COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH
UNIVERSITY GRANTS COMMISSION

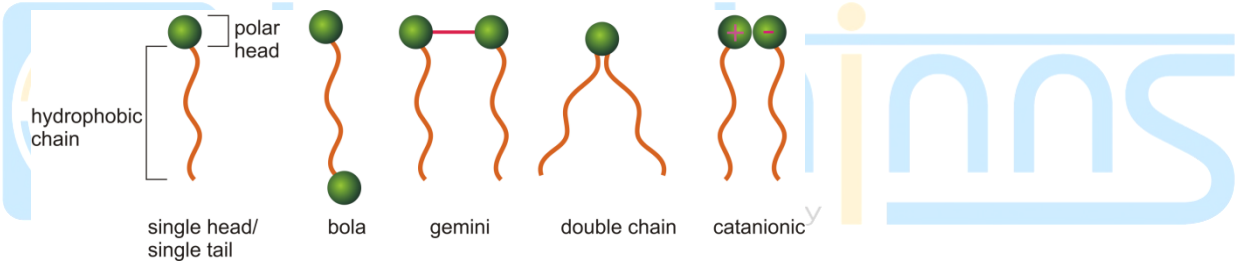
CHEMICAL sCIENCES code:01

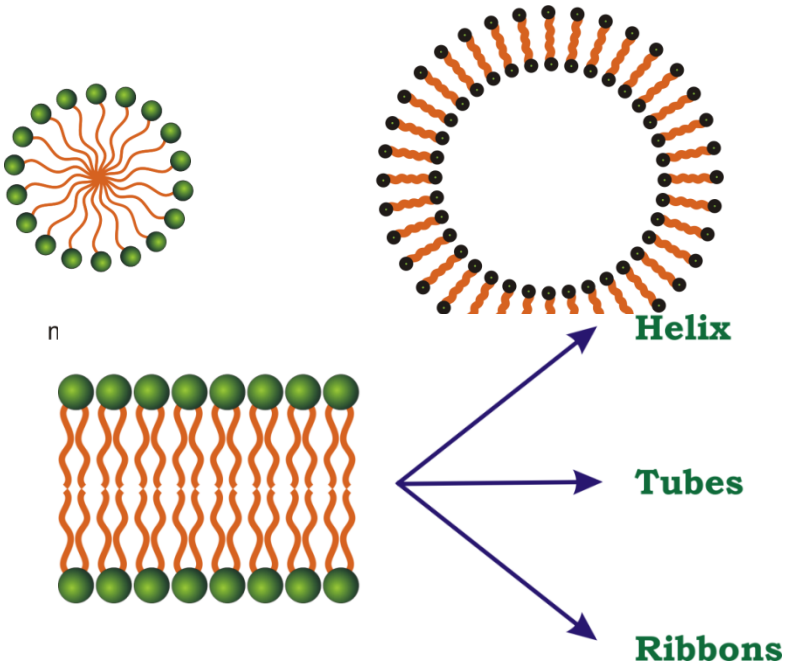
4.4. Supramolecular Chemistry

Self-assembly

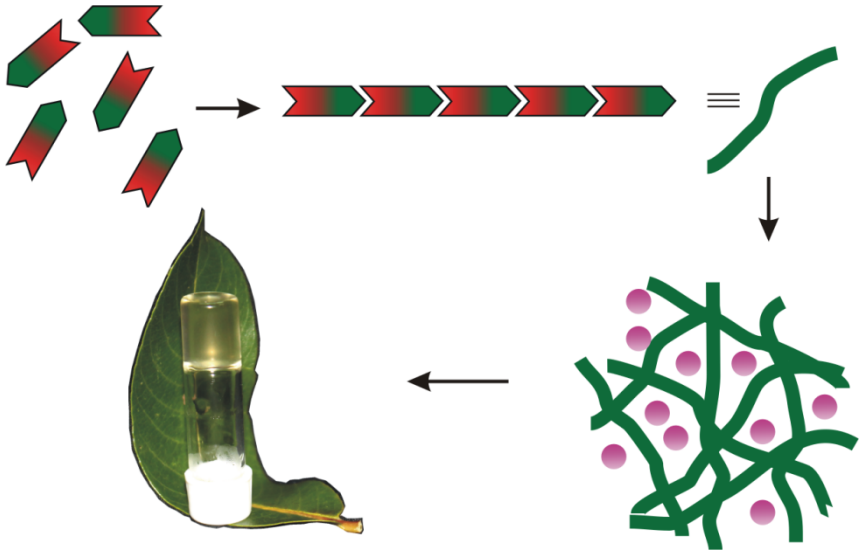
Self-assembly is a type of process in which a disordered system of pre-existing components forms an organized structure or pattern as a consequence of specific, local interactions among the components themselves, without external direction. When the constitutive components are molecules, the process is termed molecular self-assembly.

Amphiphiles





Formation of supramolecular gel via self-assembled fibrillar network

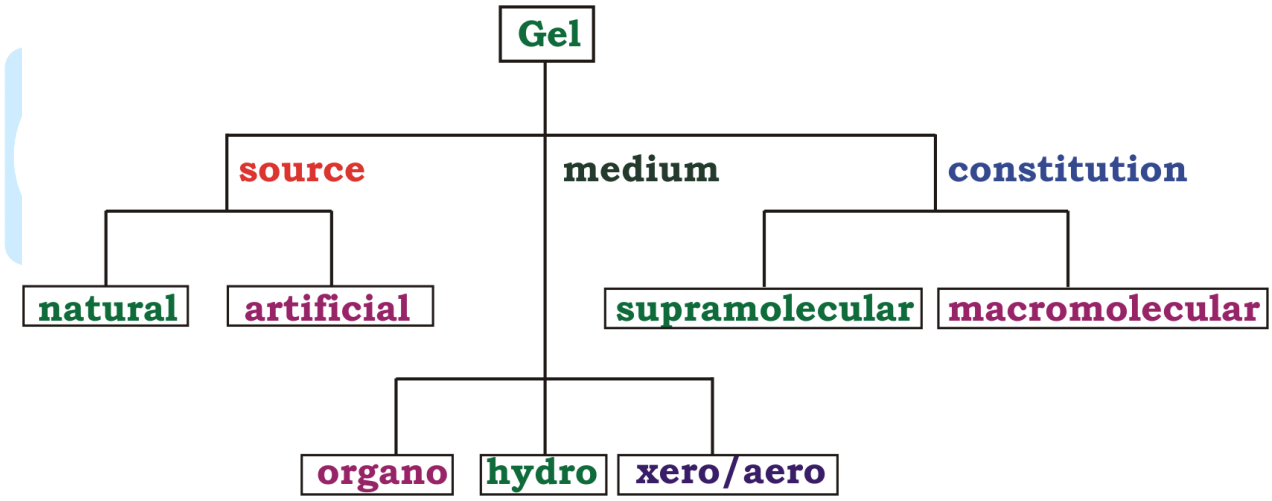


Supramolecular Gels

Gels are unique soft materials, well known in our daily life and having a broad range of applications in food, medicines, cosmetics, separation technology, etc. Typical examples are for instance gelatin pudding, anti-insect gel, hair styling gel, detergent gels, etc. Despite the fact that gels have been known and studied since the end of the 18th century, up till now '…. the gel is one which is easier to recognize than to define…'. In general, gels are soft solid-like materials in which a liquid (the major component) is entrapped inside the three-dimensional network of a solid (minor component). The solid phase forms a network of interconnected fibers, which prevents the fluid from flowing on a macroscopic scale, whereas on a microscopic scale the liquid is mobile. The fluid phase fills the pores of the network and prevents the network from collapsing.

As a result of this structure, the gel possesses both solid-like and liquid-like characteristics. For instance, a gel is resistant to mechanical stress, a large solid-liquid interfacial area is present within the gel, solutes can be entrapped within the pores formed by the solid-component or slowly diffuse through the gel and the fluid component can be used as a reaction medium. Due to these unique characteristics gels, are very interesting, both from a scientific and an industrial perspective.

Classification of Gels



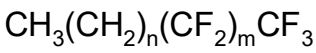
Among various types of gelators, the studies of low molecular mass organogelators (LMOGs) have gained renewed interest in recent years because of their various potential applications as well as their importance in supramolecular chemistry.

Representative LMOGs:

A: LMOG's based upon elongated hydrocarbons

n = 1 - 13

1



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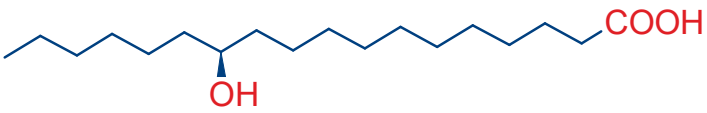

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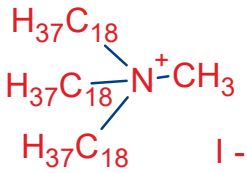

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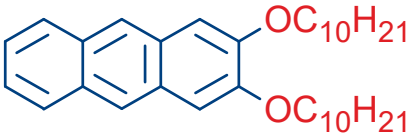
B: LMOG's based upon aromatic units



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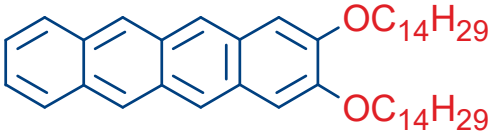

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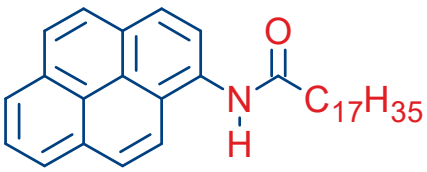

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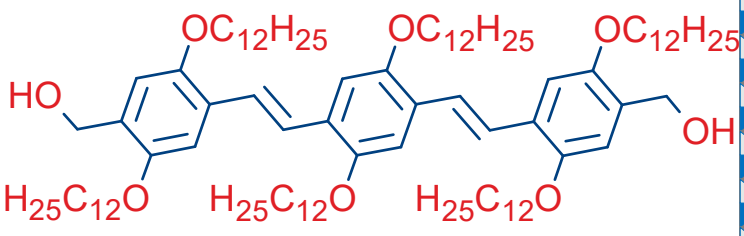

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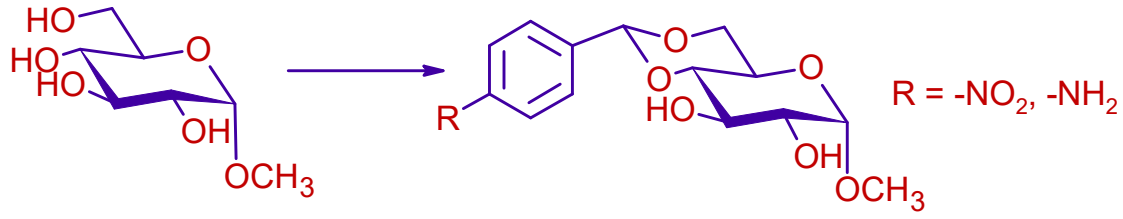
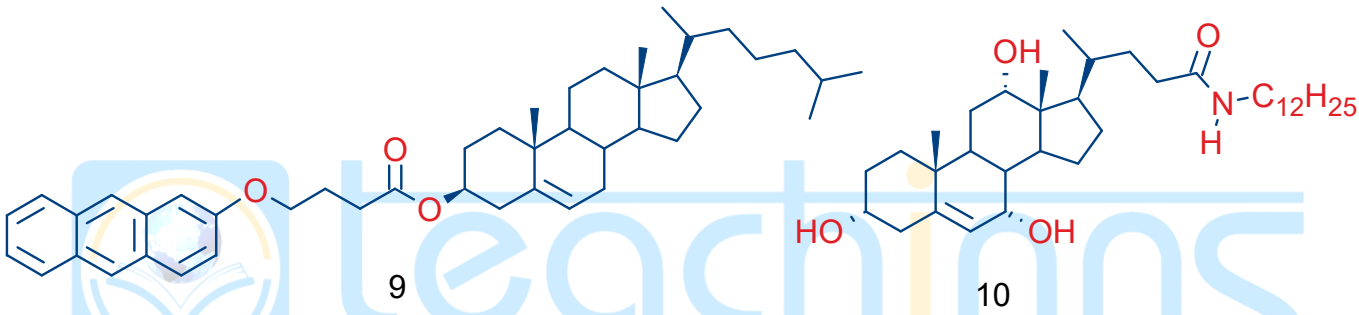
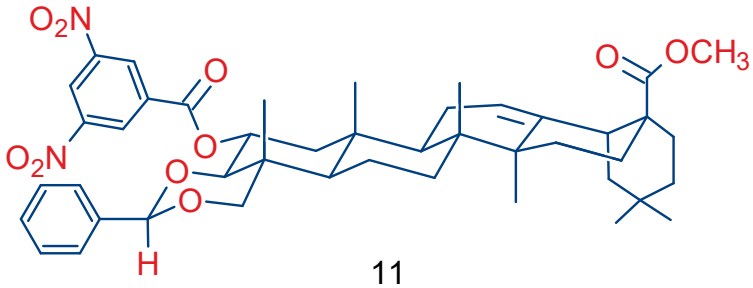
C: LMOGs based upon sugars

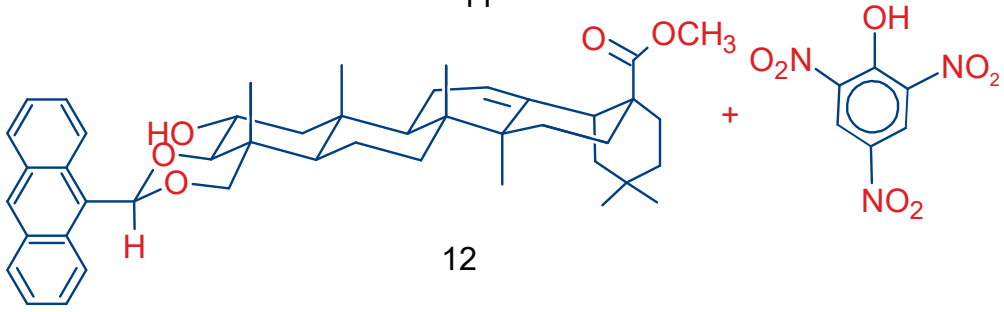


D: LMOG's based on Steroids



E: LMOG's based on Terpenoids





Preparation of Gel:

Gels from low molecular mass organic compounds are usually prepared by heating the gelator in an appropriate solvent and then allowing the resulting solution to cool at room temperature. When the solvent does not flow under gravity, the resulting soft solid-like material is called gel. The low molecular mass organic compounds self-assemble in one dimension to form a fibrous network. The solvent molecules are then trapped inside the network and in macroscopic scale their movements are lost.

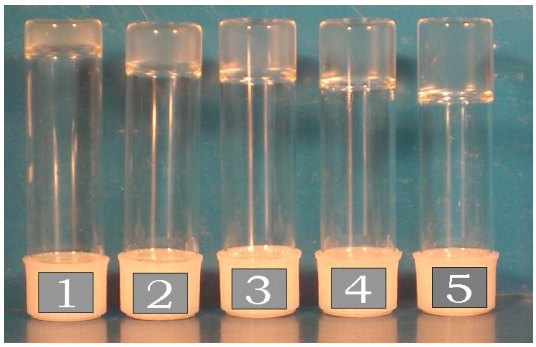
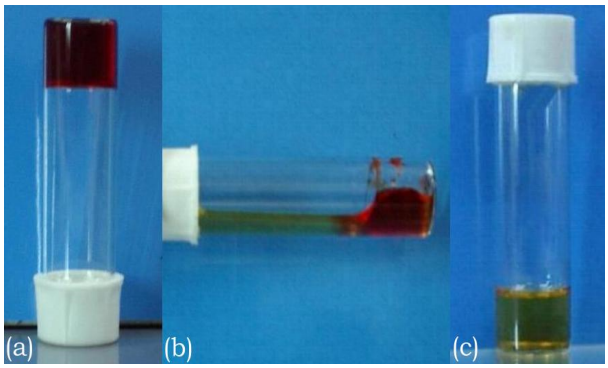


Figure: Inverted vials containing gels from **11** and propan-2-ol

Gel Melting:

A plot of the gel-to-sol transition temperature T_{gel} is shown in figure. With increasing gelator concentration, the T_{gel} values increase indicating stronger intermolecular interactions.

Thermochromic behavior has been demonstrated in the case of two component organogel system **12** (see fugure). A new charge-transfer band is formed during gelation which disappears during melting. Efficient gelation takes place when both the components are present in 1:1 stoichiometric ratio.



Morphology:

The morphology of the gels are studied by various microscopic techniques like SEM, TEM, AFM etc. All these studies reveal a fibrous network structure formed by self-assembly of the molecules in one dimension.

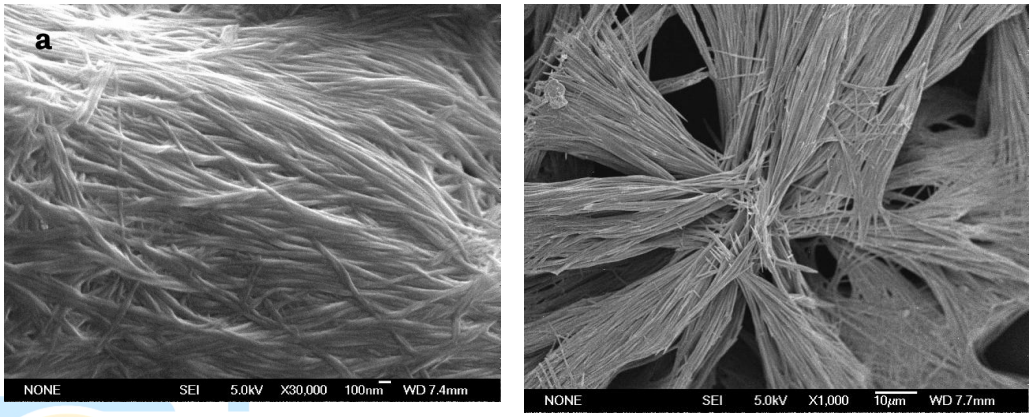


Figure: Scanning Electron Micrographs

References:

(i) M. George, R.G. Weiss, *Acc. Chem. Res.* (2006), 39, 489.

(ii) N.M. Sangeetha, U. Maitra, *Chem. Soc. Res.,* (2005), 34, 821.

(iii) B.G. Bag, G.C. Maity, S.K. Dinda, *Org. Lett.* (2006), 8, 5457.