Journal of Physical Sciences, Vol. 11, 2007, 156-171

Low Molecular Mass Gelators of Organic Liquids

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Received September 29, 2007; accepted November 5, 2007

ABSTRACT

In recent years there has been a considerable interest in developing new types of low molecular mass organogelators because of their potential technological applications. Several classes of *low molecular weight compounds* form stable and efficient gels with various organic solvents at low concentrations**.** One-component and two-component gelators are grouped separately. Each group is self-assembled by various noncovalent to form various structures with nanometer and micrometer dimension.

Key word : *Supramolecular gel; one-component and two-component gelators; nanometer and micrometer dimension; Entangled Fibrillar Gel-Phase Network.*

1. Introduction

Gels are considered as viscoelastic solid-like or liquid-like material. When the bulk solvents are entrapped within an appropriate three dimensional network under suitable condition it form gel. Gels have been used in our everyday life in the form of commercial products such as soaps, shampoo, toothpaste, hair gel and cosmetics, as well as contact lenses and gel pens etc. These types of gels are derived from polymeric compounds. Polymeric gels[1] have been known for centuries and applications in fields as diverse as food, medicine, materials science, cosmetics, pharmacology etc. Gels can be classified in different ways based upon their origin constitution, the type of cross-linking and the medium (*Figure 1*).[2, 3] Depending upon source, gel can be classified into natural gel and artificial or synthetic gel. Gels derived from synthetic compounds can be subdivided into macromolecular (polymer) and molecular gel based on their constitution. Macromolecular gel can be formed either by chemical cross-linking or physical interactions. When the gels are formed by strong chemical bonds, they cannot be re-dissolved and are thermally irreversible whereas gels formed by weak noncovalent interactions (physical interaction) are reversible. Depending upon the solvents, gel can be classified into organogel and hydrogel. The compound form gel with organic solvents is called organogel whereas gel with water is called hydrogel. Depending upon the drying process, gels can be subdivided into aerogel, Cryogel and xerogel. Materials in which the

typical pore structure and network are largely maintained when the pore liquid of a gel is replaced by air are called aerogels. However, it is not always clear to what extent the structure is maintained. Aerogels are highly porous solid materials with extremely low densities, open pores, and high specific surface areas. These result in interesting physical properties, such as extremely low thermal conductivity and low sound velocity, combined with high optical transparency. Cryogels are obtained when the pore liquid is removed by freeze drying. A *xerogel* is formed by conventional drying of the wet gels, that is, by increasing the temperature or decreasing the pressure with concomitant large shrinkage (and mostly destruction) of the initially uniform gel body. Shrinkage upon drying of a wet gel body is showed in *Figure 2*.

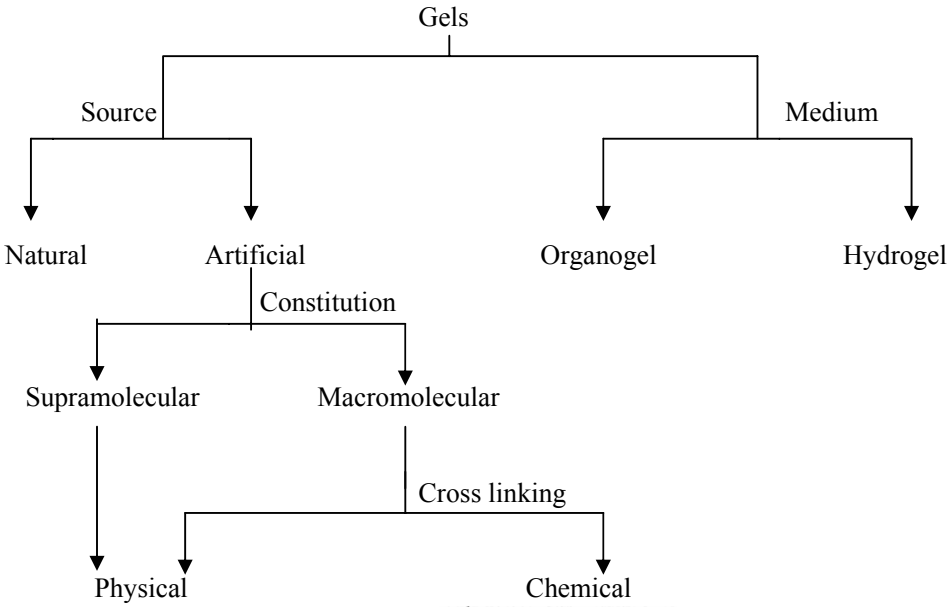


Figure 1. Classification of gels.

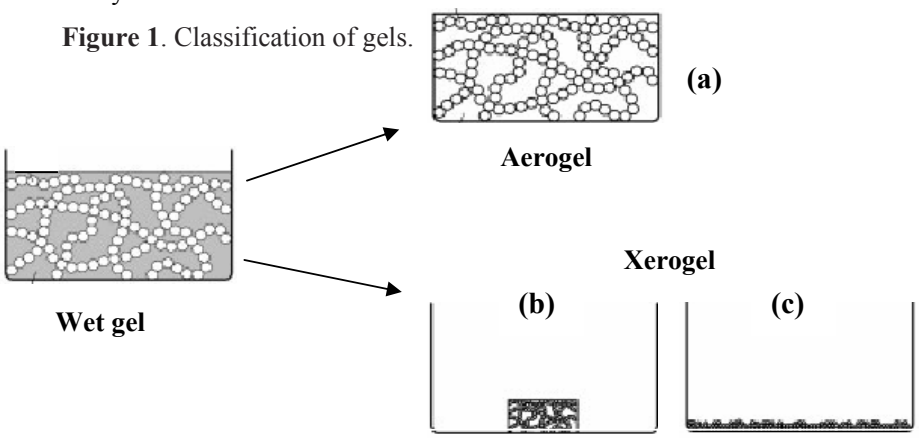


Figure 2. Shrinkage upon drying of a wet gel body to give an aerogel (a) and xerogel (b, c)

The organogels are in common with other gel systems that the gelling agent forms a continuous three- dimensional entangled network in the solvent, thereby preventing the flow of liquid. Gels derived from low molecular mass compounds are called supramolecular gel. Although, the formation of organogels from small organic molecules is an excellent example of supramolecular self-assembly process, most the organogelators have been found by serendipity rather than design and many aspects of organogels are still poorly understood. In recent year, *low molecular mass gelators* attracted considerable interest due to molecules of a great structural diversity. Their discovery and development are particularly important due to potential applications. Low molecular mass organogelators are self-assembled to form fibers, strands, tapes, helix via one-dimensional growth of the molecules. The aggregation of gelator molecules is driven by multiple, weak interaction such as hydrogen bonding interaction, π- π stacking,[4] metal coordination,[9, 5, 6, 7] van der waals interaction.[8] A gel can be broken down into a primary, secondary, and tertiary structure like a protein to understand the mechanism of gel formation.[9] The primary structure (angstrom to nanometer scale) is determined by the molecular level recognition. As a result gelator molecules are aggregated in one dimension. The secondary structure (nano- to micrometer scale) is defined as the morphology of the aggregates like micelles, vesicles, fibers, ribbons or sheets. This secondary structure is directly influenced by the molecular structure. Finally the tertiary structure of a gel (micro- to millimeter scale) involves the interaction of individual aggregates and ultimately determines whether a gel is formed or instead, fibers (or other aggregates) precipitated from solution rather than trapped it.[10] The aggregation of gelator molecules occurred through the both branched fibers and entrangled fibers. The long, thin, flexible fibers are better able than shorter fibers to trap the solvent molecules, leading to gelation.[11]

The transition from molecular to primary and secondary structure has been explained by several methods.[12] As for example, Boden and co-workers have modeled the hierarchical self-assembly of rod-like chiral molecules, such as peptides in a β-strand conformation, into ribbons and fibers.[12a] The transition from secondary to tertiary structure is determined by the type of interactions that can occur among the fibers.

Gels derived from low molecular mass compound are usually prepared by heating the compounds in appropriate solvent and cooling the resulting saturated solution at room temperature. When the hot solution is cooled, the molecules start to condense and three situations are possible i.e a highly ordered aggregation giving rise to crystals, a random aggregation resulting in an amorphous precipitate and an aggregation process intermediate between these two gives rise to a gel (*Figure 3*).

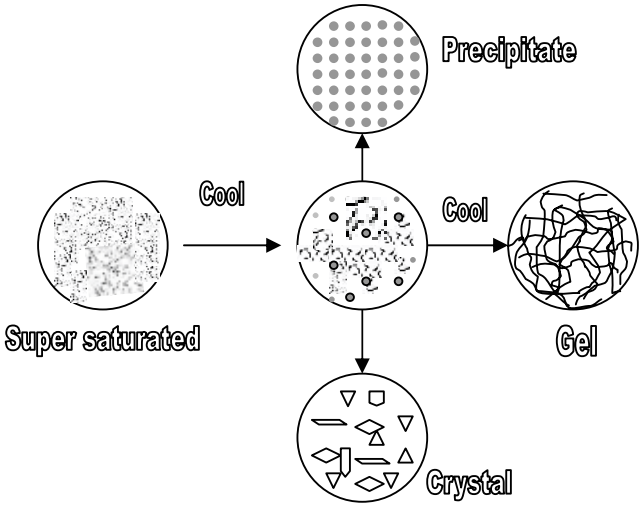


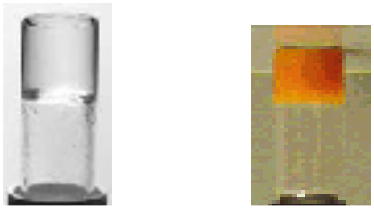
Figure 3. Schematic representation of aggregation modes.

2. Gelation Test

The gelator is dissolved with appropriate amount of solvent (organic solvent or water) by warming in capped test tube or vial. By this procedure the solvent boiling point becomes higher than that under standard atmospheric pressure. Then the vial containing the solution is allowed to cool in air at room temperature, left for 2-3 h at this temperature. When a gel is formed, the homogeneous transparent substance did not flow when the vial is inverted (*Figure 4*).[13] The gel is denoted by "G". The inverted vial approach[14] is used as a general criterion for gel formation.

3. Gel Transition Temperature (T_{gel})

The gel transition temperature is the required temperature below which flow of the gel no longer is discernible over long periods. The gel transition temperature was determined by the ball dropped method. A glass ball was carefully placed on top of the gel and the temperature was slowly raised. The gel transition temperature was determined[15] as the temperature at which gel was unable to bear the glass ball and it dropped down. Gel transition temperature is denoted by 'T_{gel}'. It is also fact that this type of measurement is highly influenced by surface tension and liquid density. To determine the thermal stability of the gels, T_{gel} is plotted against the gelator concentrations. The gel transition temperature increases with increasing in the gelator concentration.



a b

Figure 4. Inverted vials containing colorless gel (a), colorful gel. (b).

4. Morphology of Gels

Molecular self-aggregation features can be observed by an electron microscope, since the initial stage of physical gelation is the self-assembly of gelator monomers. The morphology of the dried gels is studied by Scanning Electron Microscopy (SEM) or Transmission Electron Microscopy (TEM) analysis. The scanning electron microscopic studies of the gel is done using a thin slice of gel on microscopic slides and dried. Then the dried sample is coated by platinum or gold and observed under the SEM apparatus. The SEM images of dried gel indicates various structures like fibers network, tape, ribbon, rod, sheets, hole, micelles, vesicles, helix etc. with micro or nano dimension. The gel networks entrapped the solvent molecules and preventing the solvent molecules when the vial containing gels was inverted (*Figure 4*).

5. One Component and two Component Organogelators

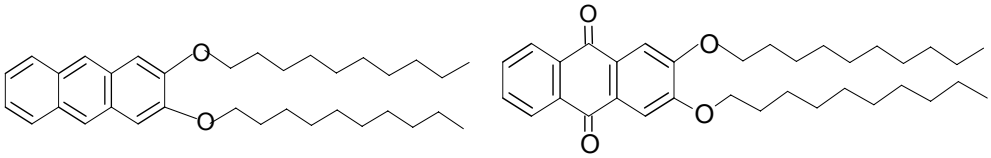
In one-component system, a compound can be present in solution and forms gel with the solvents. Whereas in true two-component systems, an individual component can be present in isotropic solution, and only on additions of the second component will a gel actually form. In case of one-component, gelators molecules are stacked one after one to form gel networks by non covalent interactions such as π- π stacking, hydrogen bonding, van der waals interaction etc.. Whereas in the case of two-component gelators, one compound form a complex with another compound through donor-acceptor interaction, hydrogen bonding interaction etc.. Then the complexes are aggregated to form various structures like *Fibrillar Gel-Phase Network*, helix, ribbons, sheets etc.. One or two-component *low molecular mass gelators* are discussed separately.

5.1. One-Component Organogelators

5.1.1. Anthryl and anthraquinone derivatives

Compound 2,3-Bis(n-decyloxy)anthracene(DDOA) **1** is a good organogelator at low concentration for a large number of solvents ranging from alkanes to alcohols, ethers,

ketones or halogenated molecules.[16,17] The molecules are self associated by dipolar force and van der waals interactions.[1] DDOA can also easily gelify various organic solvents including propylene carbonate (PC) at low concentrations by forming a three-dimensional network of fibers.[18] The electrochemical properties of organogel based on DDOA are reported.[19] The related anthraquinone (**2**) is also an efficient gelator of organic solvents.[20]



1 **2**

Scheme 1. Anthryl derivative-based gelators.

DDOA has recently been used to replicate non-functionalised silica fibres having double-scale porosity.[21] The organogelator DDOA has ability to grow organically modified hybrid silica fibres.[22] The modified derivative 2,3-dialkoxy phenazine gelate various organic solvents such as, methanol, ethanol, DMF, and acetonitrile. The gel in acetonitrile could be fine tuned by reversible protonation of the nitrogen on the gelator. A further increase in the concentration of acid, T_{gel} value was decreased. The compounds 2,3-didecyloxytetracene (DDOT) and 2,3-dihexadecycloxytetracene (DHDOT), which are the more efficient organogelator in various organic solvents like cyclohexane, DMSO, acetone, dichloromethane solvent due to enhance π-stacking ability of tetracenes.[23]

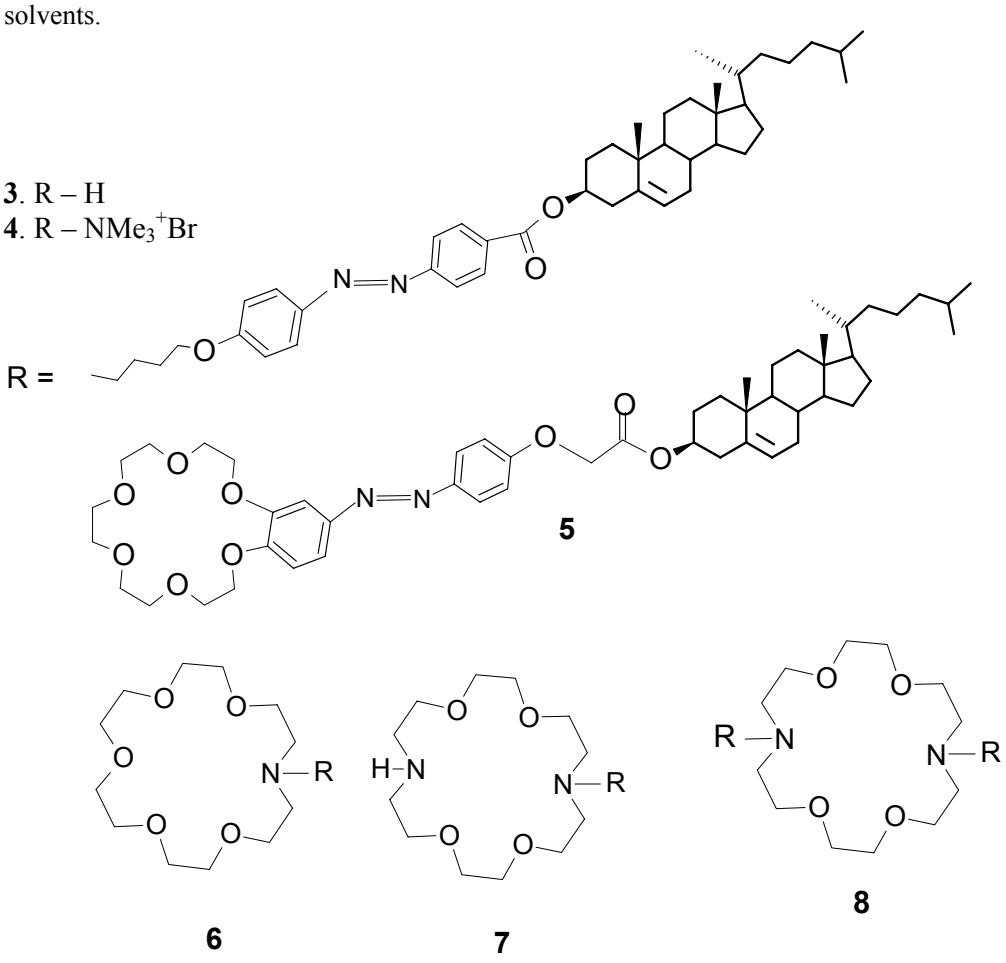
5.1.2 Gelators containing steroidal and condensed aromatic rings

Another class of molecules (**ALS)** which are also efficient gelators of many organic solvents. These molecules consist of an aromatic group (**A**) connected to steroidal moiety (**S**) via a linking group (**L**). The organogelators based on cholesterol in which a chromophore unit is attached.

5.1.2.1 Azobenzene steroid-based and crown ether steroid-based gelators

A cholesterol derivative with an azobenzyl group is an organogelator with various organic solvents.[24,25] The trans form of the compound aggregates readily to form a gel and the cis form does not give the gelation properties. The irradiation of the butanol gel of the cis form of the compound transformed into trans form. Cholesterol-based gelator bearing a 4-pyridyl group was a very versatile gelator whereas cholesterol bearing 3- or 2-pyridyl group gelled very few number of solvents.[26] Compound 3 and 4 shows the gelation properties in various organic solvents as well as the silanol compound TEOS

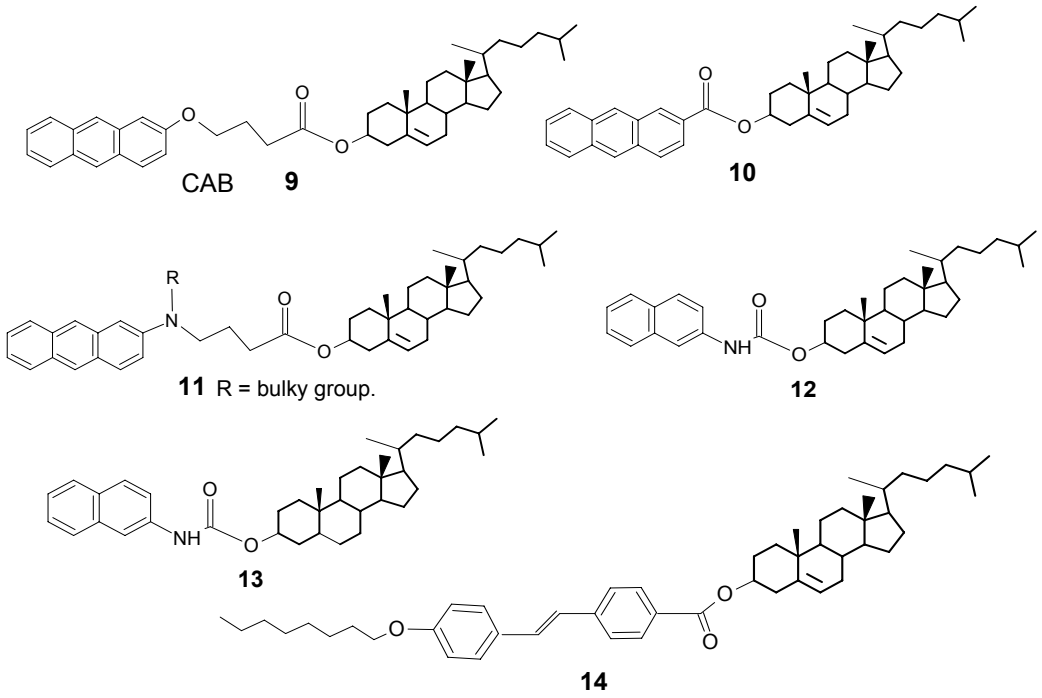
(*Scheme 2*).[27] The SEM studies of the compound 4 showed a network of fibers structure with diameters ranging from 50 to 200 nm. The crown-appended cholesterol derivative act as an amphiphilic gelator for organic solvents.[28] Gel derived from azacrown derivative of cholesterol 5 (*Scheme 2*) in a mixture of methylcyclohexane and benzene solvent responded to added alkali metal or ammonium ions.[9] It is found that T_{gel} increases with increase in the concentration of various alkali metal cations (such as Li^+, Na^+, K^+, Rb^+ and NH_4^+). It is interesting to note that this increase was not continuous and after a saturation point reached, the T_{gel} was decreased. Compounds 6, 7 and 8 which consist of cholesterol moieties linked to azacrown capable of forming gels with various organic solvents.



Scheme 2: Cholesterol-based gelators containing crown ether and azobenzene moiety.

5.1.2.2 Anthryl and anthraquinone appended steroid-based gelators

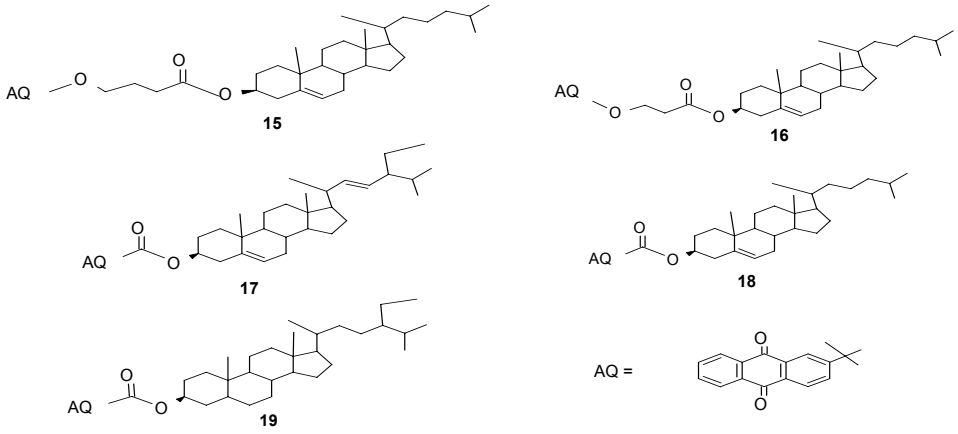
Cholesteryl 4-(2-anthryloxy) butyrate (CAB) could gelate a wide range of solvents including alkanes, alkenes, alcohols, aldehyde, carboxylic acid esters, amines, and aromatic solvents.[29] Three-dimensional *self-assembled fibrillar networks* (SAFINs) was observed by the microscopy studies of CAB. The compound 10 gives gelation properties with organic solvents. The replacement of 2-anthryl part of compound 10 by phenanthryl, pyrenyl, or 9-anthryl did not give the gelation properties with organic solvents. Compound 11 is an efficient gelator whereas the replacement of R- group by NH group is not a successful gelator with organic solvents.[30] Steroid containing napthyl unit via a linking group (13) formed three-dimensional SAFINs through the gelation with various solvents like 1-propanal, 1-butanol, 1-pentanol, n-decane, n-hexanedecane, cyclohexane whereas compound 12 form three-dimensional SAFINs through gelation with organic solvents like ethanol, 1-propanal, 1-butanol, 1-pentanol, n-octanol, n-decane, n-hexanedecane, cyclohexane, benzyl alcohol, ethyl acetate.[31] The presence of one extra double bond at C_5 position of steroid unit (12) compared with 13, changes the gelation properties. It is difficult to trace the specific reason(s) for these differences.



Scheme 3: cholesterol containing chromophore unit based gelators.

However, the range of liquids gelated by each suggests that the presence or absence of a double bond at C5 has some influence on the overall solubility of these LMOGs. Cholesterol containing azobenzene moiety linked via ester group (14) gelled with various organic solvents.[32]

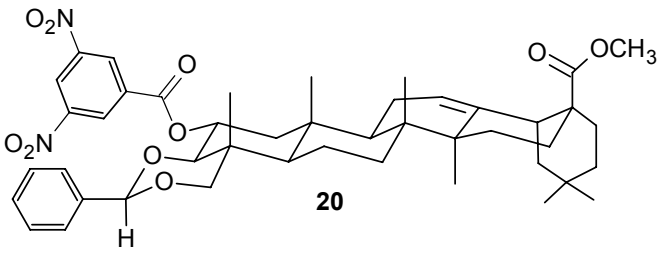
Anthraquinone-steroid based gelators 15-19 gives the gelation properties with various organic solvents (*Scheme 4*).[39,33]The compounds 17, 19 were efficient gelator among the other compounds. The driving force for the aggregation of the gelator molecules was assigned by π- π stacking, van der waals interaction and other non covalent interactions. The gel transition temperature values of gel obtained from 15 and n-alkanes were considerably higher than those from 15 and alkan-1-ols. Various examples include both structurally complicated (ALS molecules with aromatic, linking, and steroidal groups) and simple LMOGs in a wide range of organic liquids were reported.[39]



Scheme 4: Anthraquinone-steroid based gelators.

5.1.3 Gelator containing terpenoid and aromatic ring

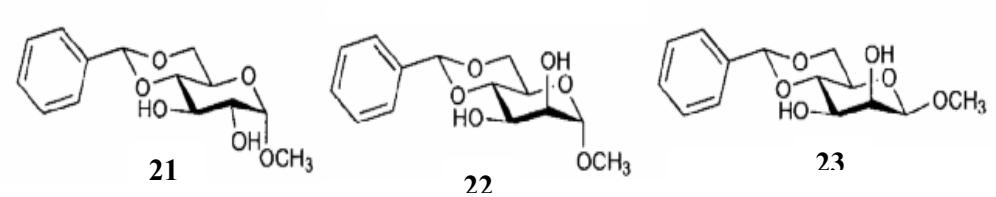
Compound 20 is able to gel with various alcoholic and mixed solvents.[34] Highly stable and efficient gels are obtained with aliphatic alcohols with <1 wt% of the gelators. For instance, methanol could be gelated with only 0.5% of compound 20 indicating that one gelator molecule is capable of immobilizing more than 3500 solvent molecules. To determine the thermal stability of the gels, T_{gel} was plotted against the gelator

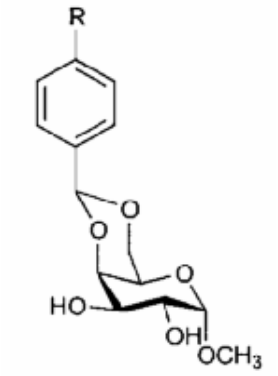


concentration (% w/v). It is also found that T_{gel} increases with increase in the gelator concentration. The increase in T_{gel} with increasing gelator concentration indicates that self-assembly is driven by strong intermolecular interactions.

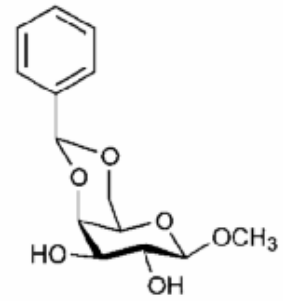
5.1.4 Sugar-based organogelators

Methyl 4,6-*O*-benzylidene monosaccharide (*Scheme 5*) can act as strong organogelators for various organic solvents.[35] For the same concentration the sol-gel transition temperature (T_{gel}) of the compounds (*Scheme 5*) always appears in the order of: 25 >23 >24 > 21 > 22. Methyl glycosides of 4,6-O-benzylidene derivative of monosaccharides aggregate the solvent molecules through the formation of a hydrogen-bonded-based gel network. The evidence of the hydrogen bond was given by FT-IR and temperature dependent NMR spectroscopy. Sugar-based gelators such as 27, 29, 31 and 32 (*Scheme 5*) are capable of gelating various polar solvents.[36] Organogelators derived from different combinations of the gelators and solvent shows the fibrous or spherical morphology on SEM study. Due to the presence of amino groups, the transcription of these organogel result in the formation of hollow fibrous or hollow spherical silica after calcinations. The transcription of the corresponding nitro analogues (26, 28, and 30) was not successful. Whereas the silica resulting from the ethanol gel of the amine-bearing α-glucose derivative 26 has a fibrous structure with a single, central channel, the silica obtained from the ethanol gel of amine-bearing β-glucose derivative 31 possesses several channels inside each silica fiber. The α-glucose-based gelator 32 could gelate a range of organic solvents as well as water and can form fibers in two different ways. In organic solvents, the polar sugar parts can form a chain of intermolecular hydrogen bonds upon stacking and exposes the aromatic parts to the solvent. In water, the molecules are presumed to form fibers through π- π stacking, thus exposing the sugar parts to the solvent.[37]





24. R =H



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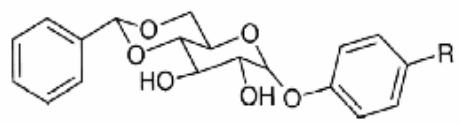
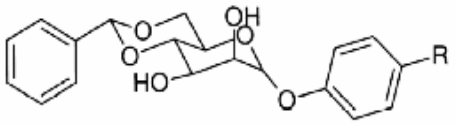


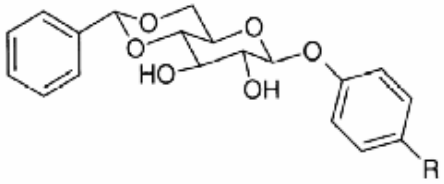
26. (α-glu): R = NO_2

27. (α-glu): R = NH_2



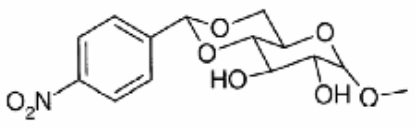
28. (α-man): R = NO_2

29. (α-man): R = NH_2



30. (β-glu): R = NO_2

31. (β-glu): R = NH_2



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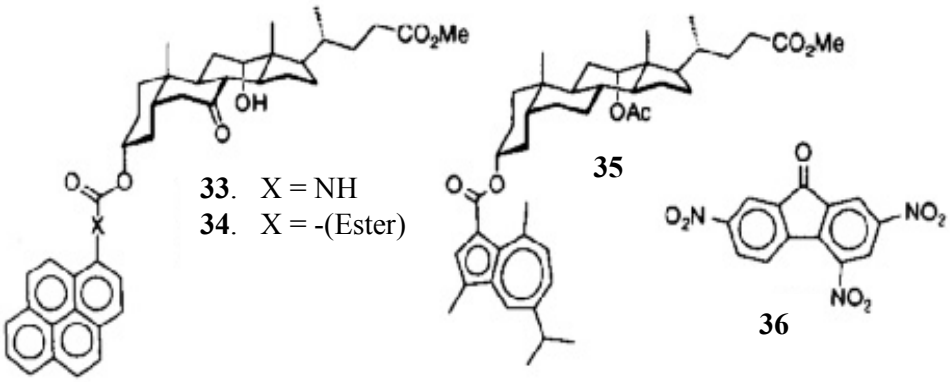
Scheme 5. Sugar-based gelators

5.2 Two component organogelators

5.2.1 Steroid-based gelators

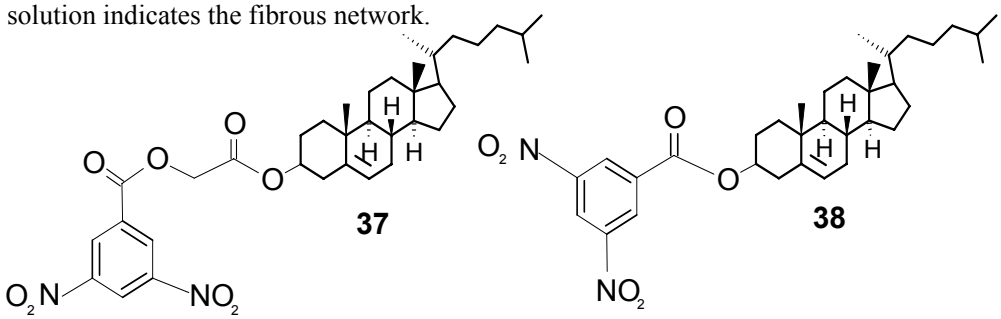
Aromatic donor substituted bile acid derivatives such as 33, 34 and 35 gives the gelation properties with various organic solvents in presence of electron deficient guest,

trinitrofluorenone (TNF) as the accepter (*Scheme 6*).[38] The major driving force is donor-acceptor interaction for the gelation. The stoichiometric requirement of the two components was established by measuring the T_{gel} as a function of the ratio of 36:33 at a constant concentration of 33. The T_{gel} values indicates that 1:1 stoichiometry are required for the effective gelation. The temperature dependence UV-VIS spectroscopy indicates the charge-transfer (CT) interaction between pyrene (donar) unit and trinitrofluorenone (acceptor). The gel formed from colorless 33 and 34 (and pale yellow 36) are colored due to charge-transfer interaction. The intensity of this band changes substantially during the gelation. SEM images of the dried gel derived from 35/36 in n-octanol shows fibrous network.



Scheme 6: Bile acid-based two-component gelators and TNF**.**

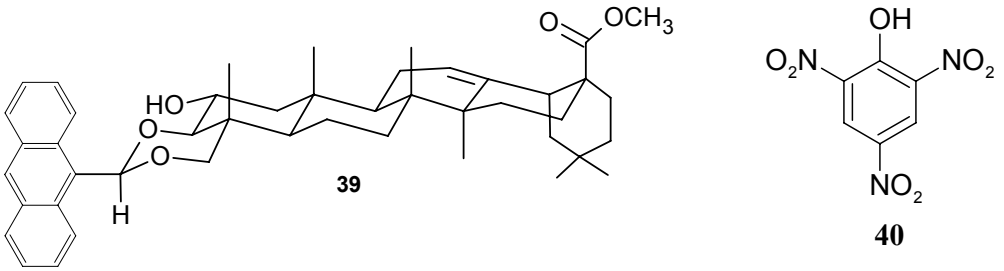
Cholesteryl [(3,5-dinitrobenzoyl)oxy]acetate 37 and cholesteryl 3,5-Dinitrobenzoate 38 (*Scheme 7*) gelify acetonitrile solvent in presence of polyaromatic hydrocarbons (PAHs).[39] The gel formation of rigid ester 38 is favored when the concentration is increased. In constrast gel formation of the less rigid ester 37 occurred at minimum concentration. SEM images of dried gel of compound 37 and anthracene in acetonitrile solution indicates the fibrous network.



Scheme 7. Dinitrobenzoyl appended gelators.

5.2.3 Terpenoid-based two-component gelator

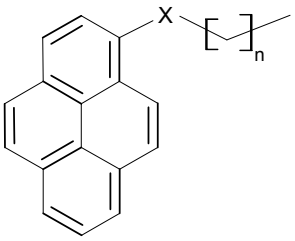
The anthylidene derivative **39** of *arjunolic acid* form thermo reversible gel with organic solvents in presence of electron deficent guest such as picric acid **40** or methyl-3,5-dinitrobenzoate.[40] The color change from yellow to deep red was observed during gelation. The temperature dependent UV-VIS spectroscopy indicates the charge transfer interaction between the anthylidene part of the triterpene derivative and picric acid. The significance of large aromatic surface as well as lypophilic triterpene backbone was discussed. To determine the stoichiometric requirement of the two components on gelation, gel transition temperature was measured with increasing concentration of picric acid at a constant concentration of anthylidene derivative. Scanning Electron Micrographs of gels reveal fibrous morphology.



Scheme 8. Terpenoid-based gelator and picric acid.

5.2.4 Pyrene-based gelators

The pyrene derivatives 41-46 (*Scheme 9*) formed gel with different organic solvents in presence of TNF due to tharge-transfer interaction between pyrine unit and trinitrofluorenone.[41] . The most of the gels were stable at room temperature for several days. Compounds 41 and 42 formed opque organogel with hydroxylic solvents whereas compound 43, 44, 45 and 46 formed transparent color gels in hydrocarbon hydroxylic solvents. The T_{gel} value was maximum at 1:1 molar ratio of acceptor and donor. At a 1:1 ratio of donor (42) to acceptor (36), the T_{gel} values increased with increasing gelator concentration. The length of hydrocarbon chain did not affect the gelation ability and thermal stability of the gels. The temperature dependence UV-VIS spectroscopy and color change during gelation indicates the charge-transfer interaction between pyrene unit and TNF.



41. X = COO , n = 15, **44**. X = CH_2, n = 10
42. X = COO, n = 7, **45**. X = CH_2, n = 0
43. X = CH_2, n = 14, **46**. X = O, n = 13

Scheme 9. pyrene based gelators.

6. Conclusions

In this article, definition, classification, driving force and mechanism for the formation of gel and gel transition temperature has discussed. As an aid to defining strategies for the molecular design of new *low molecular mass* gelators, organogelators have been grouped separately. Each group of *low molecular mass* compound forms gel with various organic solvents. The first terpenoid-based one-component and two-component gelators are reported here. The study of supramolecular gel phase materials has led to a revolution in the ability of chemists to engineer nanoscale structures that have macroscopic soft materials properties.

REFERENCES

1. (a) "Polymer Gels; fundamentals of Biomedical Application" D. Derossi, K. Kajiwara, Y. Osada, A. Yamauchi, *Plenum Press, New York*, 1991; (b)"Thermoreversible Gelation of polymers and Biopolymers" J. M guenewt, *Academic press, London*(1992). (C) Corriu, R. J. P.; Leclercq. D. *Angew Chem.. Int. Ed. Engl*. 1996, *35*, 1420,
2. Osada, Y.; Kajiwara, K.; (ed.) Fushimi, T.; Hirasa, O.; Hirokawa, Y.; Matsunaga, T.; Snimomura, T.; wang, L. (assoc. ed.).; Ishida, H. Gels hand book. *Vol. 1-3,* Academic Press. San Diego. 2001.
3. Sangeetha, N. M.; Maitra, U. *Chem. Soc. Rev*., 2005, *34*, 821–836
4. Tam, A. Y-Y.; Wong, K. M-C.; Wang, G.; Yam, V. W-W. *Chem. Commun*., 2007, 2028–2030
5. (a) Terech. P.; Schaffhauser, V.; Maldivi, P.; Guenet J. M. *Langmuir*, 1992, *8*, 2104. (b) Dammer, P.maldivi, P. Terech and J. Guenet, *Langmuir*, 1995, *11*, 1500.
6. (a) Yam, V. W.W. Chan, K. H. Y. ; Wong, K.M.C. and Zhu, N. *Chem.Eur.J*., 2005, *11*, 4535. (b) Yu, C.; Wong, K. M. C.; Chan, K.H.Y. and. Yam, V. W. W. Angew. *Chem., Int. Ed.*, 2005, *44*, 791. (c) Yam, V.W.W.; Chan, K.H.Y.; Wong, K. M. C.; and Chu, B.W.K. *Angew. Chem., Int. Ed*., 2006, *45*, 6169.

7. (a) Kishimura, A.; Yamashita, T. and Aida, T. *J. Am. Chem. Soc*., 2005, *127*,179. (b) Camerel, F.;.Bonardi, L; Schmutz, M.and Ziessel, R. *J. Am. Chem. Soc.*, 2006, *128*, 4548. (c) Weng, W., Beck, J. B., Jamieson, A.M.; Rowan, S.J. *J. Am. Chem. Soc*.,2006, *128*, 11663. (d) Camerel, F.; Ziessel, R.; Donnio, B.; Bourgogne, C.; Guillon, D.; Schmutz, M.; Iacovita, C. Bucher, J. P. *Angew. Chem., Int. Ed*., 2007, *46*, 2659. (e) Naota, T.; Koori, H.; *J. Am. Chem. Soc*., 2005, *127*, 9324.
8. Sugiyasu, K.; Numata, M.; Fujita, N.; Park, S. M.; Yun, Y. J.; Kim, B. H.; Shinkai, S. *Chem. Commun*. 2004, 1996.
9. Simmons, B. A.; Taylor, C. E.; Landis, F. A.; John, V. T.; McPherson, G. L.; Schwartz, D. K.; Moore, R. *J. Am. Soc*. 2001, *123*, 2414.
10. Estroff, L. A.; Hamilton, A. D. *Chemical Review*, 2004, *104*, 1201.
11. Flory, P. *J. Faraday Discuss*. 1974, *57*, 7.
12. (a) Israelachvili, J. N.; Intermolecular and Surface Fources, 2nd ed.; *Academic Press: New York*, 1991. (b) Schnur, J. M. *Science* 1993, *262*, 1669. (c) Nandi, N.; Bagchi. B. *J. Am. Chem. Soc*. 1996, *118*, 11208.
13. (a) Hirst, A. R.; Smith, D. K. *Chem. Eur. J*. 2005, *11*, 5496 – 550. (b) Beck, J. B.; Rowan, S. J. *J. Am. Chem. Soc*. 2003, *125*, 13922-13923. (c) Kuroiwa, K.; Shibata, T.; Takada, A.; Nemoto, N.; Kimizuka, N. *J. Am. Chem. Soc*. 2004, *126*, 2016-2021.
14. Murata, K.; Aoki, M.; Suzuki, T.; Harada, T.; Kawabata, H.; Komori, T.; Ohseto, F.; Ueda, K.; Shinkai, S. *J. Am. Chem. Soc.* 1994, *116*, 6664-6676.
15. Takahashi, A.; Sakai, M.; Kato, T. *Polymer*. *J*. 1980, *12*, 335-341.
16. Brotin, T.; Utermohlen, R.; Fages, F.; Bouas-Laurent, H.; Desvergne, J. P. *Chem. Commun.* 1991, 416.
17. Terech, P.; Bouas-Laurent, H.; Desvergne, J. P. J. *Colloid Sci*. 1995, *174*, 258.
18. Placin, F.; Desvergne, J.-P.; Lassegues, J.-C. *Chem. Mater*. 2001, *13,* 117.
19. Placin. F.; Desvergne, J.-P.; Belin, C.; Buffeteau, T.; Desbat, B.; Ducasse, L.; Lassegues, J.-C. *Langmuir* 2003, *19*, 4563.
20. Terech, P.; Weiss, R. G.; *Chemical Review*, 1997, 97, 3133.
21. Clavier, G.M.; Pozzo, J. L.; Bouas-Laurent, H.; Liere, C.; Roux , C.; Sanchez, C. *J. Mater. Chem.* 2000, *10*, 1725.
22. LIusar, M.; Roux, C.; Pozzo, J. L.; Sanchez, C., *J. Mater. Chem*., 2003, *13,* 442-444.
23. Reichwagen, J.; Hopf, H.; Guerzo, A. D.; Belin, C.; Bouas-Laurent, H.; Desvergne, J.-P. *Org. Lett*., 2005, *7*, 6
24. Murata, K.; Aoki, M.; Nishi, T.; Ikeda, A. and S. Shinkai. *J. Chem. Soc., Chem. Commun*. 1991, 1715.
25. Murata, K.; Aoki, M.; Suzuki, T.; Harada, T.; Kawabata, H.; Komri, T.; Olrseto, F.; Ueda, K.; Shinkai, S. *J. Am. Chem. Soc*. 1994, *116*, 6664-6676.
26. Kawano, S-i.; Fujita, N.; Bommel, K. J. C.; Shinkai, S. *Chemistry Letter*, 2003, *32*, 12.
27. For a review on the gelation of liquids by cholesterol derivatives, (a) Shinkai, S.; Murata, K.; *J. Mater. Chem*. 1998, *8*, 485-495. (b) The aggregation structure of these gels has

been studies by using small angle X-ray scattering: Sakurai, K.; One, Y.; Jung, J. H.; Okamoto, S.; Sakurai, S.; Shinkai, S. *J. Chem. Soc. Perkin Trans. 2* 2001, 108-112.

28. Jung, J. H.; Kobayashi, H.; Masuda, Shimizu, T.; Shinkai, S. *J. Am. Chem. Soc*. 2001, *123*, 8785.
29. Lin, Y.-C.; B. Kachar and. Weiss, R. G *J. Am. Chem. Soc*., 1989, *111*, 5542.
30. .(a) Lu, L.; Cocker, T. M.; Bachman, R. E.; Weiss, R. G. *Langmuir*, 2000, *16*, 20-34. (b) Lu, L Ph.D. Thesis, Georgetown University, Washington, DC, 1997.
31. George, M.; Weiss, R. G. *Accounts of Chemical Research,* 2006, *39*, 489.
32. (a) Mukkamala, R.; Weiss, R. G. *J. Chem. Soc., Chem. Commun*., 1995, 375-376. (b) Wang, R.; Geiger, C.; Chen, L.; Swanson, B.; Whitten, D. G. *J. Am. Chem. Soc*. 2000, *122*, 2399-2400.
33. Mukkamala, R.; Weis, R. G. *Chem. Commun*. 1995, 375.
34. (a) Bag, B. G.; Maity, G. C.; Pramanik, S. R. *Supramol*. *Chem*. 2005, *17*, 383. (b) Bag, B. G.; Maity, G. C.; Pramanik, S. R. *Pramana*, 2005, *65*
35. (a) Gronwald, A.; Shinkai, S. *Chem. Eur. J*. 2001*, 7*, 20. (b) Yoza, K.; Amanokura,b N.; Ono, Y.; Akao, T.; Shinmori, H.; Takeuchi, M.; Shinkai, S. Reinhoudt, D. N. *Chem. Eur. J. 1999*, *5*, 2722 - 2729; (c) Luboradzki, R.; Gronwald, O. Ikeda, M.; Shinkai, S.; Reinhoudt, D. N. *Tetrahedron* 2000, *56*, 8697 -8701;(d) Gronwald, O.; Sakurai, K.; Luboradzki, R.; Kimura, T.; Shinkai, S. *Carbohydr. Res.* 2001, *331*, 307-318.
36. (a) Jung, J. H.; Amaike, M.; Shinkai, S. *Chem. Commun*. 2000, 2343-2344. (b) Jung, J. H.; Amaike, M.; Nakashima, K.; Shinkai, S. *J. Chem. Soc. Perkin Trans. 2* 2001, 1938-1943. (c) Jung, J. H.; Amaike, M.; Shinkai, S. *Trans. Mater. Res. Soc. Jap*. 2001, *26*, 527-530.
37. Gronwald, O.; Shinkai*,* S. *J. Chem. Soc. Perkin Trans. 2* 2001, 19933-1937.
38. Mitra, U.; Vijay Kumar, P.; Chandra, N.; D`Souza, L. J.; Prasanna, M. D.; Raju, A. R. *Chem. Commun*. 1999, 595.
39. Rizkov, D.; Gun, J.; Lev, O.; Sicsic, R.; Melman, A. *Langmuir*, 2005, *21*, 12130-12138.
40. "Donar-Acceptor Interaction Promoted Gelation: Visual Observation of Color Change", Bag, B. G.; Maity, G. C.; Dinda, S. *Organic Lett.* 2006*, 8,* 5457.
41. Bablu, P.; Sengeetha, N. M.; Vijaykumar, P.; Mitra, U.; Rissanen, K.; Raju, A. R. *Chem. Eur. J*. 2003, *9*, 1922-1932.