Chapter 1. A Brief Overview of Low Molecular Mass Gels and their Applications

This chapter deals with molecular gels derived from the self-assembly of small organic molecules (typical molecular weight < 2000 daltons), endowed with appropriate functions to promote anisotropic growth of supramolecular aggregates, by means of various non-covalent interactions like van der Waals, π-π stacking, H-bonding etc., leading to a self-assembled fibrillar network (SAFIN). Several representative examples from the literature (Chart 1) are discussed to demonstrate the structural diversity of the gelator molecules which form self-assembled organogels or hydrogels.

Besides emphasizing on the diverse molecular structures of the gelators, applications of gel phase materials as functional nanostructures are also discussed (Scheme 1). Some of
the aspects that have been elaborated in this context include the use of gels as reaction media, as sensors, in light harvesting, as biomaterials and in optoelectronic applications.

![Scheme 1](image)

**Chapter 2. Supramolecular Chirality in Organogels: Spectroscopic, Morphological and Rheological Investigations of Gels/Xerogels derived from Alkyl Pyrenyl Urethanes**

This chapter addresses the formation of chiral supramolecular structures in the organogels derived from chiral 1R (or 2R), and its mixture with its enantiomer (1S) and a series of achiral analogues (3-9) by extensive circular dichroism (CD) spectroscopic measurements (Chart 2). Morphological studies by atomic force microscopy (AFM) and scanning electron microscopy (SEM) were complemented by the measurements of their bulk properties by thermal stability and rheological studies. Specific molecular recognition events (1/3 vs 2/3) and solvent effects (isooctane vs dodecane) were found to be critical in the formation of the chiral aggregates. Computational studies were carried out to understand the interactions responsible for the formation of chiral superstructures.

![Chart 2](image)
Chapter 3. Self-assembled Composite Organogels based on a Thermo-reversible Photoactive $n$-Acene Fibrillar Scaffold and Organic Ligand stabilized ZnO Nanoparticles

Organic/inorganic composite organogels were obtained in $n$-BuOH by the self-assembly of 2,3-di-$n$-decyloxyanthracene (DDOA, Chart 3) in this solvent in the presence of ZnO nanoparticles (NPs) capped with different organic ligands (Chart 4). When ligands (oleic acid or 2,3-substituted anthracenic acid/oleic acid mixed shell) having structural similarity with the gelator molecule were used to cap the NPs, a homogeneous dispersion of the NPs in the gel matrix was obtained, as confirmed by microscopy (TEM and confocal fluorescence microscopy) experiments. The efficient integration of these NPs into the gel fibers resulted in a significant quenching (20-25%) of DDOA emission, even with extremely small loading of these NPs (~ $10^{-4}$ mol% compared to DDOA) into the gel fibers. The mechanical properties (rheology experiments) and thermal stability (thermal gel melting experiments) of the composite gels were unaffected relative to the pristine DDOA organogel. However, the presence of the NPs lowered the critical gelation concentration and accelerated the gelation kinetics. Attempts to disperse these NPs (the ones without fluoro capping) on the aerogel fibers of DDOA by dissolving both DDOA and the NPs in supercritical (sc) CO$_2$ were not successful (Fig. 1), since the NPs could not be dissolved in scCO$_2$.

![Figure 1](image)

**Figure 1.** (a) TEM images of DDOA aerogels obtained from scCO$_2$, containing A23-NPs, scale bar 200 nm; (b) SEM image of DDOA aerogel obtained in the presence of OL-NPs, scale bar 10 µm.
Chapter 4. Donor-Acceptor Interaction Promoted Gelation of Organic Fluids by Anthracene Carboxamides/2,4,7-Trinitrofluorenone

Tris carboxamides of anthracene were found to form charge-transfer driven organogels in a range of aliphatic alcohols in the presence of an equivalent of (electron-deficient) 2,4,7-trinitrofluorenone (TNF) (Chart 5). Intense color developed in the gel state during the sol to gel phase transition process (Fig. 2). Besides, none of these carboxamides were able to form gel in the absence of TNF, suggesting the importance of charge-transfer interaction in the gel formation. Importantly, most of these gels formed only through rapid cooling of the hot solution, otherwise leading to the precipitation of the CT complex from the solvent. This result indicated that the kinetics is very important for the formation of these gels. Optimum stoichiometry of the donor and acceptor was found to be 1:1. At this molar ratio of the donor and the acceptor, the gels not only showed the highest thermal stability (thermal gel melting experiments), they also displayed the highest values of the mechanical strength and the yield stress (rheology experiments). All the gels showed extensive quenching of the emission of the monomeric anthracenic donor. For the gels derived from the 2-substituted donor, a low energy emission at high wavelength indicated the formation of an emissive CT exciplex. X-ray powder diffraction studies of these xerogels revealed the presence of layered, fibrillar structures in the xerogel phase.

**Chart 5**

**Figure 2.** The gelation event: (a) The 2-substituted carboxamide and TNF taken in 1-propanol (b) The mixture was heated to obtain a homogeneous solution (pale yellow) (1:1 of donor and acceptor, 16.6 mM each). (c) Rapid cooling of the hot solution to 0 °C followed by warming up to room temperature led to a transparent, cherry colored gel.