Chapter 2

π-Conjugated Organogels: A Novel Class of Supramolecular Materials Derived from Self-Assembled Oligo(p-phenylenevinylene)s

Abstract

A new class of π-conjugated organogels based on oligo(p-phenylenevinylene) (OPV) derivatives are reported. A variety of all-trans OPVs containing hydroxymethyl groups and hydrocarbon side chains were prepared and shown to form organogels in apolar hydrocarbon solvents. A cooperative interaction between H-bonding, π-stacking and van der Waals forces leads to the self-assembly and gelation which are strongly influenced by the structure of the gelator and the nature of the solvent. The length and position of the hydrocarbon side chains and the presence of the hydrogen bonding groups are crucial for the efficient gelation. The gelation properties and the morphology of the gels are established from the DSC, \(^1\)H NMR, XRD, OPM, SEM, TEM and AFM analyses of the gels from different solvents. Variable temperature \(^1\)H NMR spectral studies revealed the thermoreversible self-assembly of the molecules in the gel state. DSC analysis provided the gel melting temperatures and gel stability under different conditions. XRD analysis revealed a lamellar type packing of the molecules whereas the OPM showed the growth of birefringent fibers. Electron microscopic studies revealed the formation of twisted and entangled supramolecular tapes of an average of 50-200 nm in width and several micrometers in length which are in agreement with
the AFM analysis. The organogels reported herein are the first examples of OPV based organogels derived from extended \( \pi \)-conjugated aromatic molecules.

2.1. Introduction

Control of the self-assembly of synthetic molecules in the creation of nanosized architectures, using the principles of supramolecular chemistry is a topic of considerable importance.\(^1\) The cooperative effect of noncovalent forces such as H-bonding, \( \pi \)-stacking, dipolar and van der Waals interactions are the driving force behind the self-assembly of molecules, leading to a variety of novel supramolecular architectures with reversible functional properties. Nature has the ability to control the architecture and function of supramolecular assemblies such as DNA double helix, collagen triple helix, ion channels and photosynthetic reaction centers which has been the major source of inspiration to scientists to mimic natural systems with the help of synthetic molecules.\(^2\)-\(^6\) In the domain of functional molecular assemblies and nanoarchitectures, supramolecular control of chromophore-linked molecular systems is a challenging task, particularly in the fabrication of nanoscale devices since chromophore orientation has tremendous influence on the optoelectronic properties.\(^7\) Organic \( \pi \)-conjugated systems play a crucial role as an integral component of supramolecular devices due to their interesting optical and electronic properties that are associated with the delocalized \( \pi \)-electrons, which can be modulated by intermolecular interactions.\(^3\),\(^8\) Therefore, self-organization of such systems with the aid of weak noncovalent associations are of extreme importance.

Even though the conjugated polymers are easy to synthesize and process into a device structure, the energetic and positional disorder of its chromophores induced by
The structural defects and entanglement of extended side chains affect the device performance. A solution to this problem is to build well-defined supramolecular structures through the self-assembly of π-conjugated oligomers, thus combining the high molecular order with ease of processing. Hence in recent years, considerable efforts are being focused to realize the concept of 'supramolecular electronics', where supramolecular assemblies of 10-100 nm lengths, from functional π-conjugated oligomers are targeted as active organic materials for the electrooptical devices.

Among various π-conjugated systems, phenylenevinylene (PVs) are one of the well studied class of molecules due to their importance in various electrooptical devices such as LEDs, photovoltaic cells and FETs. Control of the HOMO-LUMO gap by donor-acceptor interaction and by varying the conjugation length of oligomers provide materials with well-defined functional properties. In this context, extensive studies have been reported in the literature, pertaining to the optical and electronic properties of oligo(p-phenylenevinylene) (OPVs). Apart from these studies, there are several reports related to the liquid crystalline behavior, solid-state packing and self-assembly of phenylenevinylene derivatives. The main objective of these studies is the control of the optical and related electronic properties as a function of the self-assembly to form supramolecular architectures of nanometer dimensions. Combining the advantages of H-bond directed supramolecular interactions with the optical properties of PVs could provide an elegant way of creating functional nanoscopic as well as macroscopic assemblies of desired properties.

Recently, Meijer and coworkers have made significant contributions to the understanding of the supramolecular organization of OPVs. They have
synthesized OPVs, which are functionalized with uriedo-s-triazine quadruple H-bonding units. These OPV derivatives are further equipped with tridodecyloxy groups and enantiomerically pure (S)-2-methylbutoxy side chains. In chloroform, monofunctional OPV derivatives (1) dimerizes through quadruple H-bonding motifs with an association constant of $K_{\text{dim}} = (2.1 \pm 0.3) \times 10^4 \text{ Lmol}^{-1}$. In nonpolar solvents like dodecane, the H-bonded dimers self-assemble into left-handed helical stacks (Figure 2.1). Temperature and concentration dependent measurements have shown that the stability of the self-assembled stacks increases with conjugation length, due to favorable π-π interactions. Most importantly, the self-assembled fibers could be successfully transferred on to solid surfaces, which is essential for the fabrication of future supramolecular electronic devices. Detailed AFM studies have shown that, single fibers could be transferred only to inert substrates like graphite and silicium oxide. In the case of repulsive surfaces (mica and glass) clustering of the stacks occurs, while at attractive surfaces (gold) the stacks are destroyed. This systematic AFM study shows the importance of inert substances for the fabrication of nanodevices. However, the bifunctional OPV derivative (2) could only form less organized frustrated polymeric stacks, due to the competition between favorable π-π interactions and restricted conformational freedom, due to the hexyl spacer (Figure 2.2). The length of these supramolecular polymers and its chirality could be controlled by the addition of the monofunctional OPV derivatives as chain stoppers.
Recently, the self-assembly of diaminotriazine substituted OPV molecules (3-4) to hexameric \( \pi \)-conjugated rosette structures and the subsequent growth into chiral tubular objects have been reported. STM images have shown that chiral hexameric rosette structures lying flat on the surface with the diaminotriazine moieties pointing towards the center forming hydrogen bonds (Figure 2.3a). AFM and CD studies have shown that in nonpolar solvents these hexameric rosette assemblies stack on each
other using π-π interactions to form tubular self-assemblies as shown in Figure 2.3b. Detailed SANS experiments revealed the formation of tubules of 7 nm in diameter and 180 nm in length.

![Figure 2.3. a) STM images of the chiral hexameric OPV rosettes and b) AFM images of the OPV rosette nanotubes derived from the self-assembly of 3.](image)

An important aspect of supramolecular assembly of certain organic molecules is their ability to entrap a large volume of the solvent within the self-assembly to form a non-flowing soft mass called 'gel'\(^\text{21}\). Though a large number of non-chromophore and chromophore containing organogels are known, extended π-conjugated systems are the least exploited class of molecules in gel chemistry\(^\text{22}\). An early report on gelation of π-conjugated systems pertains to urea functionalized oligo(thiophene)s (5) (Figure 2.4).

![Figure 2.4. a) Bisurea-appended thiophene oligomer 5 and b) possible supramolecular arrangement of 5 through urea-urea H-bonding interactions.](image)
Though there are a number of reports on the self-assembly of OPV based systems, none of them describes the gelation properties of these molecules. Therefore, it is of considerable importance and curiosity to design OPVs which self-assemble to form organogels, to investigate on the properties and morphology of the resultant supramolecular assemblies. In the present chapter, we describe the detailed studies of the synthesis, gelation behavior and morphological analysis of OPV based organogelators which belong to a new class of supramolecular materials.

2.2. Results and Discussion

2.2.1. The Design Strategy

The actual cause of gelation of organic molecules is still a matter of debate though it is known that supramolecular noncovalent organization to form entangled structures, which are different from the simple molecular aggregates, are mainly responsible. Therefore, gelation can be considered as a delicate balance between crystallization, precipitation and solubility of noncovalently interacting molecules in a suitable solvent. Keeping this view in mind, we set to design π-conjugated molecules in such a way that they satisfy most of the conditions necessary for the formation of an extended self-assembly required for gelation (Figure 2.5). In this design, an appropriate π-conjugated system is equipped with two weak H-bonding end groups and sufficient number of long hydrocarbon side chains. Thus, a variety of tailor-made OPV derivatives were synthesized, the structures of which are shown in Figure 2.6. The presence of the two hydroxymethyl end groups will allow the molecules to self-assemble via weak nondirectional 2-point H-bonding, which will give sufficient freedom to the molecules to organize themselves. The presence of long hydrocarbon side chains facilitates the packing of the molecules, assisted by the weak van der
Waals interaction. These interactions will be reinforced by \( \pi \)-stacking of the rigid aromatic OPV backbone. A cooperative interaction of all these forces will eventually lead the molecules to form ordered assembly, resulting in the formation of entangled nanoscopic structures which are able to hold large amount of appropriate solvent molecules within the self-assembly, thereby forming a gel.

**Figure 2.5.** Design features of the OPV based organogelators showing various noncovalent interactions.

**Figure 2.6.** Library of OPV organogelators under investigation.
2.2.2. Synthesis of OPVs

The bisalcohols, BH-OPV1a-e, BH-OPV2 and BH-OPV3 were synthesized by the controlled Wittig reaction of the appropriate bisaldehydes and bisphosphonium salts, followed by the reduction of the resulted OPV bisaldehydes with NaBH4 (Scheme 2.1). Controlled Wittig-Horner reaction between the bisaldehyde (6) and the benzyl phosphonate (7) afforded the OPV monoaldehyde 8 in 35% yield, which in turn was reduced to MH-OPV by NaBH4 in 95% yield (Scheme 2.1). Synthesis of S-OPV was based on a literature procedure (90% yield).23 Preparation of the hydroxyl protected derivatives BM-OPV and BA-OPV were accomplished by the alkylation of BH-OPV1a with the corresponding alkyl halides in 95% and 60% yields, respectively (Scheme 2.2). All the OPV derivatives under investigation were characterized by spectral analyses. The all-trans configurations of the OPVs are confirmed by the \( J \) values (16.5 Hz) of the vinylic protons in their respective \( ^1H \) NMR spectra.

**Scheme 2.1.** Synthesis of the mono- and bishydroxymethyl OPV derivatives.
Scheme 2.2. Synthesis of the hydroxyl protected OPVs.

2.2.3. Gelation Studies

Gelation behavior of the newly synthesized OPV derivatives was examined in a range of organic solvents by dissolving different amounts in a specific volume (1 mL) of the solvent under heating and cooling. It has been observed that either gelation, precipitation or a clear solution could be obtained depending upon the solvent and structure of the compound. Gel formation could be detected readily by the failure of the resultant mass to flow when the vial was tilted upside down and also from the soft and transparent appearance. The results of the gelation experiments are presented in Table 2.1, which reveal that the bishydroxy compounds BH-OPV1a-c, having long linear hydrocarbon chains are efficient gelators of nonpolar hydrocarbon solvents such as hexane, decane, dodecane, cyclohexane, benzene and toluene. They could also gelate hydrocarbon fuels such as diesel and petrol. The maximum gelation efficiency is obtained for BH-OPV1a with a hexadecyloxy side chains and the critical gelator concentrations (CGC) in dodecane, decane and cyclohexane were 0.8, 0.9 and 1.1 mM, respectively. This means that BH-OPV1a can entrap approximately 10,000 molecules of dodecane per gelator molecules and falls under the category of supergelators.24
Table 2.1. Critical gelator concentrations (mM)\textsuperscript{a} of the OPV derived organogelators BH-OPV\textsubscript{1a-e}, BH-OPV\textsubscript{2} \textbf{\textit{} and BH-OPV\textsubscript{3}} in different solvents

<table>
<thead>
<tr>
<th>Gelator</th>
<th>Dodecane</th>
<th>Decane</th>
<th>Cyclohexane</th>
<th>Hexane</th>
<th>Toluene</th>
<th>Benzene</th>
<th>Chloroform</th>
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<tr>
<td>BH-OPV\textsubscript{1a}</td>
<td>0.8</td>
<td>0.9</td>
<td>1.1</td>
<td>1.7</td>
<td>2.8</td>
<td>3.0</td>
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<td>(s,tr)</td>
<td>(s,tr)</td>
<td>(s, tr)</td>
<td>(s, tr)</td>
<td>(th,o)</td>
<td></td>
</tr>
<tr>
<td>BH-OPV\textsubscript{1b}</td>
<td>1.0</td>
<td>1.1</td>
<td>1.4</td>
<td>2.1</td>
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<td>(s,tr)</td>
<td>(s,tr)</td>
<td>(s,tr)</td>
<td>(s,tr)</td>
<td>(th,o)</td>
<td></td>
</tr>
<tr>
<td>BH-OPV\textsubscript{1c}</td>
<td>4.5 (PG)</td>
<td>4.8 (PG)</td>
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<td>1</td>
<td>12.6</td>
<td>11.6</td>
<td>S</td>
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<td>(s,tr)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>BH-OPV\textsubscript{1d}</td>
<td>1</td>
<td>1</td>
<td>10.6</td>
<td>1</td>
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<td>(s,tr)</td>
<td>(s,tr)</td>
<td>(s,tr)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BH-OPV\textsubscript{1e}</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
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<td>P</td>
<td>15.4</td>
<td>11.5</td>
<td>23.0</td>
<td>P</td>
<td>P</td>
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<tr>
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<td>(s,o)</td>
<td>(s,o)</td>
<td>(s,o)</td>
<td>(s,o)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BH-OPV\textsubscript{3}</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>S</td>
<td></td>
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\textsuperscript{a}CGC = Critical gelator concentration, which is the minimum concentration required for the formation of a stable gel at room temperature. In parenthesis, s = stable, tr = transparent, th = thixotropic, o = opaque. S = soluble, I = insoluble, P = precipitation, PG = partial gelation at room temperature.

The gelation was selective for hydrocarbon solvents even from an emulsion with water. Photographs of the gels prepared under different conditions are shown in Figure 2.7. The gels obtained were transparent and stable so that the glass vial could be turned upside down without damaging the structure (Figures 2.7b and 2.7c). This is clear from Figure 2.7e where a gel of BH-OPV\textsubscript{1a} in diesel could hold an equal amount of water without falling (water is stained to distinguish from the diesel). The gelation ability of BH-OPV\textsubscript{1d}, carrying hexyloxy side chains is relatively poor (CGC is 10 mM in cyclohexane) whereas BH-OPV\textsubscript{1e} having branched 2-ethylhexyloxy side chain gave a homogeneous solution in all the solvents investigated. Nature of the solvents has considerable influence on the gelation behavior of BH-OPV\textsubscript{1a-d}. 
(Table 2.1). For example, the CGC of BH-OPV1a in chloroform is 5.6 mM and the resulting gels are unstable upon shaking (thixotropic). However, in a slightly less polar solvent like toluene, BH-OPV1a forms a reasonably stable gel with a CGC of 2.8 mM. Another factor, which influences the gelation ability of OPV derivatives, is the number of the hydrocarbon side chains present on the conjugated backbone (Table 2.1). For example, the CGC of BH-OPV2 having side chains only at the terminal phenyl rings is 15.6 mM in cyclohexane resulting in a turbid gel, whereas BH-OPV3, with side chains only at the central phenyl ring, does not gelate any of the solvents investigated. Hence, it is clear that for an OPV derivative to form a gel, it is necessary to maintain a balance between crystallization, solubility and precipitation where the length and position of the hydrocarbon side chains play an important role.

![Figure 2.7](image)

**Figure 2.7.** BH-OPV1a in decane a) before and b) after gelation. c) A toluene gel of BH-OPV1a. d) and e) BH-OPV1a in a mixture of water and diesel before and after gelation respectively. Water is stained with a dye to distinguish the two layers.

In order to investigate on the role of H-bond assisted π-stacking in the gelation process, we extended our studies to other OPV derivatives where the H-bonding groups are either protected or replaced by other functional groups. The results of the gelation studies of BM-OPV, BA-OPV, S-OPV and MH-OPV are summarized in Table 2.2. Interestingly, in the case of BM-OPV and BA-OPV, gelation occurred only
at high concentrations when compared to the corresponding bisalcohol derivative BH-OPV1a. The critical gelator concentration of BM-OPV is 3.3 mM in cyclohexane, and the resulting gels are thixotropic. BM-OPV failed to fully gelate solvents such as chloroform and THF, which may be due to the absence of H-bond donor groups that are necessary for the positional locking of the molecules within the π-stacked assembly. Compound BA-OPV, having the hexyloxy end groups, could gelate only nonpolar solvents such as dodecane and decane. In the case of MH-OPV with only one hydroxymethyl group, gel formation was observed in nonpolar solvents though it is not as efficient as in the case of BH-OPV1a and BH-OPV1b. However, S-OPV, without any end functional groups, could not gelate any of the solvents investigated, instead aggregate formation was observed which are not able to trap the solvents. These studies indicate the crucial role of H-bonding in assisting the weak interactions such as π-stacking and van der Waals associations in the process of self-assembly and gelation.

Table 2.2. Critical gelator concentrations (mM) of the OPV derived organogelators S-OPV, BM-OPV, BA-OPV and MH-OPV in different solvents

<table>
<thead>
<tr>
<th>Gelator</th>
<th>Dodecane</th>
<th>Decane</th>
<th>Cyclohexane</th>
<th>Hexane</th>
<th>Toluene</th>
<th>Benzene</th>
<th>Chloroform</th>
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<tbody>
<tr>
<td>S-OPV</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>BM-OPV</td>
<td>1.6</td>
<td>1.8</td>
<td>3.3</td>
<td>4.4</td>
<td>7.2</td>
<td>6.8</td>
<td>16.5</td>
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<td>(th, tr)</td>
<td>(th, tr)</td>
<td>(th, tr)</td>
<td>PG</td>
</tr>
<tr>
<td>BA-OPV</td>
<td>4.9</td>
<td>5.2</td>
<td>10.4</td>
<td>10.4</td>
<td>S</td>
<td>S</td>
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</tr>
<tr>
<td></td>
<td>(th, tr)</td>
<td>(th, tr)</td>
<td>(th, o)</td>
<td>(th, o)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MH-OPV</td>
<td>1.4</td>
<td>1.5</td>
<td>2.3</td>
<td>4.6</td>
<td>4.6</td>
<td>4.2</td>
<td>S</td>
</tr>
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<td></td>
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</table>

In parenthesis, s = stable, tr = transparent, th = thixotropic, o = opaque. S = soluble, l = insoluble, P = precipitation, PG = partial gelation at room temperature.
2.2.4. Thermotropic Behavior

The thermotropic behavior of the gels formed by BH-OPV1a-c, BM-OPV and MH-OPV were investigated by dropping ball method\textsuperscript{25} and by differential scanning calorimetry to understand the impact of the structure of the OPVs and the nature of the solvents on the gel stability. In the case of BH-OPV1a-c, a regular increase in the gel melting temperature ($T_{gel}$) with increasing concentration of the gelator molecules was observed (Figure 2.8). Phase diagrams of the gels of BH-OPV1a-c in cyclohexane were obtained by plotting the $T_{gel}$ at different concentrations (Figure 2.8a). The phase above each curve is a solution, whereas the phase below is a gel. The increase in $T_{gel}$ with increase in alkyl chain length shows increased stability of the gels, which could be due to the solvation assisted intermolecular packing of the long alkyl chains. Phase diagrams of BH-OPV1a gels from dodecane, cyclohexane, toluene and chloroform are shown in Figure 2.8b, which indicate that BH-OPV1a form strong gels in dodecane and cyclohexane, which showed higher melting temperatures even at very low concentrations. This observation is in accordance with the gelation studies presented in Table 2.1. Figure 2.8c shows the plots of the gel melting temperatures of the cyclohexane gels of BH-OPV1a, BM-OPV and MH-OPV, at different concentrations. These plots show remarkable stability for BH-OPV1a gel, due to H-bonding between the hydroxymethyl groups. For example, a cyclohexane gel of the methoxy derivative BM-OPV at a concentration of 10 mgmL$^{-1}$ melts at 47 °C, which is 15 °C lower than the corresponding BH-OPV1a gel. It is also clear that the gels of the monohydroxy derivative MH-OPV is more stable than that of the hydroxyl protected BM-OPV gel, however less stable than the BH-OPV1a gel. These results clearly indicate that the stability of the gels strongly depends upon the length and position of the side chains, polarity of the solvents and the presence of H-bonding
groups. Thermodynamic parameters calculated from the plots of the $T_{gel}$ vs. concentration using equation 1, which is derived from the Schrader’s relation,\(^2\) showed $\Delta H$ values of 258 kJmol\(^{-1}\), 196.32 kJmol\(^{-1}\) and 110.4 kJmol\(^{-1}\) for the cyclohexane gels of BH-OPV1a, BH-OPV1b and BH-OPV1c, respectively.

\[
\ln C = -\frac{\Delta H}{R} \frac{1}{T_{gel}} + \text{constant} \quad \ldots \ldots \ (1)
\]

In this equation $C$, $\Delta H$, $T_{gel}$ and $R$ are molar concentration, melting enthalpy, gel melting temperature and gas constant, respectively. The $\Delta H$ values of BH-OPV1a in cyclohexane, toluene and in chloroform were 258 kJmol\(^{-1}\), 143 kJmol\(^{-1}\) and 114 kJmol\(^{-1}\), respectively. These values show a maximum stability for BH-OPV1a in cyclohexane. Though this equation is often used to determine the $\Delta H$ values in polymeric and low molecular mass gels,\(^2\) ambiguity exists in the validity of equation 1 in the case of the sol-gel process of small molecules. Therefore, we have presented these values only for the purpose of comparison.

Differential Scanning Calorimetric (DSC) studies of the methylcyclohexane gels of BH-OPV1a-c, BM-OPV and MH-OPV are shown in Figure 2.9. These studies showed a similar trend in the stability of the gels as observed by the dropping ball methods. A broad exothermic transition was observed during the heating process, which is characteristic of a noncovalently associated supramolecular assembly. In the case of BH-OPV1a-c, the transition temperatures of the heating exotherms and the cooling endotherms increase in the order BH-OPV1a > BH-OPV1b > BH-OPV1c (Figure 2.9a). As in the case of the dropping ball experiment, the DSC analysis showed increased stability for the gels in hydrocarbon solvents of higher chain length. For example, among the three solvents used, the dodecane gel showed maximum
thermal stability (Figure 2.9b). The role of H-bonding is also evident from the DSC thermograms where BH-OPV1a showed a melting temperature of 63.5 °C which is 12.5 °C and 14 °C higher than that of the MH-OPV and BM-OPV, respectively (Figure 2.9c). In all these cases, it is interesting to note that the cooling transitions are sharper and occurred approximately 15-16 °C lower than the heating transition curves, indicating a better cooperativity in the formation of the self-assembly in the cooling process, leading to the gelation.

Figure 2.8. Binary phase diagrams of the OPV organogels showing the effect of side chains, solvents and H-bonding on stability. a) cyclohexane gels of BH-OPV1a (■), BH-OPV1b (●) and BH-OPV1c (▲), b) BH-OPV1a gels in dodecane (▼), in cyclohexane (●), in toluene (■) and in chloroform (▲) and c) cyclohexane gels of BH-OPV1a (■), MH-OPV (●) and BM-OPV (▼).
Figure 2.9. DSC thermograms of a) BH-OPV1a-c in methylcyclohexane, b) BH-OPV1a in different solvents and c) BH-OPV1a, MH-OPV and BM-OPV in methylcyclohexane (8 mg mL⁻¹). The heating and cooling rates are 5 °C/min in all experiments.

2.2.5. Variable Temperature ¹H NMR Studies

The ¹H NMR spectra of BH-OPV1a-b in CDCl₃ and benzene-d₆ (5 mM) showed distinctly different features when recorded at room temperature. For example, the ¹H NMR spectrum of BH-OPV1a in CDCl₃ gave well resolved resonance signals in accordance with the structure of the molecule, whereas in benzene-d₆, the spectrum did not show any of the characteristic resonance signals corresponding to the aromatic and vinylic protons. These observations point towards the strong intermolecular interaction due to the aggregation of the OPV units through noncovalent self-assembly of the molecules in benzene-d₆. In such cases, the ¹H NMR signals are too broad and weak to be distinguished due to the long correlation time. Changes in the resonance
signals of the aromatic and vinylic protons between the temperature ranges of 10 °C to 70 °C are shown in Figure 2.10a. As the temperature increases, the resonance signals corresponding to the aromatic protons appeared gradually at δ = 7.49, 7.37 and 7.05 ppm, along with the vinylic protons at δ = 8.05 ppm. The corresponding changes to the aliphatic protons are shown in Figure 2.10b. The benzylic and the –OCH₂ protons which appeared as broad unresolved peaks at δ = 4.79 and 3.65-3.9 ppm, respectively became well resolved when the temperature is increased to 50 °C. Further heating did not show any considerable change except for a small upfield shift of vinylic protons from 8.05 ppm to 7.95 ppm. Variable temperature ¹H NMR spectra of BH-OPV1a in cyclohexane-d₁₂ showed similar temperature dependency though the resolution of the resonance peaks occurred above 60 °C, indicating a higher stability of the self-assembly in cyclohexane.

Figure 2.10. Temperature dependent ¹H NMR spectra of BH-OPV1a in benzene-d₆ (5 mM) on the heating cycle.
2.2.6. X-ray Diffraction Studies

X-ray diffraction patterns of the xerogels obtained from BH-OPV1b show well resolved diffraction patterns characteristic of the long range ordering of the molecules (Figure 2.11a). In addition, a strong diffraction signal corresponding to a d-spacing of 23.2 Å, which is very close to the calculated molecular length (21.2 Å) of BH-OPV1b could be seen in the small angle region. A prominent reflection that is characteristic of a typical π−π stacking distance is observed in the wide-angle region at 3.8 Å. The strong intensity of the wide-angle peaks at 4.2 and 4.9 Å indicates the ordered packing of the dodecyl side chains in a layer type assembly. Figure 2.11b shows the intense diffraction peak of BH-OPV1a,b and d at the short angle region, which corresponds to the d-spacing of 41.7 Å, 35.2 Å and 16.5 Å, respectively. These distances match with the calculated width of the respective molecules with extended side chains. This is an indication of the lamellar packing distance that should vary with the length of the side chains. This argument is clear from the comparison of the observed d-spacing. Based on these data, it appears that the xerogel of BH-OPV1b most likely consists of a lamellar type packing through a cooperative H-bonding, π-stacking and van der Waals interactions as shown in Figure 2.12. In the lamellar packing, BH-OPV1b adopts a planar structure, in which the aryl units are coplanar and the alkyl side chains are laterally extended with a complete stretching of the side chains within the same plane of the conjugated backbone. The diffraction patterns of BM-OPV carrying hexadecyl side chains, where the H-bonding of the two hydroxymethyl groups were blocked, showed relatively broad reflections (Figure 2.11a). The absence of higher order reflections and the presence of broad reflections in the wide-angle region point toward a low degree of ordering in this case. The wide-angle region showed broad diffraction at 3.8 and 4.8 Å corresponding to a weak π−π stacking. These observations
are in agreement with the observed gelation behavior of BH-OPV1a and BM-OPV as indicated in Table 2.1 and Table 2.2.

Figure 2.11. a) X-ray diffraction patterns (room temperature) of the xerogels of BH-OPV1b and BM-OPV. b) Diffraction patterns in the short angle region corresponding to the lamellar packing distance of BH-OPV1a, BH-OPV1b and BH-OPV1d.

Figure 2.12. Schematic view of the lamellar packing of BH-OPV1b in the gel state. a) Structure of BH-OPV1b, b) side view and c) molecular model of the top view of the lamellar packing.
2.2.7. Optical Polarizing Microscopy

When viewed through crossed polarizers, the neat bishydroxy derivatives BH-OPV1a-c showed birefringent textures below the isotropic melting temperature. For example, when the neat BH-OPV1a is allowed to cool from the isotropic melt, spontaneous growth of long birefringent tape like textures could be observed at 114 °C as shown in Figures 2.13a and b. Presence of these textures indicates the linear growth of anisotropic H-bonded assemblies of the OPV molecules. Interestingly, it is observed that the length of the hydrocarbon side chains strongly influences the evolution of the textures. For example, the OPM picture of BH-OPV1d with hexyl side chains showed characteristic of crystalline textures when compared to the long fibrous textures of BH-OPV1a (Figure 2.13c). The role of H-bonded supramolecular assemblies in the growth of the tape-like structures is justified by comparing the OPM textures of the neat S-OPV (Figure 2.13d) with that of the BH-OPV1a (Figure 2.13a). Cooled melt of S-OPV at 106 °C showed the presence of crystallites due to the lack of H-bond assisted self-assembly. The birefringent tape-like textures obtained for the neat BH-OPV1a is very similar to that reported in the case of some helicenes and such textures are rare in the literature.\(^{27}\)

Figures 2.14a and 2.14b represent the optical micrographs of a BH-OPV1b gel in decane under different magnification, which are obtained under a moderate cooling rate of 5 °C/min\(^{-1}\). When cooled from the isotropic solution, birefringent fibrous aggregates emanating from random nucleation centers could be seen. The individual strands are difficult to discern within the bundles of fibers. The strong birefringence of the fibers indicates a well-defined molecular arrangement during the gelation as noticed in the case of the neat gelators, which is the result of the three-dimensional
organization of the ordered aggregates. When the same experiment was performed at a very low cooling rate of 0.5 °C/min, slow growth of elongated, birefringent fibers were observed which is evident from Figures 2.14c and 2.14d, indicating that the cooling rate is critical in the directional growth of the fibrous assembly. Fast cooling induces large number of nucleation sites leading to the radial growth of aggregates whereas slow cooling produces fewer nucleation centers leading to the directional linear growth of long fibers. Similar textures were observed for the decane gels of other bisalcohols, although the aggregate size varies with the structure and concentration of the OPVs. Decane gels of MH-OPV also showed birefringent fibers, even though they are short, thin and less directional (Figure 2.14e). Interestingly, the decane gels of the methyl ether derivative BM-OPV upon slow cooling form microcrystallites from several nucleation centers as shown in Figure 2.14f which
failed to form long fibrous aggregates in contrast to BH-OPV1b. The difference in the morphology of the structures obtained from the gels of BH-OPV1b and BM-OPV reveals that hydroxymethyl groups are essential for the formation of the extended supramolecular assemblies with long range ordering, leading to fiber growth and efficient gelation.

Figure 2.14. Optical micrographs of the decane gels of BH-OPV1b under moderate cooling a) 100x and b) 400x and by slow cooling c) 100x and d) 400x. Optical micrographs of the decane gels of e) MH-OPV and f) BM-OPV observed under moderate cooling (100 x).
2.2.8. Electron Microscopic and Atomic Force Microscopic Studies

Representative Scanning Electron Microscopic (SEM) images of the dried BH-OPV1a gels from toluene are shown in Figures 2.15a and b. These micrographs show the presence of entangled network of twisted supramolecular tapes formed by the self-assembly of BH-OPV1a. Careful analysis showed that these twisted tapes are approximately 50-100 nm in width and several micrometers in length. SEM pictures indicate that the fibers split and fuse with other fiber bundles, leading to the formation of junction zones, which stabilize the three-dimensional entangled network structures. Figures 2.15c and d are the SEM pictures of the dried gels of BH-OPV1a from decane. In this case the fibers are more dense, entangled and twisted. A magnified image indicates that entangled textures have the morphology of twisted tapes. The width of the tapes obtained from the decane gel is larger than that of the toluene gel, which indicates that intermolecular interaction is much stronger in the former case. In addition, the solvent-gelator interaction and as a result, the interactions between individual tapes are much strong in decane thereby leading to the formation of longer twisted tapes. Thus the observed gelation efficiency and the stability of the OPV gels are in agreement with the observed morphology.

Figure 2.16 represents the SEM pictures of a drop casted film of the bisalcohol BH-OPV1a, which showed fibrous morphology irrespective of the solvent used for the preparation of the film. In this case, large bundles of fibers with diameters varying from 0.2-0.8 μm are obtained which might be formed from small tapes and fibers. Figure 2.16b shows the SEM image of such a large bundle of fibers comprising of several coiled and entangled small fibers.
Figure 2.15. Scanning electron microscopic pictures of BH-OPV1a gels from toluene (a, b) and decane (c, d).

Figure 2.16. Scanning electron microscopic pictures of the BH-OPV1a drop casted from chloroform solution. a) magnification 5,000 and b) magnification 20,000.

A comparative study of the SEM pictures of the different OPV derivatives provided insight to the role of the H-bonding functionality on the morphology of the self-assembled structures. In the case of the methyl ether derivative BM-OPV, short ‘feather-like’ aggregates are obtained which are in contrast to the several micrometers long fibers of the bisalcohol derivatives (Figure 2.17a). This observation is in agreement with the OPM studies of BM-OPV, which showed the presence of short
fibers resulting from the lack of cooperative interactions of an anisotropic growth. However, the gelation of BM-OPV in hydrocarbon solvents reveals that long fibrous morphology is not a crucial factor in the formation of organogels, particularly in long hydrocarbon solvents, although this may affect the efficiency of gelation and the stability of the gels to a considerable extent. A SEM picture of a film of S-OPV having no end substituents showed a completely different morphology, in which randomly clustered aggregates of 0.5-1.0 μm in size are present (Figure 2.17b). These aggregates failed to trap organic solvents and hence S-OPV was not able to form gels. Interestingly, the SEM picture of BH-OPV1b showed the formation of fibrous aggregates in chloroform-methanol solvent mixtures, the morphology of which is entirely different from the gel fibers obtained from toluene or cyclohexane (Figure 2.17c). The above observations indicate that H-bond formation between the terminal hydroxymethyl groups is a key factor for the efficient gelation of OPVs, leading to the formation of supramolecular textures of definite shape and size.

![Figure 2.17](image)

Figure 2.17. Scanning electron microscopic pictures of a) cyclohexane gel of BM-OPV, b) S-OPV as a casted film and c) aggregates of BH-OPV1b from chloroform-methanol solvent mixture.

The transmission electron micrograph (TEM) of BH-OPV1a from a dilute toluene solution provided more information on the morphology of the self-assembled textures. The TEM picture in this case shows the presence of isolated twisted tapes of 50-100 nm in diameter and several micrometers in length (Figure 2.18). In a
magnified image (Figure 2.18b) the presence of several thin fiber-like structures of 10-20 nm in diameter could also be seen in addition to the large twisted structures. The alternate dark and bright regions observed are the indication of the twisted morphology of the fibers.

![Figure 2.18](image)

**Figure 2.18.** TEM pictures of the twisted fibers of BH-OPV1a gels from toluene.

AFM images of the BH-OPV1a self-assembly from toluene shows the presence of supramolecular tapes which consists of intertwined bundles of 50-150 nm in width and several micrometers in length (Figures 2.19a and 2.19b). It is also clear that the fiber bundles are built up from thinner fibers of 10-20 nm width. The width of the smallest fiber bundle that can be distinguished is 50-70 nm. Several isolated fibers could be observed under the AFM, when a dilute solution of the BH-OPV1a is deposited by drop casting. The morphology of such a single fiber is shown in Figure 2.19c. The presence of an array of the dark and bright areas of approximately 2 nm in width shows the molecular level lamellar organization of the individual OPV units. AFM analysis of the toluene gels MH-OPV (Figure 2.20a) and BM-OPV
(Figure 2.20b) showed the presence of fibrous and plate-like morphologies, respectively which are in agreement with the SEM results.

![Figure 2.19. AFM of BH-OPV1a from toluene under different magnification.](image)

![Figure 2.20. AFM of a) MH-OPV and b) BM-OPV from toluene.](image)

Based on the results obtained by the $^1$H NMR, DSC, X-ray, OPM, SEM, TEM and AFM studies, it is clear that the gelation of the BH-OPV1a-d is due to the cooperative supramolecular organization of the OPV units which is assisted by H-bonding, π-stacking and van der Waals interactions. The weak nondirectional H-bonding interaction of the hydroxymethyl end groups allows the formation of linear H-bonded assemblies as shown in Figure 2.12. These linear H-bonded assemblies will form supramolecular layer-like assemblies through the lamellar packing. The layered assemblies will be reinforced by π-stacking and van der Waals interactions leading to
the formation of supramolecular tapes. H-bonding may also be possible between the stacked layers which may act as reversible noncovalent crosslinking, resulting in a three-dimensional network. Further growth will result in the twisting of the tapes thereby forming elongated fibrous network leading to the immobilization of large volume of solvents within and between the networks, resulting in the gelation. The morphological analysis of the self-assemblies obtained from other OPV derivatives under investigation clearly established the role of the H-bonding motifs and the length and position of the side chains in the gelation process.

2.3. Conclusions

The OPV based organogelators reported here is a novel class of hydrocarbon gelators derived from rigid aromatic π-conjugated molecules. The presence of weak H-bonding hydroxymethyl groups and long hydrocarbon side chains are crucial for the gelation. Formation of strong gels even at a concentration below 1 mM shows that OPVs are efficient gelators of hydrocarbon solvents. The gelation properties and the morphology of the resultant supramolecular systems can be controlled by suitable modification of the OPV structures. Detailed morphological studies using OPM, SEM, TEM and AFM techniques revealed the formation of birefringent, entangled nanostructures of 50-100 nm in width and several micrometers in length. Evolution of the self-assembled fibrous network and the consequent gel formation is attributed to a cooperative interaction of H-bonding, π-stacking and van der Waals association of the individual OPV units leading to linear arrays of molecular stacks. The present study illustrates the importance of weak nondirectional H-bonding motifs for the design of strong gelators of hydrocarbon solvents. The different morphologies induced by the
gelation and the consequent reversible changes in the macroscopic properties endow these OPV organogels as a novel class of materials with tunable properties.

2.4. Experimental Section

2.4.1. Synthesis and Characterization

Unless otherwise stated, all starting materials and reagents were purchased from commercial suppliers and used without further purification. The solvents used were purified and dried by standard methods prior to use. Melting points were determined with a Mel-Temp-II melting point apparatus and are uncorrected. $^1$H and $^{13}$C NMR spectra were measured on a 300 MHz Bruker Avance DPX spectrometer using TMS as internal standard. FT-IR spectra were recorded on a Nicolet Impact 400D infrared spectrophotometer. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Perseptive Biosystems Voyager DE-Pro MALDI-TOF mass spectrometer. High-resolution mass spectra were recorded on a JEOL JM AX 505 HA mass spectrometer. The OPV bisaldehydes 6, were prepared using a reported procedure.$^{28}$

General Procedure for the Preparation of the Bisalcohols BH-OPV1a-e, BH-OPV2 and BH-OPV3. The appropriate precursor bisaldehyde$^{28}$ (6, 0.2 mmol) was dissolved in a mixture of methanol (10 mL) and dichloromethane (35 mL). To this solution, sodium borohydride (0.4 mmol) was added and stirred at room temperature for 45 minutes. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was dried and concentrated to give the corresponding alcohols. Yields, melting points, and spectral details of each product are given below.
**BH-OPVla.** Yield: 92%. mp 113-114 °C. FT-IR (KBr) \( \nu_{\text{max}} = 851, 965, 1011, 1068, 1202, 1259, 1341, 1388, 1418, 1460, 1511, 2845, 2918, 3381 \) cm\(^{-1}\). \(^1\)H NMR (300 MHz, CDCl\(_3\), TMS): \( \delta 0.85-0.87 \) (m, 18H, \(-\text{CH}_3\)), 1.25-1.83 (m, 168H, \(-\text{CH}_2\)), 2.3 (s, br., 2H, \(-\text{OH}\)), 3.97-4.04 (m, 12H, \(-\text{OCH}_2\)), 4.68 (s, 4H, \(-\text{CH}_2\text{OH}\)), 6.86 (s, 2H, aromatic), 7.12 (s, 2H, aromatic), 7.14 (s, 2H, aromatic), 7.45 (s, 4H, vinylic) ppm. \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta 14.10, 22.69, 26.21, 26.26, 28.70, 28.95, 29.37, 29.57, 29.58, 29.72, 31.93, 62.31, 68.57, 69.49, 69.70, 109.10, 110.73, 114.00, 122.69, 123.33, 127.25, 127.35, 129.29, 150.64, 151.05 \) ppm. MALD-TOF MS (MW = 1785.12): \( m/z = 1785.55 \) [M]⁺.

**BH-OPVlb.** Yield: 93%. mp 115-116 °C. FT-IR (KBr) \( \nu_{\text{max}} = 851, 963, 1072, 1207, 1258, 1344, 1389, 1421, 1466, 1510, 2847, 2920, 3056, 3349 \) cm\(^{-1}\). \(^1\)H NMR (300 MHz, CDCl\(_3\), TMS): \( \delta 0.87 \) (m, 18H, \(-\text{CH}_3\)), 1.25-1.83 (m, 120H, \(-\text{CH}_2\)), 2.4 (s, br., 2H, \(-\text{OH}\)), 3.98-4.04 (m, 12H, \(-\text{OCH}_2\)), 4.67 (s, 4H, \(-\text{CH}_2\text{OH}\)), 6.86 (s, 2H, aromatic), 7.12 (s, 2H, aromatic), 7.14 (s, 2H, aromatic), 7.45 (s, 4H, vinylic) ppm. \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta 14.09, 22.67, 26.20, 26.25, 26.31, 29.36, 29.46, 29.59, 29.68, 31.91, 62.28, 68.58, 69.50, 69.70, 109.08, 110.67, 114.00, 122.64, 123.34, 127.21, 127.36, 129.32, 150.65, 151.07 \) ppm. HRMS-ES⁺: [M+Na]⁺ calcd for C\(_{96}H_{166}O_{2}Na\), 1470.2480; found, 1470.2490.

**BH-OPVlc.** Yield: 95%. mp 126-127 °C. FT-IR (KBr) \( \nu_{\text{max}} = 851, 964, 1026, 1073, 1207, 1253, 1340, 1392, 1423, 1474, 1515, 2850, 2922, 3339 \) cm\(^{-1}\). \(^1\)H NMR (300 MHz, CDCl\(_3\), TMS): \( \delta 0.87-0.89 \) (m, 18H, \(-\text{CH}_3\)), 1.27-1.85 (m, 72H, \(-\text{CH}_2\)), 2.6 (s, br., 2H, \(-\text{OH}\)), 3.97-4.06 (m, 12H, \(-\text{OCH}_2\)), 4.68 (s, 4H, \(-\text{CH}_2\text{OH}\)), 6.87 (s, 2H, aromatic), 7.12 (s, 2H, aromatic), 7.15 (s, 2H, aromatic), 7.45 (s, 4H, vinylic) ppm.
BH-OPV1d. Yield: 96%. mp 134-135 °C. FT-IR (KBr) νmax = 854, 965, 1053, 1208, 1259, 1344, 1391, 1425, 1466, 1511, 2859, 2930, 3416 cm⁻¹. 1H NMR (300 MHz, CDCl₃, TMS): δ 0.90-0.91 (m, 18H, -CH₃), 1.26-1.85 (m, 48H, -CH₂), 3.89-4.06 (m, 12H, -OCH₂), 4.68 (s, 4H, -CH₂OH), 6.87 (s, 2H, aromatic), 7.13 (s, 2H, aromatic), 7.15 (s, 2H, aromatic), 7.45 (s, 4H, vinylic) ppm. 13C NMR (75 MHz, CDCl₃) δ 14.04, 22.64, 25.93, 29.48, 31.64, 62.31, 68.55, 69.47, 69.66, 109.06, 110.56, 113.93, 118.91, 123.27, 123.38, 125.5, 127.15, 150.65, 151.05 ppm. HRMS-FAB: [M]+ calcd for C₆₀H₉₄O₈, 942.6949; found, 942.6921.

BH-OPV1e. Yield: 85%. mp 74-75 °C. FT-IR (KBr) νmax = 852, 965, 1077, 1201, 1259, 1341, 1385, 1424, 1465, 1511, 2845, 2920, 3367 cm⁻¹. 1H NMR (300 MHz, CDCl₃, TMS): δ 0.87-0.89 (m, 18H, -CH₃), 1.27-1.85 (m, 72H, -CH₂ and -CH), 2.4 (s, br., 2H, -OH), 3.97-4.06 (m, 12H, -OCH₂), 4.67 (s, 4H, -CH₂OH), 6.86 (s, 2H, aromatic), 7.12 (s, 2H, aromatic), 7.14 (s, 2H, aromatic), 7.44 (s, 4H, vinylic) ppm. 13C NMR (75 MHz, CDCl₃) δ 11.32, 14.06, 23.08, 24.27, 29.15, 30.81, 39.74, 62.19, 70.63, 71.50, 71.89, 108.10, 109.44, 113.65, 112.39, 122.54, 127.05, 127.23, 129.35, 150.67, 151.13 ppm. MALDI-TOF MS (MW = 1110.88): m/z = 1110.82 [M]+.

BH-OPV2. Yield: 93%. mp 95-96 °C. FT-IR (KBr) νmax = 852, 960, 1017, 1073, 1104, 1212, 1269, 1337, 1393, 1424, 1470, 1511, 2856, 2928, 3381 cm⁻¹. 1H NMR (300 MHz, CDCl₃, TMS): δ 0.85-0.87 (m, 12H, -CH₃), 1.25-1.85 (m, 112H, -CH₂),
3.47 (s, br., 2H, -OH), 4.03-4.06 (m, 8H, -OCH₂), 4.71 (s, 4H, -CH₂OH), 6.80 (s, 2H, aromatic), 7.10 (s, 2H, aromatic), 7.34-7.39 (d, J = 16.5 Hz, 2H, vinylic), 7.46-7.51 (d, J = 16.5 Hz, 2H, vinylic), 7.56 (s, 4H, aromatic) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 14.10, 22.68, 26.21, 29.36, 29.42, 29.69, 62.24, 68.67, 69.68, 107.60, 113.90, 123.31, 126.45, 126.79, 128.41, 129.61, 137.09, 150.77, 151.04 ppm. MALDI-TOF MS (MW = 1303.13): m/z = 1303.03 [M⁺].

BH-OPV3. Yield: 95%. mp 96-97 °C. FT-IR (KBr) νmax = 847, 965, 1017, 1104, 1207, 1264, 1336, 1393, 1424, 1475, 1516, 2850, 2918, 3283 cm⁻¹. ¹H NMR (300 MHz, CDCl₃, TMS): δ 0.85-0.87 (m, 6H, -CH₃), 1.25-1.86 (m, 56H, -CH₂), 3.49 (s, br., 2H, -OH), 4.03-4.07 (t, J = 6.39 Hz, 4H, -OCH₂), 4.70 (s, 4H, -CH₂OH), 7.10-7.15 (d, J = 16.4 Hz, 2H, vinylic), 7.12 (s, 2H, aromatic), 7.34-7.37 (d, J = 7.8 Hz, 4H, aromatic), 7.45-7.50 (d, J = 16.5 Hz, 2H, vinylic), 7.51-7.54 (d, J = 7.7 Hz, 4H, aromatic) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 14.11, 22.68, 26.21, 26.62, 29.37, 29.57, 29.65, 29.69, 31.92, 65.21, 69.61, 105.47, 110.72, 123.61, 126.69, 126.88, 127.39, 137.49, 139.99, 151.13 ppm. MALDI-TOF MS (MW = 822.65): m/z = 822.60 [M⁺].

Preparation of MH-OPV. MH-OPV was prepared by the reduction of the monoaldehyde derivative 8 as described above for the syntheses of BH-OPVs. Yield: 95%. mp 112-113 °C. FT-IR (KBr) νmax = 852, 964, 1071, 1206, 1259, 1343, 1387, 1420, 1462, 1511, 2842, 2922, 3322 cm⁻¹. ¹H NMR (300 MHz, CDCl₃, TMS): δ 0.86-0.87 (m, 18H, -CH₃), 1.18-1.95 (m, 120H, -CH₂), 2.4 (s, br., 2H, -OH), 3.97-4.04 (m, 12H, -OCH₂), 4.67-4.69 (d, J = 6.3 Hz, 4H, -CH₂OH), 6.87 (s, 1H, aromatic), 7.12 (s, 2H, aromatic), 7.16 (s, 4H, vinylic), 7.33-7.38 (m, 3H, aromatic), 7.45 (s, 2H,
vinyllic), 7.48 (s, 3H, aromatic), 7.52-7.54 (d, J = 7.8 Hz, 2H, aromatic) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ 14.09, 22.62, 25.62, 28.95, 29.37, 29.49, 29.62, 29.82, 31.68, 60.65, 68.21, 69.51, 69.73, 109.11, 114.37, 114.65, 115.90, 122.34, 126.0, 127.11, 128.36, 129.32, 131.24, 150.65, 151.07, 155.11 ppm MALDI-TOF MS (MW = 1520.45): m/z = 1520.27 [M]$^+$. 

**Preparation of BM-OPV.** The bisalcohol BH-OPV1a (0.1 mmol) was dissolved in dry THF and NaH (0.3 mmol) in dry THF was added in portions. Methyl iodide (0.3 mmol) was added to this solution while cooling. The reaction mixture was stirred for 12 h and poured into water and then extracted with dichloromethane. Concentration of the organic layer followed by the column chromatography (hexane/chloroform, 3:1) over silica gel (100-200 mesh) gave the pure product BM-OPV. Yield 95 %. mp 99-100 °C. FT-IR (KBr) $\nu_{\text{max}}$ = 846, 955, 1011, 1068, 1094, 1125, 1202, 1248, 1336, 1382, 1418, 1465, 1511, 2850, 2923 cm$^{-1}$. $^1$H NMR (300 MHz, CDCl$_3$, TMS): δ 0.85-0.89 (m, 18H, -CH$_3$), 1.25-1.85 (m, 168H, -CH$_2$), 3.45 (s, 6H, -OCH$_3$), 3.97-4.05 (m, 12H, -OCH$_2$), 4.51 (s, 4H, -CH$_2$OCH$_3$), 6.96 (s, 2H, aromatic), 7.11 (s, 2H, aromatic), 7.14 (s, 2H, aromatic), 7.45 (m, 4H, vinyllic) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ 14.04, 22.68, 26.20, 26.62, 28.70, 28.95, 29.34, 29.71, 29.69, 31.91, 58.4, 68.32, 69.27, 69.52, 109.46, 110.68, 113.63, 123.29, 126.92, 127.28, 127.42, 150.70, 151.05 ppm. MALDI-TOF MS (MW = 1813.03): m/z = 1813.55 [M]$^+$. 

**Preparation of BA-OPV.** Reaction of the bisalcohol BH-OPV1a (0.1 mmol) and 1-bromohexane (0.3 mmol) as per the procedure described for the preparation of BM-OPV provided the BA-OPV in 60% yield after purification. mp 88-89 °C. FT-IR (KBr) $\nu_{\text{max}}$ = 855, 965, 1032, 1078, 1207, 1264, 1346, 1387, 1428, 1416, 1516, 2855, 2922 cm$^{-1}$. $^1$H NMR (300 MHz, CDCl$_3$, TMS): δ 0.85-0.90 (m, 24H, -CH$_3$), 1.24-1.85
Conjugated Organogels

(m, 184H, -CH₂), 3.50-3.55 (t, J = 6.63 Hz, 4H, -OCH₂C₆H₁₁), 3.98-4.05 (m, 12H, -OCH₂), 4.55 (s, 4H, -CH₂OC₆H₁₃), 6.99 (s, 2H, aromatic), 7.10 (s, 2H, aromatic), 7.14 (s, 2H, aromatic), 7.45 (m, 4H, vinylic) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 14.06, 14.11, 22.69, 26.01, 26.24, 26.32, 29.37, 29.50, 29.53, 29.58, 29.68, 29.72, 29.83, 31.77, 31.93, 67.30, 68.84, 69.51, 69.56, 70.83, 109.37, 110.63, 113.58, 123.15, 123.46, 126.70, 127.38, 127.87, 150.65, 151.02 ppm. MALDI-TOF MS (MW = 1953.30): m/z = 1952.84 [M]+.

**Preparation of S-OPV.** S-OPV was prepared by Wittig-Horner reaction according to a reported procedure.²³ Yield 90%. mp 106-107 °C. FT-IR (KBr) νmax = 847, 965, 1074, 1223, 1254, 1347, 1398, 1429, 1465, 1506, 2840, 2923 cm⁻¹. ¹H NMR (300 MHz, CDCl₃, TMS): δ 0.85-0.87 (m, 18H, -CH₃), 1.25-1.84 (m, 168H, -CH₂), 3.97-4.01 (m, 12H, -OCH₂), 6.7s (s, 2H, aromatic), 6.82 (d, J = 8.7 Hz, 2H, aromatic), 7.14 (s, 2H, aromatic), 7.18 (d, J = 8.5 Hz, 2H, aromatic), 7.47 (s, 4H, vinylic) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 14.09, 22.68, 26.12, 26.22, 26.28, 29.36, 29.48, 29.58, 29.63, 29.71, 31.92, 68.63, 69.54, 69.61, 110.79, 112.24, 114.00, 1223.44, 123.87, 127.41, 128.32, 129.29, 150.93, 153.34 ppm. MALDI-TOF MS (MW = 1724.93): m/z = 1724.58 [M]+.

**2.4.2. General Procedure for Gelation Studies**

A weighed amount of the compound in an appropriate solvent was placed in a glass vial, which was sealed and heated until the compound was dissolved. The solution was allowed to cool to room temperature and the gel formation was confirmed by the failure of the transparent soft mass to flow by inverting the glass vial. The reversibility of the gelation was confirmed by repeated heating and cooling.
2.4.3. Description on Experimental Techniques

**Differential Scanning Calorimetry.** An accurately weighed amount of the gel from appropriate solvents was analyzed on a Mettler Toledo Star DSC instrument under nitrogen atmosphere at the heating and cooling rates of 5 °C per minute.

**X-ray Diffraction.** Gels of the different OPVs from hexane or toluene were coated on glass plates and the solvents were slowly evaporated. X-ray diffractograms of the dried films were recorded on a Phillips diffractometer using Ni filtered Cu Kα radiation.

**Optical Polarizing Microscopy.** The gel texture was observed on a polarizing light microscope (Nikon HFX 35 A Optiphot equipped with a Linkan THMS 600 heating and freezing stage connected to Linkan TP 92 temperature programmer).

**Scanning Electron Microscopy.** Sheared gels from decane, cyclohexane or toluene were placed on sample studs and coated with gold by ion sputtering. SEM pictures were obtained either on a JEOL 5600 LV scanning electron microscope with an accelerating voltage of 10 kV, or a Hitachi S 2004 at an accelerating voltage of 15 kV.

**Transmission Electron Microscopy.** Transmission Electron Microscopy was performed on a Hitachi H-7100 microscope. Samples were prepared by drop casting the OPV solution from toluene on carbon coated copper grids and the TEM pictures were obtained without staining.

**Atomic Force Microscopy.** Atomic Force Microscopy images were recorded under ambient conditions using a Digital Instrument Multimode Nanoscope IV operating in the tapping mode regime. Micro-fabricated silicon cantilever tips (NSG01/Pt) with a
resonance frequency of approximately 150 kHz and a spring constant of about 5.5
Nm\(^{-1}\) were used. The scan rate varied from 0.5 to 1.5 Hz. The set-point amplitude ratio
\(r_{sp} = A_{sp}/A_o\), where \(A_{sp}\) is the amplitude setpoint, and \(A_o\) is the amplitude of the free
oscillation) was adjusted to 0.9. All AFM images shown here were subjected to a first-
order plane-fitting procedure to compensate for sample tilt. AFM analysis was done
offline. AFM samples were prepared by drop casting the OPV solution on freshly
cleaved muscovite mica.

2.5. References

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7. See the references 4-28 cited in Chapter 1 of the thesis.


21. See the references 29-108 cited in Chapter 1 of the thesis.


25. In a dropping ball method, a steel ball (150 mg) was placed on the top of a 1 mL volume gel in a sealed glass vial. Then the gels are slowly heated, while the position of the ball on the top of gel is continuously observed, until the gel no longer bears the ball. The temperature at which the ball reaches the bottom of vial is taken as the sol-gel phase transition temperature ($T_{gel}$).

