Abstract

Supramolecular chemistry is one of the most fascinating fields of chemistry, which is defined as the ‘chemistry beyond the molecule’ or ‘chemistry of noncovalent interactions’. Inspired by the unrivalled imagination of nature, supramolecular chemists are pursuing the translation of the principles of supramolecular self-assembly into novel organic materials with specific functions. In this chapter, a review of functional supramolecular assemblies is presented with special emphasis on H-bonded chromophore assemblies and low molecular weight organogels. Finally, the aim and the outline of the thesis are presented.

1.1. Supramolecular Chemistry

In nature, large and complex biological systems such as the lipid bilayers, the DNA double helix, the collagen triple helix and the tertiary and quaternary structures of proteins are formed by defined supramolecular organization of natural building blocks with the help of various noncovalent interactions. This unrivalled complexity and elegance of natural assemblies through molecular recognition and the desire to understand and mimic the structure and functions of such architectures were the inspiration to chemists to the development of supramolecular chemistry. It is generally defined as the ‘chemistry beyond the molecule’ and deals with the design and
synthesis of novel supramolecular architectures via spontaneous self-assembly of molecules, governed by various noncovalent interactions between or within molecules. The concept and terms of supramolecular chemistry were coined by Lehn in 1978. According to him supramolecular chemistry may be divided into two broad and partially overlapping areas as supermolecules and supramolecular assemblies. Supermolecules are well-defined, discrete oligomolecular species formed by the intermolecular association of a few components based on the principles of molecular recognition. Supramolecular assemblies are polynuclear entities that result from the spontaneous self-assembly of a large undefined number of components into a specific phase having more or less well-defined microscopic organization and macroscopic characteristics depending upon its nature, as in the case of membranes, vesicles, micelles etc.

Started only as a scientific curiosity nearly 30 years ago by the pioneers in this field Donald Cram, Jean-Marie Lehn and Charles Pedersen (Figure 1.1), supramolecular chemistry has emerged into one of the most fascinating and active fields of research of modern chemistry. The contributions of Cram, Lehn and Pedersen were recognized by conferring the Nobel prize for chemistry in the year 1987. The roots of the supramolecular chemistry lie on molecular recognition and host-guest interaction. However, the modern supramolecular chemistry stretches from molecular recognition in natural and artificial complexes to the design of functional supramolecular materials for applications in biology, medicine and material science. Therefore, supramolecular chemistry is an interdisciplinary area of research and plays a crucial role to the development of the emerging area of nanoscience and technology.
1.2. Noncovalent Interactions and Noncovalent Synthesis

One of the most important aspects of supramolecular chemistry is its ability to utilize noncovalent interactions for the controlled, reversible assemblies of functional building blocks. Noncovalent interactions can be of attractive and repulsive intermolecular forces, with interaction energies ranging from 4-400 kJmol$^{-1}$, as can be observed from Table 1.1. These are in the order of decreasing strength (a) electrostatic interactions (ion-ion, ion-dipole and dipole-dipole interactions) (b) hydrogen bonding (c) π-π stacking (d) solvent effects and (e) van der Waals interactions.

Ion-ion, ion-dipole and dipole-dipole interactions are basically electrostatic (coulombic) interactions, which arise due to the delocalization of charges on organic ions. Ion-ion interactions are the strongest noncovalent interaction, having strength comparable to the covalent bonding and are resulted from the attraction between opposite charges (Table 1.1-entry 1). The bonding of an ion, such as Na$^+$, with a polar molecule, such as water, due to the attraction of oxygen lone pairs to the cation positive charge is known as ion-dipole interactions. A typical example is the binding of cations by crown ethers (Table 1.1-entry 2). Dipole-dipole interactions are resulted from the opposite alignment of two adjacent dipoles leading to an electrostatic attraction between the opposite poles (Table 1.1-entry 4).
Table 1.1. Average interaction energies of various noncovalent interactions frequently used in supramolecular chemistry

<table>
<thead>
<tr>
<th>Entry</th>
<th>Interaction</th>
<th>Energy/ kJmol(^{-1})</th>
<th>Illustration/Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Ion-ion</td>
<td>50-400</td>
<td><img src="image" alt="Ion-ion Interaction" /></td>
</tr>
<tr>
<td>2.</td>
<td>Ion-dipole</td>
<td>50-200</td>
<td><img src="image" alt="Ion-dipole Interaction" /></td>
</tr>
<tr>
<td>3.</td>
<td>Hydrogen bond</td>
<td>4-120</td>
<td><img src="image" alt="Hydrogen Bond" /></td>
</tr>
<tr>
<td>4.</td>
<td>Dipole-dipole</td>
<td>4-40</td>
<td><img src="image" alt="Dipole-dipole Interaction" /></td>
</tr>
<tr>
<td>5.</td>
<td>(\pi-\pi) stacking</td>
<td>4-20</td>
<td><img src="image" alt="(\pi-\pi) Stacking" /></td>
</tr>
<tr>
<td>6.</td>
<td>Solvent effects</td>
<td>4-40</td>
<td><img src="image" alt="Solvent Effects" /></td>
</tr>
<tr>
<td>7.</td>
<td>van der Waals forces</td>
<td>&lt;5</td>
<td><img src="image" alt="van der Waals Forces" /></td>
</tr>
</tbody>
</table>

\(^{a}\)Cations (M), anions (X), electronegative element (D), elements with lone pair of electrons (A), host (H) and guest (G).
A hydrogen bond, D—H···A, is formed between a hydrogen atom attached to an electronegative donor atom (D) and a neighboring acceptor atom with lone pair of electrons (A), which will be discussed in detail in section 1.3 (Table 1.1-entry 3).

\[ \text{π-π Stacking interactions are the weak electrostatic interactions between aromatic rings. There are two general types of π-stacking interactions: face-to-face and edge-to-face. A well known example is the stacking of nucleobases to stabilize the DNA double helix (Table 1.1-entry 5).} \]

Solvent effects in supramolecular chemistry mainly consist of hydrophilic and hydrophobic interactions. Hydrophobic interactions are generally the exclusion of large molecules or those that are weakly solvated from polar solvents, particularly from water. This can produce attraction between organic molecules and play a crucial role in the binding of organic guest molecules by cyclodextrin or cyclophane host molecules in water (Table 1.1-entry 6). Hydrophilic interactions are the interaction between water and organic molecules so that the molecules are attracted to water. This is an important reason for the good solvent properties of water. van der Waals interactions arise from the temporary polarization of an electron cloud by the proximity of an adjacent nucleus, resulting in a weak electrostatic interaction. They are usually non-directional and can be of attractive or repulsive in nature (Table 1.1-entry 7).

Despite the weakness of noncovalent interactions, the cooperative action of several such interactions may lead to thermodynamically and kinetically stable supramolecular assemblies under a variety of conditions. Moreover, the reversibility of these noncovalent interactions will allow self-correction during the organization process leading to well-defined supramolecular architectures. The term ‘noncovalent synthesis’ refers to the use of noncovalent interactions to design macromolecular architectures of reversibility and complexity. Noncovalent synthesis enables one to
synthesize supramolecular entities having molecular mass of several kDa, that are extremely difficult to prepare by covalent synthesis.

1.3. Hydrogen Bond – The Favorite in Supramolecular Chemistry

Among different noncovalent interactions, hydrogen bonds are the most crucial and favorite glue to stick molecules together. The advantage of H-bonds is their tunable strength, directionality and specificity. Hydrogen bonds are attractive electrostatic interaction between a positively charged hydrogen atom bonded to an electronegative element (the donor: D<sup>-</sup> - H<sup>+</sup>), and a negatively charged atom with a lone pair of electrons (the acceptor: A<sup>-</sup>). The strength of a single H-bond is related to the acidity of the hydrogen bonding donor group and the basicity of the hydrogen bonding acceptor group involved, which ranges from 10-65 kJmol<sup>-1</sup> for neutral molecules, to 40-190 kJmol<sup>-1</sup> for an ionic acid-base hydrogen bond. H-Bonds are responsible for the existence of H<sub>2</sub>O as a liquid and DNA as a double helix which means that they are vital for the existence of life. Apart from this fundamental significance of H-bonds, they in cooperation with other noncovalent forces can lead molecules to organize in different ways to form stable supramolecular architectures of definite shape and properties. Therefore, the study of H-bonds and its use in the creation of supramolecular architectures are of fundamental and technological importance, particularly in the area of advanced materials science.

1.4. Hydrogen Bonded Chromophoric Assemblies – The Door to Functional Materials

Highly organized arrays of π-conjugated chromophore and organic dyes are of great interest as mimics of natural photosynthetic systems. The beautiful examples found in nature, for example the photosynthetic light harvesting antenna complexes
and reaction centers in bacteria and green plants, contain highly organized self-assemblies of chlorophyll molecules held together by protein scaffolds. The natural photosynthesis begins with the capture of sunlight by light harvesting antenna complexes, which then excite the reaction centers indirectly via energy transfer. This is followed by a series of electron transfer events within the photoreaction centers. Inspired by these naturally occurring architectures, much attention is currently focused on the design of supramolecular chromophoric model systems and nanosized chromophoric assemblies which may find application in solar energy conversion devices. In addition chromophoric assemblies are also considered to be the key to introduce novel optical and electronic properties to organic materials for potential applications in molecular and supramolecular electronic devices.3

Learning lessons from the nature’s self-assembly process, supramolecular chemists have succeeded to a small extent to create a variety of artificial nanoarchitectures of chromophoric molecules using noncovalent interactions such as H-bonding, π-π stacking, electrostatic and van der Waals associations. These studies have generated a wealth of knowledge to the design of a variety of materials with intriguing properties. Among various noncovalent interactions, H-bonding plays a crucial role in controlling the supramolecular organization of the individual building blocks. In this section, an overview is given on H-bonded chromophoric and dye assemblies such as porphyrin, phthalocyanine, perylene and cyanine based assemblies and π-conjugated oligomeric assemblies.

1.4.1. Porphyrin Assemblies

Porphyrins represent an important class of dyes with promising application in many areas such as optoelectronics, chemosensors and catalysis. These dyes exhibit
strong absorption and emission in the visible region and show electrochemical activity. The self-assembly of porphyrins is mainly inspired by the photosynthetic systems in nature and is not only important to the better understanding of natural processes, but also valuable towards application in optoelectronic devices.⁴

A variety of energy and electron donor or acceptor molecules have been used to create H-bonded complexes with porphyrins as mimics of photosynthetic systems. In a pioneering work, Hamilton and coworkers have designed porphyrin based multichromophoric hydrogen bonded dyads and triads comprised of various fluorescent or redox active naphthalene, ferrocene and dansyl chromophores and studied the energy and electron transfer processes.⁵ The self-complementary interactions were based on the hexa-hydrogen bonding complementarity between barbiturate derivatives and two 2,6-diaminopyridine units linked through an isophthalate unit \( (K_a = 1.1 \times 10^{-6} \text{ M}^{-1}) \) as shown in Figure 1.2.

![Figure 1.2. Porphyrin derived H-bonded donor-acceptor dyads developed by Hamilton.](image)

Later Sessler et al. exploited the Watson-Crick nucleobase pairing H-bonding interactions between guanosine and cytidine to design a trimeric array 1 of two zinc porphyrins and one free base porphyrin in CD₂Cl₂.⁶ The protected ribosyl sugar groups present on the nucleobase act as solubilizing groups. The Zinc(II) and free base porphyrins act as the donor and acceptor molecules respectively and both singlet and
triplet energy transfer occurred within these porphyrin H-bonded arrays. More recently, many hydrogen bonded assemblies, where porphyrins are complexed with naphthalene bisimides\textsuperscript{7} and phenoxy napthacenequinoines\textsuperscript{8} are reported. In the 1:1 triple H-bonded supramolecular dimer 2 composed of a diacetylaminopyridine bearing zinc porphyrin and naphthalene tetracarboxylic acid diimide, Osuka and Okada have studied in detail the electron transfer dynamics within the self-assembly.\textsuperscript{7} Photoinduced electron transfer in the H-bonded assembly occurs in benzene with rates of charge separation and recombination of $k_{CS} = 4.1 \times 10^{10} \text{s}^{-1}$ and $k_{R} = 3.7 \times 10^{9} \text{s}^{-1}$, respectively.

![Chart 1.1](image)

An interesting one-dimensional H-bonded porphyrin assembly in nonpolar solvents such as cyclohexane and chloroform, based on bis(imidazol-4-yl)porphyrin (3) to mimic natural light harvesting antennae function was reported by Kobuke and coworkers.\textsuperscript{9} Even though the H-bond interactions are very weak, the cooperative effect of multiple H-bonding, hydrophobic and $\pi-\pi$ interactions stabilize the one-
dimensional assembly of 3 (Figure 1.3b). The resultant assembly showed an efficient excited state energy transfer followed by electron transfer to quenchers like chloranil. However, the bis(imidazoyl) porphyrin 4, in which alkoxy phenyl substituents of 3 is modified with carboxyl groups, was found to self-assemble in water to form liposomes, as a result of cooperative H-bond, π-stack and solvophobic forces (Figure 1.3c). Detailed AFM and TEM studies revealed liposomes of an average diameter 20-30 nm.

![Figure 1.3. a) Structures of bis(imidazoyl) porphyrins, b) self-assembly of 3 to one-dimensional assemblies and c) self-assembly of 4 in water to form liposomes.](image)

The self-assembly of monopyrazolylporphyrins (5) to form a dimer and tetramer in chloroform due to the intermolecular H-bonding interactions between pyrazole units have been reported (Figure 1.4a). The association constants of the dimer [5]_2 and the tetramer [5]_4 were found to be 39 M⁻¹ and 9.3 x 10³ M⁻³ respectively, which are relatively low. However, more stable and interesting cyclic porphyrin H-bonded architectures have been reported by functionalizing the porphyrin with multiple H-bonding motifs. A cyclic porphyrin rosette (6) composed of three triaminotriazine units bearing two appended tetraphenyl porphyrins or their zinc complexes and three complementary dialkylbarbituric acid derivatives (BBA) was reported by Lehn, which closely resembles B850 chlorophylls architectures present in the light harvesting complexes of photosynthetic bacteria (Figure 1.4b).
A large variety of multiporphyrin H-bonded arrays with different spatial relationships in predefined geometries, such as discrete squares and linear tapes, have been reported. When two porphyrins substituted with complementary H-bonding groups of uracil and diacetamido pyridyl in a 90° topology, are mixed in a 1:1 stoichiometry, a tetrameric supramolecular square (7) was formed by triple H-bonding hetero-complementary interactions. On the other hand 180° topology of the complementary H-bonding groups, each on a different porphyrin, results in the self-assembly of linear porphyrin tapes in toluene. Another series of self-assembled discrete squares of porphyrins (8) are formed by the self-complementary quadruple H-bonding interactions between diacetamido pyridyl groups rigidly linked to the chromophores. $K_a$ values of the order $10^9$ and $10^{12}$ have been reported for the tetrameric squares 7 and 8, respectively.
Recently, Aida and coworkers have reported the fullerene triggered unidirectional supramolecular association of acyclic zinc porphyrin dimer (9) having six carboxylic acid functionality, resulting in the so-called ‘supramolecular peapods’, with high aspect ratio and good thermal stability (Figure 1.5). The porphyrin derivative 9 also bears large (G4)-poly(benzyl ether) dendritic wedges, which provide solubility to the zinc porphyrin.

![Chart 1.2](image)

**Chart 1.2**

Recently, Shinkai et al. have reported the one-dimensional self-assembly of sugar, urea or amide-appended porphyrins leading to the gelation of solvents. These studies will be discussed in detail under the section of porphyrin derived organogels (section 1.7.3).
1.4.2. Phthalocyanine Assemblies

H-Bonded self-organization of amphiphilic copper phthalocyanine molecules substituted with eight diol groups into nanoscale fibrous assemblies, have been reported by Kimura et al.\textsuperscript{16} Both the racemic (10) and the optically active (11) phthalocyanine complexes produce fibrous assemblies from aqueous solution through two noncovalent interactions, \(\pi-\pi\) interaction among phthalocyanine rings and hydrogen bonding among diol units. However the detailed CD, XRD and TEM studies have revealed different types of long range ordering of molecules for the two phthalocyanine derivatives within the fibrous assemblies as shown in Figure 1.6. The racemic copper phthalocyanine 10 forms columnar stacks, which then self-assembles spontaneously to the two-dimensional hexagonal lattice. On the other hand, the chiral phthalocyanine molecules (11) are arranged in a left-handed helical sense within the column, which then self-assembles into a lamellar structure as the chirality of the side chains affect the intercolumnar structure.

![Figure 1.6. Schematic representation of the self-assembly in Kimura's phthalocyanine molecules.](image-url)
Temperature dependent self-organization of hydrogen bonded dimers of Zinc(II) phthalocyanines (12) decorated with six optically active side chains and one chiral diol groups resulted in the formation of two different supramolecular structures. At room temperature, the polymeric H-bond among the diol groups allowed the construction of a lamellar sheet. However, the cleavage of the H-bond network at 130 °C caused the structure to change to a hexagonal columnar phase, in which zinc phthalocyanine molecules are arranged in a left-handed helical manner (Figure 1.7).

![Figure 1.7](image)

Figure 1.7. Schematic representation of the self-assembly in phthalocyanine hydrogen bonded dimers.

### 1.4.3. Perylene Bisimide Assemblies

Perylene bisimides are one of the well studied classes of dyes for optoelectronic functional applications because of their promising optical properties such as the strong absorption in the visible range, fluorescence quantum yields of almost 100% as well as its high stability towards photooxidation. In addition, perylene bisimides feature a relatively low reduction potential, which enables them to act as an electron acceptor in photoinduced charge transfer reactions. Because of their striking
properties, they have been extensively used in various optoelectronic applications such as field effect transistors, photovoltaic devices and light emitting devices. A variety of H-bonded functional supramolecular architectures, incorporating perylene imides as the functional building blocks, have been reported. This section focuses on some of these interesting examples.

Würthner et al. have extensively studied the hierarchical self-organization of perylene based complementary building blocks to nano- and mesoscopic superstructures, which are expected to show supramolecular functional properties such as light harvesting and long range vectorial transport of excitation energy within the superstructures. Hierarchical self-organization of the perylene bisimide (13) and the melamine (14) by multiple orthogonal intermolecular interactions lead to fluorescent mesoscopic structures as shown in Figure 1.8. The complementary H-bonding between perylene bisimides and melamines initially form linear polymeric chains that subsequently aggregate to extended supramolecular systems as a result of cooperative \( \pi-\pi \) stacking and alkyl chain interactions.

**Figure 1.8.** Formation of functional perylene superstructures by hierarchical self-organization.
The chiral molecule 15, having long side chains consisting of octadecyl esters of alanine and phenylalanine, when mixed with the ditopic perylene bisimides (13), gave extended superstructures. The perylene chromophores are arranged in a helical manner, whose helicity is determined by the stereoisomerism of the corresponding melamines (Figure 1.9). Circular dichroism (CD) experiments, which showed an exciton coupled CD signal for perylene absorption, characteristic of its helical arrangement, revealed that $(S,S)$ melamines lead to a left-handed helical and $(R,R)$ enantiomers lead to a right-handed helical arrangement of the chromophores.

![Image](image.png)

*Figure 1.9. Helical organization of perylene chromophores with chiral melamine molecules.*

1.4.4. Cyanine Assemblies

Cyanines are a class of dyes containing heterocyclic rings such as imidazole, pyridine, pyrrole, quinoline and thiazole. They are commonly used as sensitizers in silver halide photography, as infrared absorbers and as photorefractive materials. Würthner and coworkers have explored the imide functional groups of merocyanine dyes, to form a variety of supramolecular assemblies such as double rosettes as well as mesoscopic and liquid crystalline materials by complementary triple hydrogen bonding interactions with a variety of melamine derivatives. Reinhoudt and
Würthner have shown that six merocyanine chromophores can be arranged in a helical sense by incorporating them into well-defined double rosette assemblies (Figure 1.10).21 These cyclic rosette assemblies, consist of two stacked rosettes, are formed by the self-assembly of three calixarene dimelamine (16) and six merocyanine (17) (a chromogenic barbiturate derivative) chromophores via 36 H-bonds. The two stacked rosettes are held together by the calixarene molecules. The helical arrangement of the merocyanine dye molecules into double rosette is controlled by the chiral configuration of the calixarene dimelamines. In addition, as a result of the strong dipole-dipole interactions between the chromophores, exciton coupling is observed giving rise to strong Cotton effects whose sign depends on its helical packing.

![Figure 1.10. Double rosette assemblies containing merocyanine dyes.](image)

Würthner et al. have reported the formation of H-bonded columnar liquid crystalline merocyanine-melamine assemblies.22 The trialkoxy functionalized ditopic melamine derivative 18, bearing long alkyl chains, and the merocyanine dye (19) together form linear extended tapes through triple H-bonding interactions. Dipole assisted π-π stacking of these tapes leads to ribbons which finally assemble into a
columnar structure by microphase segregation and steric effects as shown in Figure 1.11. The columnar mesophase is characterized by OPM, XRD and DSC.

![Diagram](image)

**Figure 1.11.** Proposed self-assembly in the merocyanine-melamine liquid crystalline phase.

A variety of merocyanines with strong electron donor groups, with the objective of increasing the electron density at the imide carbonyl groups for achieving stable merocyanine-melamine assemblies even in dilute solutions, have also been reported. However, despite the pronounced differences of the charge transfer properties within the dyes, identical binding constants of $K_s = 120 \text{ M}^{-1}$ were observed for the H-bonding interactions with the melamine derivatives in chloroform. UV/Vis spectral changes observed in methylcyclohexane indicate the formation of colloidal assemblies through a cooperative effect of H-bonding and dipolar aggregation between merocyanine dyes.

### 1.4.5. Azo Dye Derived Assemblies

Azo dyes contain at least one azo group that can be in the *trans* or *cis* form, the switching between these two isomeric forms is possible with light. Surprisingly, hydrogen bond interactions have been rarely applied in tuning the properties of these
dyes. Ammonium head group-appended azobenzene cyanuric acids and glutamate derivatized melamines have been organized in water\textsuperscript{24,25} and at the air water interface\textsuperscript{26} by complementary hydrogen bonding. In water, helical superstructures were formed and the aggregation process could be controlled by photoisomerization of the azobenzene dye resulting in segregation of the two components.

Recently, Yagai and Kitamura \textit{et al.} reported the photoswitching properties of \textit{trans}-azobenzene incorporated melamine 20 and barbiturate 21 H-bonded assemblies (Figure 1.12).\textsuperscript{27} Photoisomerization of azobenzene units on melamine enhances the thermodynamic stability of the rosette assembly in chloroform solution and suppress its transformation into insoluble tape-like polymers. Interestingly, the resulting stable rosette supramolecular structure could be retained in the solid state when the solvent is removed.

![Figure 1.12. Schematic representation of the photoswitchable aggregation process of melamine-barbiturate H-bonded assembly.](image)

In another report, carboxylic acids have been used to self-assembleazo dyes, which could be controlled by photoisomerization of the azo moiety.\textsuperscript{28} The \textit{trans}-azobenzene isomer 22 of this dye associates into infinitely hydrogen bonded linear tapes, while the \textit{cis}-azobenzene 23 yields hydrogen bonded self-assembled tetramers that form rod-like aggregates by additional π-π stacking interactions (Figure 1.13).
1.5. Low Molecular Weight Organogels – The World of Soft Materials

Certain organic molecules spontaneously self-assemble to form soft solid-like mass called ‘gel’ by entrapping a large volume of the solvent between the self-assembled structures. Even though gel-like materials are familiar in everyday life in the form of food or cosmetics, a proper definition of a gel is difficult as stated by Jordan Lloyd, “gel is easier to recognize than to define”.\textsuperscript{29} Flory’s definition of gels as two component, colloidal dispersion with a continuous structure of macroscopic dimensions that is permanent on the time scale of the experiment and is solid-like in its rheological behavior, is the most accepted one, despite the difficulty of applying it on a routine basis.\textsuperscript{30} However, it seems more appropriate to define gels as pervasive materials that are composed of a fibrous three-dimensional network whose interstitial spaces are filled with solvents and hence behave like soft solids. Historically, most gels are composed of covalently crosslinked polymers having very high molecular
weights.\textsuperscript{31} These gels can be swollen or shrunk by the addition or removal of the solvent, and by temperature. However, the formation of these gels is irreversible. More recently there has been an enormous increase of interest in the design of low molecular weight organogelators, which immobilize various organic fluids as a result of three-dimensional supramolecular network formation.\textsuperscript{32} This novel class of supramolecular materials exhibit striking properties with respect to self-assembly phenomena leading to diverse supramolecular architectures. The diversity of nanostructures provided by organogels makes them promising candidates for several potential applications ranging from cosmetics, photography, food, petroleum industries and catalysis to optoelectronics and related areas.

In contrast to the macromolecular gels, low molecular weight organogel network is held together solely by noncovalent interactions such as H-bonding, π-stacking, solvophobic effects and donor-acceptor interactions rendering the gelation process completely reversible. The directional nature of intermolecular interactions allows gelator molecules to self-organize in one-dimensional arrays producing elongated fibrous structures. Entanglement of the fibers subsequently produces a three-dimensional network capable of trapping the solvent and yielding the gel (Figure 1.14). Usually, low molecular weight organogels are formed by dissolving a small amount of the gelator in hot solvents and the subsequent cooling below gel transition temperature ($T_{gel}$). The gelation of organic molecules can be visualized by the formation of a thick non-flowing mass, even when turned upside down. Organogels are usually characterized by a variety of analytical techniques, particularly spectroscopic and microscopic techniques.
Even though there are numerous approaches towards the design of organogelators, most gelators are found rather by serendipity than by design. However, the following features are considered to be of importance in the design of organogelators: (1) formation of one-dimensional aggregates via anisotropic growth process, (2) intertwining of these one-dimensional aggregates to form three-dimensional network and (3) the prevention of crystallization or precipitation of the self-assembled aggregate through a delicate balance between order and disorder. Therefore, the designing of new gelling agents have to account for all these aspects and hence continues to be a challenging task.

The huge library of low molecular weight organogelators known to date can be classified into two broad categories according to the difference in the mode of self-organization, namely, non-hydrogen bonded gelators and hydrogen bonded gelators. Organogels formed by van der Waals, π-π stacking, dipole-dipole and donor-acceptor interactions are classified into the first category. Cholesterol based gelators are typical examples of this category. Hydrogen bonding interactions are well exploited for the designing of gels, which mainly include amide, urea, sugar, amino acid and nucleobase derivatives constituting the second category of gels.
Among various non-hydrogen bonded gelators cholesterol based gelators are the most extensively studied molecules.\textsuperscript{32,33} In cholesterol based gelators, the C-3 hydroxyl group of the steroid molecule is appropriately functionalized with a variety of aromatic moieties through linkers. The driving force for the self-assembly of such molecules is the aggregation of the cholesterol skeleton, as a result of dipole-dipole and van der Waals interactions, which is assisted by the $\pi-\pi$ interactions between the aromatic moieties. A schematic representation of the cholesterol based gel assemblies are shown in Figure 1.15, in which the cholesterol groups are stacked in a helical manner to form the central core thereby directing the aromatic groups outwards to form a spiral staircase assembly. A large variety of functional aromatic groups such as anthracene, azobenzene, squaraine, porphyrin and stilbene, have been appended to the cholesterol for designing new gelator molecules, which will be discussed in detail in the following section on chromophore derived organogels.

![Figure 1.15. Schematic representation of the self-assembly of cholesterol derived organogelators.](image)

Other non-hydrogen bonded gelators include anthracene\textsuperscript{34} (24) and anthraquinone\textsuperscript{35} (25) derivatives, the self-assembly of which is directed by the dipolar and $\pi-\pi$ stacking interactions. Surprisingly, simple organogelators such as long linear hydrocarbons (C24, C26, C32 and C38) are known to form organogels through
London dispersion forces, which are the weakest of all noncovalent interactions.\textsuperscript{36} In addition, simple gelators such as semifluorinated alkanes\textsuperscript{37} (26) and alkanes containing one heteroatom,\textsuperscript{38} including quaternary ammonium salts with long aliphatic chains\textsuperscript{39} (27-30) are also known. Charge transfer interactions have also been exploited by Maitra\textsuperscript{40} and Shinkai,\textsuperscript{41} for the creation of donor-acceptor two component organogels.

![Chart 1.3](image)

Many of the H-bonded organogelators reported in literature contain functional groups such as urea and amide. It was established that multiple urea and amide groups are essential to drive the self-assembly to a completion. The urea-urea H-bonding interactions, which are known to have high directionality and less conformational flexibility, have been extensively exploited in the laboratories of Feringa\textsuperscript{42} and Hanabusa\textsuperscript{43} to design one-dimensional gel assemblies (Figure 1.16). It has been shown that two urea groups in one molecule are sufficient enough to enforce aggregation in dilute solutions of a range of organic solvents. Organogelators comprised of acyclic\textsuperscript{42a,42c,43} (31), cyclic\textsuperscript{42d} (32, 33), geminal\textsuperscript{42e} (34) and tripodal urea\textsuperscript{44} (35) groups have been reported. Hamilton and coworkers have reported the gelation behavior of bisurea-dicarboxylic acid\textsuperscript{45} (36) and monoure a serine\textsuperscript{46} (37) derivatives.
Hanabusa and coworkers have shown that amide-amide H-bonding interactions can also be used to design a variety of gelators such as \textit{trans}-1,2-diaminocyclohexane$^{47}$ (38), 1,3,5-benzenetricarboxylic acid$^{48}$ (39) and \textit{cis}-1,3,5-cyclohexanetricarboxylic acid$^{49}$ (40) derivatives. More recently, gelation of a series of C$_3$-symmetrical trisamide (41, 42) and corresponding trisurea substituted disc-shaped molecules have been studied by Meijer and coworkers.$^{50}$ The gelation of a series of oligoamides (43) was also reported from Mésini’s group.$^{51}$
Reinhoudt and Shinkai have synthesized a library of methyl-4,6-\(O\)-benzylidene monosaccharide derived organogelators (44-47) and carried out their detailed structural studies.\(^{52}\) Aldopyranoside amphiphilic hydrogelators (48) from Shimizu’s group\(^{53}\) and gluconamide based aminosugars (49) from Nolte’s group\(^{54}\) are also present in the literature. More recently, Shinkai and coworkers reported a series of sugar-appended porphyrin and azobenzene based gelators which will be reviewed later in this chapter.
In addition, a large variety of amino acid\textsuperscript{55} and nucleobase\textsuperscript{56} based H-bonded gelators are also present in literature. However, detailed discussion of all classes of organogels is not the objective of the present review. Instead a short description on some of the applications of organogels is given followed by a detailed discussion on functional dyes and chromophore based organogels.

1.6. Application of Organogels – As Templates in Materials Synthesis

In recent years, there has been considerable interests in the design of organogels for specific application in the field of advanced materials, apart from their well known traditional applications in industry, food and cosmetics, which rely mainly on polymeric gels. Thus, various organogel derivatives have been successfully used in molecular imprinting,\textsuperscript{57} lasing,\textsuperscript{58} electrolytes for solar cells\textsuperscript{59} and electrochemical cells,\textsuperscript{60} drug delivery,\textsuperscript{61} humidity sensing\textsuperscript{62} and enantioselective separation.\textsuperscript{63} For example, organogelators 50 and 51 have been used to gel the electrolytic solutions of solar cells and electrochemical cells, respectively, thereby avoiding the potential danger of leakage of electrolyte solution.\textsuperscript{59,60} Measurements have shown that, for the gel electrolytes, virtually the same ion mobility and conductivity are obtained as in the normal liquid phase. Organogelators, 52 and 53, that gel supercritical CO\textsubscript{2} have been used to construct pressure and thermoreversible aerogels.\textsuperscript{64} Molecular imprinting of organogels has been reported, by gelling methyl methacrylate or styrenes with 29, 49 and 54, followed by polymerization and removal of the gelator molecules.\textsuperscript{57} This will give a rigid polymer matrix whose pores are one order of magnitude larger than the cross sections of the gel nanostructures. Kato et al. have gelled liquid crystalline molecules such as 4'-octyl-4-biphenylcarbonitrile, by a variety of organogelators such as 24, 38, 49 and 51, to give anisotropic gels, which are a novel class of functional
materials. These liquid crystalline gels are proved to be potential candidates for electrooptical switching devices.

Shinkai and coworkers have succeeded in using organogels as templates for the growth of a variety of inorganic nanostructures. This was achieved by the gelation of liquid tetraethyl orthosilicate (TEOS), with cholesterol derived gelators and the subsequent sol-gel polymerization of TEOS. During the polymerization, the gel fibrils transcribe its nanostructures to the polymerized silica, which will retain the ‘imprint’ even after the removal of the gelator by calcination. Strong electrostatic attraction or H-bonding interactions between gelator functional groups and TEOS is required for the silica transcription. Most remarkably, even the chirality of the gelator component could be transferred successfully to the resulting silica superstructures. Using this approach, a variety of novel silica architectures such as multilayered
vesicular silica, chiral spiral silica, multilayered rolled paper-like silica, and helical ribbons could be obtained (Figure 1.17).

Figure 1.17. Schematic representation of the mechanism of silica transcription from organogel fibrils and TEM images of various transcribed silica nanostructures.

There are several exciting reports from the group of Stupp at the Northwestern University on the use of gel forming rod-coil and peptide molecules as templates for the synthesis of inorganic nanostructured materials. They have shown that, 'dendron rod-coil' triblock molecule (55) can self-assemble through hydrogen bonds between the hydroxyl and carbonyl groups of the hydrophilic dendron segments and the π-π stacking interactions of the aromatic rod segment resulting in supramolecular twisted nanoribbons, causing the gelation of organic solvents. The rod-coil dendron nanoribbons have been further used as templates for the mineralization of CdS to form coiled-coil helices, as a result of preferential growth of CdS along one face of the twisted ribbon template (Figure 1.18).
Stupp and coworkers have used the pH-induced self-assembly of a peptide amphiphile (56) to make a nanostructured fibrous gel scaffold reminiscent of extracellular matrix (Figure 1.19). The design of this peptide amphiphile facilitates the direct mineralization of hydroxy appetite to form a composite material which is aligned the same way as collagen fibrils and hydroxy appetite crystals in bone.

In addition to the above mentioned applications, in recent years there has been considerable interest in the supramolecular organization of chromophores (see section 1.7) through gelation which has potential optical and electronic applications.
1.7. Organogels Based on Functional Dyes and Chromophores

Gels based on functional chromophores and dyes have attracted immense interest as novel functional materials for optoelectronic applications. Supramolecular alignment of functional molecules constructed through the gelation process, can provide novel chromophoric assemblies with tunable optoelectronic properties which have potential applications in molecular and supramolecular electronic devices. In addition, the highly organized arrays of electron conducting molecules can be used for the formation of conducting supramolecular wires. This section presents a detailed review on the chromophore and dye based gels reported in literature so far.

1.7.1. Anthracene Derived Organogels

Control of the molecular organization of [n]acenes such as anthracene, tetracene and pentacene has attracted much attention, because of their significant charge mobility, intense absorption and emission, and photochromism which have potential applications in the fields of organic electronics and photovoltaic devices. Keeping this in mind, the groups of Weiss and Desvergne have contributed extensively to the self-assembly and gelation of anthracene derivatives.

The serendipitical observation of the gel formation of 3-β-cholesteryl-4-(2-anthryloxy)butanoate (57, CAB) in a variety of organic liquids has led to a novel class of steroid based gelators. They consist of an aromatic group (A), connected to a steroidal moiety (S) via a linking group (L) and hence are called ALS gelators (Figure 1.20). The kinetics of gel formation and the gel melting temperature (T\textsubscript{gel}) have been determined from the fluorescence and CD spectral changes. Detailed studies indicated a helical face-to-face stacked arrangement of CAB molecules within the gel aggregates. Electron microscopic studies of the CAB gels revealed that they consist of
molecular domains of helically twisted fibrous bundles having several micrometers in length. A series of ALS gelators have been synthesized by modifying the structural features of each part of the ALS molecules. In the case of the 2-substituted-9,10-anthraquinone (58, CAQ) the gelation ability is favored by a (S)-chirality at the C-3 position of the steroidal part, while changes at C-17 does not have much influence.

![Figure 1.20](image)

**Figure 1.20.** a) Structures of CAB (57) and CAQ (58) ALS gelators and b) TEM image of the helical fibers of the propanol gels of CAB.

Desvergne and coworkers have reported that 2,3-bis-\(n\)-decyloxyanthracene (24, DDOA) can form fluorescent gels in various alkanes, alcohols, aliphatic amines and nitriles, through dipole-dipole interactions, van der Waals forces and \(\pi-\pi\) stacking. DDOA showed a ground state dipole moment of 1.9 Debye showing the presence of dipolar forces in the resulting gels. Gel formation is accompanied by significant changes in the absorption and emission properties of the anthracene chromophores, which suggested an anti-parallel head-tail arrangement for the aromatic rings with partial overlap between them. Furthermore, freeze-fracture electron micrographs of DDOA gels showed a dense three-dimensional random network of fibrous rigid bundles (Figure 1.21b). Detailed studies have shown that slight structural variations on DDOA, such as shortening the length of the alkyl side chains, removing the oxygen atom, mismatching the alkyl side chains or truncating the aromatic part to naphthyl
chromophores considerably reduce the gelation properties. However, hydrogenation of one of the anthryl rings (59 and 60) or replacement of it by a phenazine (61) or an anthraquinone (25) produced efficient organogelators and are studied in detail. 2,3-Di-n-alkoxyphenazine organogels (61) showed reversible acid sensitive properties, at ambient temperatures in acetonitrile. Terech et al. synthesized a new class of 2,3-di-n-decyloxy-6,7-dichloroanthracene derivatives (62) with a higher dipole moment (3.4 D). Recently, Pozzo and coworkers have shown that highly oriented DDOA gel fibers showing strong anisotropic features can be obtained by applying a mechanical stress during the cooling of hot isotropic solutions, which is evident from the optical polarizing microscopy (OPM) and TEM images (Figures 1.21c and d). These anisotropic organic materials are expected to show enhanced mechanical, photonic, magnetic and electronic properties along a given direction.

![Structures and images](image)

**Figure 1.21.** a) Structures of various anthracene gelators, b) TEM image of the gel fibers of DDOA, c) OPM and d) TEM images of aligned DDOA gel fibers.

### 1.7.2. Azobenzene Derived Organogels

A new class of gelators containing substituted azobenzenes as the aromatic part has been studied extensively by Shinkai and coworkers. In their first report, two types of gelators, with either a natural (S)-configuration (63) or the inverted (R)-
configuration (64) at the C-3 position of the steroidal part have been reported. Among them, the gelators bearing a p-alkoxyazobenzene moiety are found to be the most efficient and they can specifically gel either nonpolar solvents (S derivatives, 63) or polar solvents (R derivatives, 64). Interestingly, it is possible to ‘read-out’ the sol-gel phase transition as well as the chirality of the supramolecular stacks using CD spectroscopy. For example, 63 showed a positive exciton coupling and 64 showed a negative exciton coupled band characteristic of the clockwise and anticlockwise orientation of the azobenzene dipoles in the gel state, respectively. This is supported by the observation of right- and left-handed helical fibers through SEM pictures. In this case, the sol-gel transition could be controlled by the cis-to-trans isomerization of azobenzene, leading to photoresponsive organogels (Figure 1.22b).

![Figure 1.22. a) Structures of azobenzene-appended gelators and b) trans-to-cis isomerization of 63.](image)

Detailed studies of a variety of azacrown substituted azobenzene-cholesterol gelators, have revealed the formation of different supramolecular architectures such as vesicles (65, Figure 1.23a) layered tubules (66, Figure 1.23b), curved lamellas (67, Figure 1.23c), cylindrical tubules (68, Figure 1.23d) and helical ribbons (69, Figure 1.23e).
The chiral azobenzene (70) containing a cyclic syn-carbonate moiety, reported by Kato and coworkers self-assembles via dipole-dipole interactions to form a photoswitchable organogelator (Figure 1.24).  

A new family of hydrogelators based on azobenzene-appended sugar bolaamphiphiles (71-74) has been reported jointly by Shinkai and Reinhoudt. These bolaamphiphiles consist of two solvophilic aminophenyl sugar skeleton, such as β-D-glucopyranoside (71), α-D-glucopyranoside (72), α-D-galactopyranoside (73) or α-D-mannopyranoside (74), as chiral-aggregate forming site and one solvophobic azobenzene moiety as a π-π stacking site. Compound 71 is found to be a ‘super’ hydrogelator, as it can form gels even at concentrations as low as 0.05 wt%, whereas
compound 72 could gelate only 1:1 (v/v) DMSO-water solvent mixtures. On the other hand, 73 and 74 could not gelate any of the solvents investigated. The chiral sugar derivatives 71 and 72 are found to form right-handed helical aggregates in 50 vol% DMSO, whereas 73 and 74 form left-handed helical aggregates as evident from the corresponding exciton coupled CD spectra. TEM studies revealed right-handed helical fibrillar structures for the aggregates of 71 and 72, reflecting the microscopic one-dimensional columnar orientation of azobenzene chromophores. However 73 and 74 tend to aggregate into vesicular structures as a result of their two-dimensional aggregation mode, which prevent them from gelation (Figure 1.25).

![Chemical structures](image1.png)

Figure 1.25. Structures of sugar-appended azobenzene organogelators and the TEM images of 72 (A) and 73 (B) in 1:1 (v/v) DMSO-water mixtures.

Feringa and coworkers reported chiral recognition in hybrid gel assemblies of 1,2-bis(uredocyclohexane) derivative 75 and the azobenzene incorporated derivative 76. Both (R)-76 and (S)-76 isomers showed concentration independent exciton coupled CD spectra corresponding to the azobenzene absorption as a result of the intramolecular stacking of the azobenzene chromophores, the sign of which depends on the absolute configuration of the molecule. Incorporation of (R)-76 into a gel of (S)-75 or (R)-75 resulted in distinctly different chiral gels, in which azobenzene...
chromophores are stacked in different orientations depending on the chirality of 75 (Figure 1.26). The CD spectra of (R)-76 in 1-butanol gel of (S)-75 showed a slightly more intense bisignated CD signal at room temperature, indicating that the environment of (R)-76 is less polar when it is incorporated into the (S)-75 gel than in 1-butanol itself as shown in Figure 1.26b. However, incorporation of (R)-76 in a gel of (R)-75 results in a strong positive Cotton effect, which is not exciton coupled, indicating that the azobenzene groups are no longer stacked but incorporated between the closely packed alkyl chains of (R)-75 as shown in Figure 1.26a. In both the cases intramolecular exciton coupled CD signal of (R)-76 reappears upon the melting of the gel. In addition, the more exposed “solvent like” environment of (R)-76 in the (S)-75 gel results in its slow isomerization when incorporated into the former gel.

Figure 1.26. Structures of the 1,2-bis(ureidocyclohexane) derivatives. Schematic representation for the incorporation of (R)-76 in a) an aggregate of (R)-75 or b) an aggregate of (S)-75 showing the different environments for the azobenzene groups.

van Esch and coworkers have studied the gelation behavior of the bisurea-appended azobenzene derived organogelators 77 and 78. 4,4'-Disubstituted derivative (77) is found to be a poor gelator, whereas the 2,2'-disubstituted derivative (78) is an excellent gelator of a variety of organic solvents at concentrations as low as 0.2 mM. Interestingly, 78 showed remarkable polymorphism in their gel state leading to two different types of supramolecular aggregates, which differ in the stacking of chromophore moiety as well as in their H-bonding patterns, as evident from the
differences in the UV/Vis absorption and IR spectra. This novel observation of polymorphism in organogels was found to depend on the solvent polarity and kinetic factors.

![Chart 1.9](image)

1.7.3. Porphyrin Derived Organogels

Terech et al. have shown that a long chained ester of *meso*-tetrakis(*p*-carboxyphenyl)porphyrin (79), can form thixotropic gel-like materials in hydrocarbon solvents. The presence of both metal ion and acidic group is found to be crucial for gelation. The gelator network consists of molecular rods with moderate length with one molecule per cross section as repeating unit. Later Shinkai and coworkers have reported a novel gelator by linking the porphyrin part to the cholesterol moiety (80). Both cyclohexane and methylcyclohexane are gelled by 80, but not by its structural epimer with (*R*)-configuration at the C-3 of the cholesterol group. Subsequently, the gelation ability of Zinc(II) porphyrin-appended cholesterol gelators could be enhanced by intermolecular interactions with fullerenes through the formation of a 2:1 Zinc(II) porphyrin/C_{60} sandwich complex (Figure 1.27). The direct bathochromic shift of the Soret absorption band and the enhancement in the negative exciton coupled CD signal in the presence of C_{60} established that intermolecular interactions do exist between Zinc(II) porphyrin and the fullerenes in the gel phase.
A variety of H-bonded one-dimensional gel assemblies, by substituting the periphery of the porphyrin chromophores with sugar, urea or amide hydrogen bonding groups, have been reported by Shinkai and coworkers. An amphiphilic porphyrin bearing four β-D-galactopyranoside groups (81) was shown to form left-handed helical coiled-coil gel nanostructures in DMF/alcohol solvent mixtures. One-dimensional assemblies of porphyrin chromophores are stabilized by the synergistic effect of the π-π stacking interaction among the porphyrin aromatic cores and the H-bonding interactions between sugar moieties, as shown in Figure 1.28.
The stability of the porphyrin based gel assemblies has been significantly increased when the peripheral sugar moieties are replaced with urea groups. The urea-appended porphyrin (82) can form stable organogels in anisole with sol-gel phase transition temperature greater than 140 °C, even at 0.125 wt/vol%. Interestingly, chiral urea derivatives such as (R)- and (S)-enantiomers of $N$-(1-phenylethyl)-$N'$-dodecyl urea (R)-83 and (S)-83, respectively, could bound to the one-dimensional porphyrin stacks to twist them in a helical sense, which is evident from the resultant exciton coupled CD spectra (Figure 1.29).

![Figure 1.29](image)

Figure 1.29. Schematic picture of the helical twisting of one-dimensional stacking of sugar-appended porphyrin organogelators upon addition of chiral urea guests and the corresponding CD spectra.

Shinkai and coworkers have synthesized the amide-appended porphyrin organogelators 84 and 85 which showed competition between ‘H’ vs. ‘J’ aggregation mode of the porphyrin in the gel assemblies. Appropriate positioning of the peripheral H-bonding amide motifs could facilitate the formation of one of the aggregates preferentially. The gelators 84 and 85 are substituted with amide groups at the 4-position and the 3,5 positions of the meso-phenyl groups, respectively. X-ray analysis of the single crystals established that the porphyrins in 84 adopt the ‘H’-aggregation mode resulting in columnar stacks, whereas those in 85 adopt the ‘J’-aggregation mode resulting in two-dimensional planar assemblies. UV/Vis absorption, XRD and SEM measurements established that the organization modes of porphyrins in the gel state of 84 and 85 are similar to that in the corresponding single crystals.
SEM analysis of the cyclohexane gels of 84 and 85 revealed one-dimensional fibrillar
and two-dimensional sheet like structures, respectively indicating that the difference
in the microscopic H-bonded organization of the porphyrin chromophores are
expressed even at the macroscopic morphology (Figure 1.30).

![Figure 1.30. a) Structures of amide-appended porphyrin gelators and the SEM images of the xerogels of b) 84 and c) 85 from cyclohexane.](image)

The porphyrin derivative 85 can self-assemble to one-dimensional
multicapsular structures in the presence of C₆₀ as a cooperative effect of strong C₆₀-
porphyrin interactions and ‘inter- and intracapsular’ H-bonding interactions between
the amide groups, which is entirely different from that of the two dimensional ‘J’-type
aggregates in the absence of C₆₀ (Figure 1.31). Detailed UV/Vis absorption,
elemental analysis, XRD, ATR-IR and computer modeling studies have shown that
four amide groups from two adjacent porphyrins form a circular H-bonding array,
which can easily encapsulate a C₆₀ molecule to give a 1:2 complex. These ‘capsules’
will further grow into a one-dimensional assembly through ‘intercapsular’ H-bonding
interactions between amide groups on the other side of the complex. SEM and TEM
analysis showed a gradual change from the sheet like morphology to a fibrous
network on increasing the concentration of the C₆₀ from 0-0.5 equivalents, which
clearly support the one-dimensional aggregation mode. The complete quenching of
the fluorescence of one-dimensional multicapsular structure indicated a novel electron transfer phenomena between porphyrin ‘walls’ and encapsulated C\textsubscript{60}.

Figure 1.31. a) Aggregation modes of 85, b) side view of the energy minimized structure of (C\textsubscript{60})\textsubscript{3}(85)\textsubscript{6} and c) the SEM images showing the morphological changes in the benzene gels of 85 on adding the fullerenes.

1.7.4. Pyrene Derived Organogels

Pyrene, due to its strong fluorescence and excimer formation is a useful probe for photophysical and photobiological studies. Pyrene can also be used as a probe to study the self-assembly properties of organic molecules. In this context, the two component system consisting of bile acid based molecular tweezers (86 and 87) and 2,4,7-trinitrofluorenone (TNF, 88) acceptor molecules are shown to form organogels in a variety of hydroxyl and hydrocarbon solvents through charge transfer interactions (Chart 1.10).\textsuperscript{40} Recently, a new class of pyrene derived organogelators in which the bile acid part is replaced by alkyl chains connecting to pyrene chromophores through a variety of linkers have been reported.\textsuperscript{91} Compounds with ester (89) or ether (90) linkages are shown to form gels only in the presence of TNF through charge-transfer interactions, which can be monitored by a substantial color change and the appearance of the charge transfer band (Chart 1.10). However, the compounds with amide (91),

\textsuperscript{40}
urea (92) and urethane (93) linkers can self-assemble into one-dimensional gels through H-bond and π-stack interactions (Chart 1.1).91,92 The chiral pyrene organogelator (94), substituted with a (R)-(−)-2-octyl urethane group, self-assembles into P-helical aggregates.

![Chart 1.10](image1)

![Chart 1.11](image2)

The groups of Ihara and Sagawa have prepared fibrous gel assemblies of porphyrin 95 and pyrene 96 substituted by L-glutamic acid.93 By amide hydrogen bonding, both chromophores self-assemble co-facially into chiral fibers of several micrometers in length which can be controlled by temperature. The porphyrin 95 forms a physical gel and optical studies confirm the presence of highly ordered aggregates even below the critical gel forming concentration. Though the pyrene 96 did not produce a gel state at room temperature, it does form aggregate in solution. Preliminary results indicate energy transfer within mixed assemblies in solution from pyrene excimers to porphyrin traps. Moreover, the L-glutamic acid induces helicity into the fibers, as can
be concluded from the observed Cotton effects for both the porphyrin and the pyrene systems.

1.7.5. Miscellaneous Chromophore Based Gelators

The stilbene-appended cholesterol derivative 97, is reported to form organogels in appropriate solvents. Time dependent evolution of the gel nanostructures of 97 has been studied using AFM technique, in order to get a direct observation on the role of solvent during the gel formation (Figure 1.32). Detailed $^1$H NMR investigation on the composition, structure and dynamics of the stilbene-cholesterol gels were also reported. The cholesterol-appended squaraine derivative 98, form a gel in butanol, which is marked by the blue shift in the absorption spectra, loss of fluorescence and the appearance of exciton coupled CD spectra, indicating that the dye molecules are arranged in a helical ‘H’-aggregate fashion. However, detailed studies of 98 at the air-water interface and in Langmuir-Blodgett films showed an unusual folded type conformation in which there are attractive noncovalent interactions between the squaraine chromophores and cholesterol.
Shinkai and coworkers have designed proton sensitive, highly fluorescent 1,10-phenanthroline-appended cholesterol based gelator (99), which acts as an efficient energy transfer system (Figure 1.33). Even in the presence of two equivalents of TFA, the purple emission (360 nm) of the gel phase of 99 is quenched completely, with the appearance of the yellow emission (530 nm) corresponding to the protonated form of 99, due to an efficient energy transfer from the neutral to the protonated form of 99. However, when the gel was converted into the solution phase at 90 °C in the presence of TFA, a blue emission with bimodal emission maxima was obtained indicating the absence of energy transfer.

**Figure 1.32.** Structures of stilbene- and squaraine-appended cholesterol gelators and time dependent AFM images of the formation of gel fibers of 97.

**Figure 1.33.** Emission changes in the phenanthroline-appended cholesterol based gelator 99 upon protonation.
In an attempt to design self-assembling molecular wires, tetrathiafulvalene (TTF) molecules were attached to bis-arborols, to provide the compound 100, which is found to be an efficient organogelator. Phase contrast microscopy revealed string-like superstructures of several micrometers in length and diameter ranging from about 30 to several hundred nanometers (Figure 1.34). Absorption spectroscopy indicated the presence of stacked TTF molecules in the gel phase, which could act as a conducting supramolecular wire.

![Figure 1.34. Phase contrast microscopic picture of the TTF gels.](image)

The triphenylene derivatives (101 and 102) substituted with six amide groups and six hydrocarbon side chains are found to form fluorescent organogels with unusual emission properties in nonpolar solvents as a result of highly directional columnar self-assemblies through a cooperative effect of π-π, H-bonding and van der Waals interactions. Detailed fluorescence measurements have shown that the triphenylenes in the gel of 102 are arranged in a staggered manner, similar to the packing in triphenylene based LCs. However, in 101 the aromatic cores are arranged in an eclipsed manner leading to an unusual observation of excimer emission in triphenylene based assemblies, at 525 nm (Figure 1.35). Furthermore, XRD analysis of the xerogels revealed a lateral rectangular and hexagonal columnar arrangement for 101 and 102, respectively indicating the crucial role of alkyl chains in controlling the packing mode.
Recently, novel photoresponsive chiral organogels, based on the dithienylethene photochromic unit functionalized with (R)-l-phenylethylamine derived amides, have been reported from Feringa's group. The dithienylethene 103 exists as two antiparallel interconvertible open forms with $P$- and $M$-helicity, which cyclize in a fully reversible manner upon irradiation with UV light to form two diastereomers of the ring closed product 104 (Figure 1.36). The open form 103 is found to be an efficient organogelator of nonpolar solvents such as toluene, benzene and hexane. CD and TEM studies of the toluene gels revealed that the molecule 103 self-assemble to helical fibers, owing to the expression of the $M$- or $P$-chirality of the open form at the supramolecular level (Figure 1.37).
Interestingly, the photocyclization of 103 in the gel state showed nearly absolute stereocontrol though there is no stereoselectivity in the non-gelled solution. Both the open 103 and closed 104 forms can exist in two different chiral gel states, denoted as α and β, leading to a four-state chiroptical supramolecular switch, since these four states can be cycled by a sequence of photochemical reactions as shown in Figure 1.37. A stable gel of (α)-103 (P-helicity) is obtained on cooling the isotropic solution of the open form 103. Photocyclization results in the formation of the metastable gel (α)-104 which will convert into the thermodynamically stable gel (β)-104 (M-helicity) upon the heating-cooling cycles. Irradiation of the gel (β)-104 with visible light results in the metastable gel (β)-103, which will then change into the original stable gel (α)-103 via an isotropic solution of 103, after a heating-cooling cycle. The optical switching between different supramolecular chiral aggregates and the interplay of molecular and supramolecular chirality in these systems is attractive for designing molecular memory systems and smart functional materials.

Recently, a highly fluorescent organogel was reported by the intermolecular H-bonding interactions between the non-emissive oxadiazole based benzene-1,3,5-tricarboxamide molecule (105, Figure 1.38). Detailed studies have shown that the intermolecular face-to-face H-bonding interactions in the columnar gel aggregates

![Figure 1.37. a) TEM image of the helical fibers of a toluene gel of 103. b) Four different chiral aggregated states and the switching processes of the chiroptical supramolecular switch consisting of the open form 103 and the closed form of 104.](image-url)
play a key role in the enhancement of fluorescence upon gelation, by providing significant singlet-triplet splitting to reduce the rate of ISC.

Figure 1.38. a) An oxadiazole based gel under UV irradiation and b) the TEM image.

Würthner and coworkers have reported the hierarchical self-organization of the merocyanine dye molecules (106-107), which are tethered to tris(n-dodecyloxy)xylene unit to form supramolecular polymers and organogels, through dipolar aggregation. AFM and cryo-TEM studies of the gels revealed long and stiff rod-type assemblies, whereas, the X-ray diffraction studies revealed columnar mesomorphism. Based on these observations, a structural model is proposed in which six helically preorganized strands of the initially formed supramolecular polymer intertwined to form a rod with a diameter of about 5 nm (Figure 1.39).

Figure 1.39. Structural model for the hierarchical self-organization of merocyanine gelators.
In addition, organogelators based on the cholesterol-appended perylene\textsuperscript{104} (108) and phthalocyanine\textsuperscript{105} (109) chromophores have also been reported, the details of which will be discussed in various chapters of the thesis.

\begin{center}
\textbf{Chart 1.13}
\end{center}

\textbf{1.7.6. Diacetylene Derived Organogels}

In recent years there has been considerable interest in the self-assembly of diacetylene derivatives as they allow the covalent fixation of supramolecular assemblies through photopolymerization reactions to give polydiacetylenes (Figure 1.40). Gel forming diacetylenes are particularly interesting because the gel network which is stabilized by the noncovalent interaction can be permanently supported by strong covalent bonds under photolytic conditions, thereby retaining the morphological characteristics with increased thermal stability. Since polydiacetylenes are attractive candidates as conducting nanowires having potential applications in molecular electronic devices, covalent fixation of the organized assembly has great significance.
Masuda et al. reported diacetylene-1-glucosamide bolaamphiphiles 110 and 111, which self-assemble to form nanofibers leading to the gelation of organic solvents.\textsuperscript{106} The self-assembly of 110 is directed by the linear amide H-bonding interactions, whereas in 111, the self-assembly is supported by the H-bonding interactions among the sugar groups (Figure 1.41). Photopolymerization of the nanofibers of 110 form a relatively low molecular weight soluble polymer (13-mer), whereas 111 produced relatively higher molecular weight polymer (64-mer), due to the higher molecular packing order in the latter.

Diacetylene dicholesteryl ester derivatives having urethane linkages (112) have been polymerized in the organogel state to form colored gels containing...
polydiacetylene nanowires.\textsuperscript{107} Gels before irradiation was stabilized by H-bonding interactions between the urethane groups which are further stabilized by van der Waals interaction between the cholesterol groups. The polymerization is accompanied by a color change from white to blue. Electron microscopy revealed that the fibrillar gel morphology was not basically changed after polymerization. A series of 10,12-pentacosadiynoic acid derived organogelators with conjugated diyene units (113) and their photopolymerization was reported by Weiss and coworkers.\textsuperscript{108} 1, 2-Aminocyclohexyl derivatives have also been polymerized in the gel network, by incorporating diacetylene linkages to the alkyl side chains (114).\textsuperscript{42b}

\begin{center}
\textbf{Chart 1.14}
\end{center}

1.7.7. \textbf{Organogels Derived from Extended Aromatic $\pi$-Conjugated Systems}

The bisurea-appended oligo(thiophene)s (115-116) have been reported to self-assemble into elongated fibers resulting in the formation of organogels in solvents such as tetralin and 1,2-dichloroethane.\textsuperscript{109} Electron microscopy and X-ray diffraction studies revealed that the fibers have a lamellar structure, in which the molecules are arranged as one-dimensional ribbons with their long molecular axis parallel to each other (Figure 1.42). Moreover, it was shown by pulse-radiolysis time resolved microwave conductivity (PR-TRMC) experiments that the good electronic overlap...
between the thiophene rings due to the H-bond assisted π-stacking of adjacent oligomers results in high charge carrier mobility of at least 0.001 cm²/Vs for 115 and 0.005 cm²/Vs for 116. These values are relatively high when compared to that of simple thiophene oligomers.

Tour and coworkers reported that the well known π-stacking forces between shape persistent cyclophanes could be enhanced through hydrogen bonding interactions by incorporating multiple H-bonding sites at the periphery of the cyclophane ring. The H-bond assisted stacking interaction in 117 results in the formation of cyclophane dimers and gels at moderate concentrations in solvents such as CH₂Cl₂ and CHCl₃. Very recently, a strong fluorescent gel comprising fibrillar self-assembly of a trifluoromethyl-based cyanostilbene derivative (118) has been reported. The gelation of 118 is attributed to the cooperative effect of the strong π-π stacking interactions of the rigid rod-like aromatic segments and supplementary intermolecular interactions induced by the four CF₃ units.
1.8. Origin, Objectives and Approach to the Thesis

Despite the interesting optical and electron transport properties of linear $\pi$-conjugated systems, which are important in the design of a variety of molecular and supramolecular devices, not much attention is given to the self-assembly induced gelation and the resultant modulation of the optical properties except in a very few recent reports (Section 1.7.7). Gel formation in the case of certain $\pi$-conjugated polymers as a result of the unwanted crosslinking and chain branching reactions, as in the case of a few phenyleneethynylene derivatives has been noticed earlier. Later, gelation is observed in the case of oligo(thiophene), cyanostilbene and phenylacetylene based cyclophane derivatives. However, the importance of $\pi$-conjugated molecules in advanced applications demands self-assembly induced gelation and the consequent changes in the morphology and optical properties. Therefore, the main objective of the present study is to have a detailed investigation on the gelation properties, morphology and optical properties of small $\pi$-conjugated oligomers. For this purpose we have chosen oligo($p$-phenylenevinylene)s (OPVs), a class of molecules which have received considerable attention due to their unique optical and electronic properties. Though a large number of reports are available in the literature on the self-
assembly properties of tailor made OPVs, none of them pertain to the design of nanostructures based on organogels. In view of this, we aimed at the creation of functional chromophoric assemblies of $\pi$-conjugated OPVs through the formation of organogels, with the objective of crafting nanoscopic assemblies of different size and shape thereby modulating their optical and electronic properties.

In order to fulfill the above objectives, the design and synthesis of a variety of OPVs with appropriate structural variations were planned. The design principle involves the derivatization of OPVs with weak H-bonding hydroxymethyl end groups and with long aliphatic hydrocarbon side chains. The noncovalent interactions in these molecules were expected to lead the formation of supramolecular assembly and gels in hydrocarbon solvents. In such an event, detailed study of gelation and extensive analysis of the morphology of the gel structures were planned using advanced microscopic techniques. Since OPVs are strongly fluorescent molecules, gelation is expected to perturb the optical properties. Therefore, detailed study on the gelation induced optical properties as a way to probe the nature and stability of the self-assembly was planned. Apart from this, the potential use of the modulation of the optical properties for the purpose of light harvesting was aimed. The approach to this problem was to entrap an appropriate energy trap to the OPV gel matrix which may lead to the efficient energy transfer from the OPV gel based donor to the entrapped acceptor. The final question that we wanted to address in this investigation was the creation of helical nanostructures through proper modification of the OPV backbone with chiral handles. The present thesis is a detailed and systematic approach to the realization of the above objectives which are presented in different chapters of the thesis.
1.9. References


Chapter 1


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