxamides: The crucial role played by the substituents. *Soft Matter* **12**, 7824–7838 (2016).
110. Bindu, H. & Palanisamy, A. Bio-based castor oil organogels and investigations

on their anion-tuning properties. *Colloid Polym. Sci.* **297**, 1411–1421 (2019).

111. Meyer, A. R. *et al.* Effect of slight structural changes on the gelation properties of N-phenylstearamide supramolecular gels. *Soft Matter* **14**, 6716–6727 (2018).
112. Mañas-Torres, M. C. *et al.* In situ real-time monitoring of the mechanism of self-assembly of short peptide supramolecular polymers. *Mater. Chem. Front.* **5**, 5452–5462 (2021).
113. Alonso, J. D. *et al.* Meglumine-based supramolecular amphiphiles: The effect of chain length. *J. Mol. Liq.* **351**, 118684 (2022).
114. Smith, M. M. & Smith, D. K. Self-sorting multi-gelator gels - Mixing and ageing effects in thermally addressable supramolecular soft nanomaterials. *Soft Matter* **7**, 4856–4860 (2011).
115. Holey, S. A., Sekhar, K. P. C., Swain, D. K., Bojja, S. & Nayak, R. R. Supramolecular Glycolipid-Based Hydro-/Organogels with Enzymatic Bioactive Release Ability by Tuning the Chain Length and Headgroup Size. *ACS Biomater. Sci. Eng.* **8**, 1103–1114 (2022).
116. Xing, P. *et al.* Utilizing dual responsive supramolecular gel to stabilize graphene oxide in apolar solvents. *Colloid Polym. Sci.* **292**, 3223–3231 (2014).
117. Cai, X. *et al.* Calix[4]arene-based supramolecular gels with unprecedented rheological properties. *Soft Matter* **8**, 3756–3761 (2012).
118. Samanta, S. K., Subrahmanyam, K. S., Bhattacharya, S. & Rao, C. N. R. Composites of graphene and other nanocarbons with organogelators assembled through supramolecular interactions. *Chem. - A Eur. J.* **18**, 2890–2901 (2012).
119. Sim, H. G. *et al.* Drug-loaded supramolecular gels prepared in a microfluidic platform: Distinctive rheology and delivery through controlled farfrom-equilibrium mixing. *J. Rheol. (N. Y. N. Y).* **18**, 13 (2017).
120. Exploring Supramolecular Gels in Flow-Type Chemistry□Design.pdf.
121. Thursch, L. J., DiGuiseppi, D., Lewis, T. R., Schweitzer-Stenner, R. & Alvarez, N. J. Exploring the gel phase of cationic glycylalanylglycine in ethanol/water. I. Rheology and microscopy studies. *J. Colloid Interface Sci.* **564**, 499–509 (2020).
122. Salzano de Luna, M. *et al.* Light-responsive and self-healing behavior of azobenzene-based supramolecular hydrogels. *J. Colloid Interface Sci.* **568**, 16–24 (2020).
123. Li, X. *et al.* Molecular nanofibers of olsalazine form supramolecular hydrogels for reductive release of an anti-inflammatory agent. *J. Am. Chem. Soc.* **132**, 17707–17709 (2010).
124. Draper, E. R. *et al.* Opening a Can of Worm(-like Micelle)s: The Effect of Temperature of Solutions of Functionalized Dipeptides. *Angew. Chemie - Int. Ed.* **56**, 10467–10470 (2017).
125. Gao, S. *et al.* Salt Tunable Rheology of Thixotropic Supramolecular Organogels and Their Applications for Crystallization of Organic Semiconductors. *Langmuir* **32**, 12805–12813 (2016).
126. Hashemnejad, S. M. & Kundu, S. Probing Gelation and Rheological Behavior of a Self-Assembled Molecular Gel. *Langmuir* **33**, 7769–7779 (2017).
127. Trivedi, D. R., Ballabh, A. & Dastidar, P. An Easy To Prepare Organic Salt as a Low Molecular Mass Organic Gelator Capable of Selective Gelation of Oil from Oil/Water Mixtures. *Chem. Mater.* **15**, 3971–3973 (2003).
128. Trivedi, D. R. *et al.* Biorefinery: A design tool for molecular Gelators. *Tetrahedron* **26**, 2218–2224 (2010).
129. Hwang, H. L., Jadhav, S. R., Silverman, J. R. & John, G. Sweet and

Sustainable: Teaching the Biorefinery Concept through Biobased Gelator Synthesis. *J. Chem. Educ.* **91**, 1563–1568 (2014).

130. Trivedi, D. R., Ballabh, A., Dastidar, P. & Ganguly, B. Structure-property correlation of a new family of organogelators based on organic salts and their selective gelation of oil from oil/water mixtures. *Chem. - A Eur. J.* **10**, 5311–5322 (2004).
131. Ballabh, A., Trivedi, D. R. & Dastidar, P. New series of organogelators derived from a combinatorial library of primary ammonium monocarboxylate salts. *Chem. Mater.* **18**, 3795–3800 (2006).
132. Xue, M., Gao, D., Liu, K., Peng, J. & Fang, Y. Cholesteryl derivatives as phase-selective gelators at room temperature. *Tetrahedron* **65**, 3369–3377 (2009).
133. Peng, J. *et al.* New dicholesteryl-based gelators: Gelling ability and selective gelation of organic solvents from their mixtures with water at room temperature. *New J. Chem.* **32**, 2218–2224 (2008).
134. Samai, S., Dey, J. & Biradha, K. Amino acid based low-molecular-weight tris(bis-amido) organogelators. *Soft Matter* **7**, 2121–2126 (2011).
135. Cho, E. J. *et al.* Terpyridine-based smart organic-inorganic hybrid gel as potential dye-adsorbing agent for water purification. *Tetrahedron Lett.* **49**, 1076–1079 (2008).
136. Debnath, S., Shome, A., Dutta, S. & Das, P. K. Dipeptide-based low-molecular-weight efficient organogelators and their application in water purification. *Chemistry - A European Journal* vol. 14 6870–6881 at https://doi.org/10.1002/chem.200800731 (2008).
137. Ray, S., Das, A. K. & Banerjee, A. pH-responsive, bolaamphiphile-based smart metallo-hydrogels as potential dye-adsorbing agents, water purifier, and vitamin B12 carrier. *Chem. Mater.* **19**, 1633–1639 (2007).
138. Adhikari, B., Palui, G. & Banerjee, A. Self-assembling tripeptide based hydrogels and their use in removal of dyes from waste-water. *Soft Matter* **5**, 3452–3460 (2009).
139. Knerr, P. J., Branco, M. C., Nagarkar, R., Pochan, D. J. & Schneider, J. P. Heavy metal ion hydrogelation of a self-assembling peptide via cysteinyl chelation. *J. Mater. Chem.* **22**, 1352–1357 (2012).
140. Carter, K. K., Rycenga, H. B. & McNeil, A. J. Improving Hg-triggered gelation via structural modifications. *Langmuir* **30**, 3522–3527 (2014).
141. King, K. N. & McNeil, A. J. Streamlined approach to a new gelator: Inspiration from solid-state interactions for a mercury-induced gelation. *Chem. Commun.* **46**, 3511–3513 (2010).
142. Okesola, B. O., Suravaram, S. K., Parkin, A. & Smith, D. K. Selective Extraction and in Situ Reduction of Precious Metal Salts from Model Waste to Generate Hybrid Gels with Embedded Electrocatalytic Nanoparticles. *Angew. Chemie - Int. Ed.* **55**, 183–187 (2016).
143. Lin, Q. *et al.* A novel supramolecular metallogel-based high-resolution anion sensor array. *Chem. Commun.* **51**, 1635–1638 (2015).
144. Shen, J. S., Cai, Q. G., Jiang, Y. B. & Zhang, H. W. Anion-triggered melamine based self-assembly and hydrogel. *Chem. Commun.* **46**, 6786–6788 (2010).
145. Shen, J. S., Li, D. H., Cai, Q. G. & Jiang, Y. B. Highly selective iodide-responsive gel-sol state transition in supramolecular hydrogels. *J. Mater. Chem.* **19**, 6219–6224 (2009).
146. Becker, T. *et al.* Proline-functionalised calix[4]arene: An anion-triggered

hydrogelator. *Chem. Commun.* 3900–3902 (2008).

147. Xia, Q., Mao, Y., Wu, J., Shu, T. & Yi, T. Two-component organogel for visually detecting nitrite anion. *J. Mater. Chem. C* **2**, 1854–1861 (2014).
148. Christoff-Tempesta, T., Lew, A. J. & Ortony, J. H. Beyond covalent crosslinks: Applications of supramolecular gels. *Gels* vol. 4 at (2018).
149. Rosario, C. *et al.* Bone critical defect repair with poloxamine-cyclodextrin supramolecular gels. *Int. J. Pharm.* **495**, 463–473 (2015).
150. Sang, L., Huang, J. & Luo, D. Bone-like nanocomposites based on self-assembled protein-based matrices with Ca2+ capturing capability. *J. Mater. Sci. Mater. Med.* **21**, 2561–2568 (2010).
151. Pakhomov, P. M., Ovchinnikov, M. M., Khizhnyak, S. D., Roshchina, O. A. & Komarov, P. V. A Supramolecular Medical Hydrogel Based on L Cysteine and Silver Ions. *Med. Polym.* **53**, 820–826 (2011).
152. Mandal, S. K., Brahmachari, S. & Kumar, P. In Situ Synthesised Silver Nanoparticle-Infused l -Lysine- Based Injectable Hydrogel : Development of a Biocompatible , Antibacterial , Soft Nanocomposite. *Chempluschem* **79**, 1733–1746 (2014).
153. Paladini, F. & Cooper, S. T. M. I. R. Silver-doped self-assembling di-phenylalanine hydrogels as wound dressing biomaterials. *J Mater Sci Mater Med* (2013).
154. Zeng, J. *et al.* A Supramolecular Gel Approach to Minimize the Neural Cell Damage during Cryopreservation Process. *Macromol. Biosci.* **16**, 363–370 (2016).
155. Zhou, M. *et al.* Biomaterials Self-assembled peptide-based hydrogels as scaffolds for anchorage- dependent cells. *Biomaterials* **30**, 2523–2530 (2009).
156. Latxague, L. *et al.* Control of Stem-Cell Behavior by Fine Tuning the Supramolecular Assemblies of Low-Molecular-Weight Gelators. *Angew. Chemie* **54**, 4517–4521 (2015).
157. Karlsson, J. O. M. & Toner, M. Long-term storage of tissues by cryopreservation : critical issues. *Biomaterials* **17**, 243–256 (1996).
158. Yamamichi, S. *et al.* Separation of proteins using supramolecular gel electrophoresis. *Chem. Commun.* **47**, 10344–10346 (2011).
159. Tazawa, S., Kobayashi, K., Oyoshi, T. & Yamanaka, M. Supramolecular gel electrophoresis of large DNA fragments. *Electrophoresis* **38**, 2662–2665 (2017).
160. Yang, Z., Xu, B., Bay, C. W. & Kong, H. A simple visual assay based on small molecule hydrogels for detecting inhibitors of enzymes. *Chem. Commun.* **1**, 2424–2425 (2004).
161. Ting He, Kun Li,* Ming-Yu Wu, Y.-X. L. and X.-Q. Y. Visual detection of amino acids by supramolecular gel collapse. *RSC Adv.* **4**, 2119–2123 (2014).
162. Yang, D., Liu, C., Zhang, L. & Liu, M. ChemComm Visualized discrimination of ATP from ADP and AMP through collapse of supramolecular gels †. **4**, 12688–12690 (2014).
163. Lee, H. H., Jung, S. H., Park, S., Park, K. M. & Jung, J. H. A metal-organic framework gel with Cd2+ derived from only coordination bonds without intermolecular interactions and its catalytic ability. *New J. Chem.* **37**, 2330–2335 (2013).
164. Saha, A., Adamcik, J., Bolisetty, S., Handschin, S. & Mezzenga, R. Fibrillar networks of glycyrrhizic acid for hybrid nanomaterials with catalytic features. *Angew. Chemie - Int. Ed.* **54**, 5408–5412 (2015).

165. Jin, Q. *et al.* Self-assembly of copper(II) ion-mediated nanotube and its supramolecular chiral catalytic behavior. *Langmuir* **27**, 13847–13853 (2011).
166. Escuder, B., Rodríguez-Llansola, F. & Miravet, J. F. Supramolecular gels as active media for organic reactions and catalysis. *New J. Chem.* **34**, 1044–1054 (2010).
167. Foster, J. A. *et al.* Anion-switchable supramolecular gels for controlling pharmaceutical crystal growth. *Nat. Chem.* **2**, 1037–1043 (2010).
168. Daly, R., Kotova, O., Boese, M., Gunnlaugsson, T. & Boland, J. J. Chemical nano-gardens: Growth of salt nanowires from supramolecular self-assembly gels. *ACS Nano* **7**, 4838–4845 (2013).
169. Henisch, H. K. & García-Ruiz, J. M. Crystal growth in gels and Liesegang ring formation. II. Crystallization criteria and successive precipitation. *J. Cryst. Growth* **75**, 203–211 (1986).
170. Foster, J. A. *et al.* Pharmaceutical polymorph control in a drug-mimetic supramolecular gel. *Chem. Sci.* **8**, 78–84 (2016).
171. Huang, G., Yu, Q., Cai, M., Zhou, F. & Liu, W. Highlighting the Effect of Interfacial Interaction on Tribological Properties of Supramolecular Gel Lubricants. *Adv. Mater. Interfaces* **3**, 1–10 (2016).
172. Yu, Q., Huang, G., Cai, M., Zhou, F. & Liu, W. In situ zwitterionic supramolecular gel lubricants for significantly improved tribological properties. *Tribol. Int.* **95**, 55–65 (2016).
173. Cai, M., Guo, R., Zhou, F. & Liu, W. Lubricating a bright future: Lubrication contribution to energy saving and low carbon emission. *Sci. China Technol. Sci.* **56**, 2888–2913 (2013).
174. Yu, Q., Li, D., Cai, M., Zhou, F. & Liu, W. Supramolecular Gel Lubricants Based on Amino Acid Derivative Gelators. *Tribol. Lett.* **61**, 1–13 (2016).
175. Cai, M., Liang, Y., Zhou, F. & Liu, W. Functional ionic gels formed by supramolecular assembly of a novel low molecular weight anticorrosive/antioxidative gelator. *J. Mater. Chem.* **21**, 13399–13405 (2011).
176. Yu, Q. *et al.* Supramolecular ionogel lubricants with imidazolium-based ionic liquids bearing the urea group as gelator. *J. Colloid Interface Sci.* **487**, 130–140 (2017).
177. Rogers, M. A. Novel structuring strategies for unsaturated fats - Meeting the zero-trans, zero-saturated fat challenge: A review. *Food Res. Int.* **42**, 747–753 (2009).
178. Rogers, M. A., Spagnuolo, P. A., Wang, T. M. & Angka, L. A potential bioactive hard-stock fat replacer comprised of a molecular gel. *Food Sci. Nutr.* **5**, 579–587 (2017).
179. Alvarez-Mitre, F. M., Mallia, V. A., Weiss, R. G., Charó-Alonso, M. A. & Toro-Vazquez, J. F. Self-assembly in vegetable oils of ionic gelators derived from (R)-12-hydroxystearic acid. *Food Struct.* **13**, 56–69 (2017).
180. Co, E. & Marangoni, A. G. The formation of a 12-hydroxystearic acid/vegetable oil organogel under shear and thermal fields. *JAOCS, J. Am. Oil Chem. Soc.* **90**, 529–544 (2013).
181. Bot, A. & Agterof, W. G. M. Structuring of edible oils by mixtures of γ-oryzanol with β-sitosterol or related phytosterols. *JAOCS, J. Am. Oil Chem. Soc.* **83**, 513–521 (2006).
182. Bairi, P. *et al.* A Co-assembled Gel of Pyromellitic Dianhydride Derivative and Polyaniline with Optoelectronic and Photovoltaic Properties A Co-assembled Gel of Pyromellitic Dianhydride Derivative and Polyaniline with

Optoelectronic and Photovoltaic Properties Partha Bair. *Langmuir* **30**, 7547–7555 (2014).

183. Shi, Y., Zhang, J., Pan, L., Shi, Y. & Yu, G. Energy gels: A bio-inspired material platform for advanced energy applications. *Nano Today* **11**, 738–762 (2016).
184. Huo, Z. *et al.* A supramolecular gel electrolyte formed from amide based co-gelator for quasi-solid-state dye-sensitized solar cell with boosted electron kinetic processes. *J. Power Sources* **359**, 80–87 (2017).
185. Huo, Z. *et al.* Quasi-solid-state dye sensitized solar cells using supramolecular gel electrolyte formed from two-component low molecular mass organogelators. *Sci. China Mater.* **58**, 447–454 (2015).
186. Duduta, M. *et al.* Semi-Solid Lithium Rechargeable Flow Battery. *Adv. energy Mater.* **1**, 511–516 (2011).
187. Lyu, F. *et al.* ChemComm of C- and N-doped hollow CuO as high-performance anode materials for Li-ion batteries †. *Chem. Commun.* **53**, 2138–2141 (2017).
188. Reddy, M. V, Rao, G. V. S. & Chowdari, B. V. R. Metal Oxides and Oxysalts as Anode Materials for Li Ion Batteries. *Chem. Rev.* **113**, 5364–5457 (2013).
189. Guo, W., Sun, W. & Wang, Y. Multi-Layer CuO @ NiO Hollow Spheres : Microwave- Assisted Metal-Organic-Framework Derivation and Highly Reversible Structure-Matched Stepwise Lithium Storage Graphical abstract. *ACS Nano* **9**, 11462–11471 (2015).
190. Liang, M., Liu, X., Li, W. & Wang, Q. A Tough Nanocomposite Aerogel of Manganese Oxide and Polyaniline as an Electrode for a Supercapacitor. *Chempluschem* **81**, 40–43 (2016).
191. Dong, X., Wang, H., Fang, F., Li, X. & Yang, Y. Effect of gelator structures on electrochemical properties of ionic-liquid supramolecular gel electrolytes. *Electrochim. Acta* **55**, 2275–2279 (2010).
192. Li, W., Gao, F., Wang, X., Zhang, N. & Ma, M. Flexible Supercapacitors Strong and Robust Polyaniline-Based Supramolecular Hydrogels for Flexible Supercapacitors Angewandte. *Angew. Chemie* **55**, 9196–9201 (2016).
193. Ye, Y., Huang, Y., Cheng, C. & Chang, F. A new supramolecular sulfonated polyimide for use in proton exchange membranes for fuel cells w. *Chem. Commun.* 7554–7556 (2010).
194. Gnana, G. *et al.* Graphene Oxide / Carbon Nanotube Composite Hydrogels — Versatile Materials for Microbial Fuel Cell Applications. *Macromol. Rapid Commun* 1–5 (2014).
195. Lu, Y., Xu, Z., Gasteiger, H. A., Chen, S. & Hamad-schifferli, K. Platinum - Gold Nanoparticles : A Highly Active Bifunctional Electrocatalyst for Rechargeable Lithium - Air Batteries. *J. AM. CHEM. SOC* 12170–12171 (2010).
196. Ma, X., Cui, Y., Liu, S. & Wu, J. A thermo-responsive supramolecular gel and. *Soft Matter* **13**, 8027–8030 (2017).
197. Ma, X., Zhang, J., Tang, N. & Wu, J. A thermo-responsive supramolecular organogel: Dual luminescence properties and luminescence conversion induced by Cd2+. *Dalt. Trans.* **43**, 17236–17239 (2014).
198. Mandal, S. K., Mandal, D. & Kumar, P. Synthesis of a Low-Molecular-Weight Fluorescent Ambidextrous Gelator : Development of Graphene- and Graphene-Oxide-Included Gel Nanocomposites. *Chempluschem* **81**, 213–221 (2016).
199. Tong, B. X., Zhao, Y., An, B. & Park, S. Y. Fluorescent Liquid-Crystal Gels

with Electrically Switchable Photoluminescence **. *Adv. Funct. Mater.* **16**, 1799–1804 (2006).
200. Suzuki, Y., Mizoshita, N. & Kato, T. Homeotropically oriented nematic physical gels for electrooptical materials. *J. Mater. Chem.* **13**, 2870–2874 (2003).
201. Edition, I. Self-healable Organogel Nanocomposite with Angle-independent Structural Colors. *Angew. Chemie* **56**, 10462 (2017).
202. Organogelators, S., Vidyasagar, A., Handore, K., Sureshan, K. M. & George, D. M. V. Soft Optical Devices from Self-Healing Gels Formed by Oil and. *Angew. Chem. Int. Ed. Engl.* **50**, 8021–8024 (2011).
203. Weingarten, A. S. *et al.* Self-assembling hydrogel scaffolds for photocatalytic hydrogen production. *Nat. Chem.* **6**, 964–970 (2014).
204. Yang, Z. *et al.* Using β-lactamase to trigger supramolecular hydrogelation. *J. Am. Chem. Soc.* **129**, 266–267 (2007).
205. Piepenbrock, M. M., Lloyd, G. O., Clarke, N. & Steed, J. W. Metal- and Anion-Binding Supramolecular Gels. *Chem. Rev.* **110**, 1960–2004 (2010).
206. Hiscock, J. R., Sambrook, M. R., Ede, J. A., Wells, N. J. & Gale, P. A. Disruption of a binary organogel by the chemical warfare agent soman (GD) and common organophosphorus simulants. *J. Mater. Chem. A* **3**, 1230–1234 (2015).

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