Chapter 4

Helical Nanostructures of Chiral Oligo($p$-phenylenevinylene) Derived Organogels

Abstract

Crafting of helical coiled-coil gel nanostructures via the self-assembly of chiral oligo(p-phenylenevinylene)s (COPV1-3) having remote chiral handles is described. The chiral side chains account for a bias of helicity by transferring the chiral information to the self-assembled chromophores as evidenced by the exciton coupled CD signal corresponding to the absorption maximum of the chromophore. The hierarchical helical growth of COPV2 into coiled-coil gel nanostructures is accompanied by an interesting observation of concentration and temperature dependent helix transition, reminiscent of the multistate folding and unfolding of the helical assemblies of biological macromolecules. Using the 'sergeant and soldiers' experiments with a mixture of chiral (COPV2-3) and achiral (BH-OPV1a-b) OPVs, it was shown that supramolecular chirality and helicity could be induced in the resulting co-assembled gel network. The helical nature of the gel nanostructures are established from the electron microscopic and AFM studies. While the observed helicity and the CD signals account for the formation of left-handed assemblies in the case of the homochiral OPVs, the induced chirality of the co-assemblies showed the opposite screw sense in the CD spectra. However, the SEM images showed the presence of the more stable left-handed helical morphology for higher order assemblies.
4.1. Introduction

Nature utilizes directional noncovalent supramolecular interactions to create helical and multiple helical complex architectures such as DNA double helix, the collagen triple helix, the α-coiled coil of myosin and the protein coating of tobacco mosaic virus, which are responsible for the control of biological functions. Using nature's self-assembly principles, chemists have been trying to design artificial supramolecular assemblies with definite shape and properties. Use of chiral molecules as building blocks to create helical supramolecular assembly is therefore a topic of considerable interest. The self-assembly of molecules or polymers into overall chiral self-assembled architectures with single handedness is referred as supramolecular chirality. The supramolecular chirality of biomolecules is determined by the configuration of the chiral centers present in their nucleotide or peptide backbone, which can bias the long range overall order to a single handedness in a well-defined self-assembled architecture. This intriguing phenomenon of generation of homochiral supramolecular architectures by nature has fascinated chemists to explore the ability of noncovalent forces such as H-bonding, π-π stacking and van der Waals interactions in chiral molecules to form a variety of aesthetically appealing helical supramolecular assemblies.\textsuperscript{1-9}

Peripheral chiral centers present in the side chains attached to synthetic molecules are known to express chirality at the supramolecular level. The resultant chiral induction could be monitored via CD spectroscopy and electron microscopy. An isolated UV/Vis-active chromophore provided with a chiral side chain does not feature a Cotton effect, as the remote chiral center cannot influence the absorption of the two helical components of light by the chromophore. However, when the molecules self-assemble into an organized supramolecular architecture, the chiral side
chains can induce a bias of one of the supramolecular diastereomers thereby expressing chirality in the chromophore stack in a helical sense that will eventually lead to a Cotton effect.

The groups of Moore and Meijer have made significant contributions to the helical self-assembly of π-conjugated oligomers derived from phenyleneethynlenes and phenylenevinylene, respectively where the chirality of the attached side chains are expressed to the conjugated oligomer backbone at a supramolecular level. A series of $m$-phenyleneethynylene oligomers containing either chiral polar (2$S$)-methyl-3,6,9-trioxadecyloxy side chains (1) or chiral apolar (S)-3,7-dimethyl-1-octyloxy side chains (2) have been synthesized and studied in detail by Moore et al. The oligomers are present in a random coil conformation in chloroform. However, under solvophobically driven conditions, they fold in a stepwise process via helical conformations into chiral helices, which will further undergo intermolecular stacking resulting in helical columns (Figure 4.1a). Meijer and coworkers have studied in detail the hierarchical self-organization of uriedo-s-triazine substituted OPVs (3) into helical stacks as a cooperative effect of π-π interactions and quadruple H-bonding interactions (Figure 4.1b).

![Figure 4.1. Schematic representations of the a) solvophobically induced stacking of $m$-phenyleneethynylene oligomers and b) H-bond and π-stack directed self-assembly of phenylenevinylene oligomers.](image-url)
A variety of helical gels based on chiral self-assembling cores such as cholesterol,\textsuperscript{12} and chiral hydrogen bond donor/acceptor groups such as urea,\textsuperscript{13} amide,\textsuperscript{14} and carbohydrates\textsuperscript{15} have been reported. In an interesting report, Oda \textit{et al.} describe the evolution of helical gel nanostructures of a gemini surfactant (4) based helical gel nanostructures, the helicity of which can be tuned by the introduction of opposite handed chiral counter anions such as tartrates (5) (Figure 4.2).\textsuperscript{7,16}

\begin{center}
\textbf{Figure 4.2.} a) Schematic representation and b) TEM images of the tuning of helical ribbons in gemini surfactant (4) derived organogels, by the addition of chiral counter anions (5).
\end{center}

There are several examples where supramolecular chirality is elegantly expressed to create helical and multiple helical nanostructures derived from chromophore based gels.\textsuperscript{4,17} Nolte and coworkers reported a disc-shaped phthalocyanine molecule (6), to which four peripheral chiral alkoxy di-substituted benzo crown ether moieties are attached.\textsuperscript{4} These molecules are shown to self-assemble in a clockwise and staggered manner to right-handed helical fibers of molecular diameter and micrometer lengths, as evident from the CD spectroscopy and TEM studies (Figure 4.3). These right-handed fibers, in turn, self-assemble to form left-handed coiled-coil helices, the helicity of which could be controlled by complexing the peripheral crown ether groups with $K^+$ ions.
In the light of the microscopic data obtained for the OPV gels, which showed the presence of randomly twisted nanostructures with no helical sense, we got interested to the design and properties of OPV based helical gels. For this purpose, chiral OPV derivatives COPV1-3 (Chart 4.1) are synthesized and characterized by spectral analysis.
The supramolecular chirality of the self-assembled stacks are controlled by the chiral (S)-3,7-dimethyloctyloxy side chains and assisted by weak hydrogen bonding hydroxymethyl motifs and long hydrocarbon chains. In this chapter, the self-assembly properties of COPV1-3, the detailed morphological investigation and circular dichroism experiments are described.

4.2. Results and Discussion

4.2.1. Synthesis and Characterization of Chiral OPVs

The chiral OPV derivatives COPV1-3 were synthesized as shown in Scheme 4.1. The chiral handles were obtained from (S)-citronellol, which was first catalytically hydrogenated and then brominated giving rise to (S)-(+)-1-bromo-3,7-dimethyloctane.\textsuperscript{5a} The chiral bistriphenyl phosphonium bromide 7 and the bisaldehydes 8a-c were prepared using standard procedures.\textsuperscript{18} Controlled Wittig reaction between chiral wittig salt 7 and the appropriate bisaldehydes 8a-c, in a 1:1 stoichiometry provided the chiral bisaldehydes 9a-c in 60% yields.\textsuperscript{18} These compounds on subsequent reduction with NaBH\textsubscript{4}, provided the corresponding bisalcohols COPV1-3 in 95% yields. All the new chiral OPV derivatives were characterized with IR, \textsuperscript{1}H NMR, \textsuperscript{13}C NMR and MALDI-TOF mass spectra.
4.2.2. Gelation Studies

Gelation behavior of the chiral OPV derivatives COPV1-3 was examined in a range of nonpolar organic solvents and the results are summarized in Table 4.1. Among the three chiral OPVs, COPV2, with dodecyl side chains, was found to be the better gelator to form yellow fluorescent gels in dodecane, heptane and cyclohexane. The critical gelator concentration of COPV2 in dodecane is high (6.5 mM) when compared to the gelation abilities of achiral OPVs, which could form gels even at a concentration of 1 mM (see Chapter 2). Though, COPV3 with hexadecyl side chain forms self-assembled aggregates in nonpolar solvents (as evidenced from the optical properties which will be discussed in section 4.2.3) they could not trap organic solvents inside their self-assembled network and hence phase separated from the solvent. However COPV1, which is substituted with six chiral side chains failed to form gels in any of the solvents investigated, and resulted a homogeneous solution due to its high solubility imparted by six branched chiral side chains.
Table 4.1. Critical gelator concentration (CGC) (mM) of chiral OPVs\textsuperscript{a}

<table>
<thead>
<tr>
<th>Compound</th>
<th>Dodecane</th>
<th>Heptane</th>
<th>Cyclohexane</th>
<th>Hexane</th>
<th>Chloroform</th>
</tr>
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<tbody>
<tr>
<td>COPV1</td>
<td>P</td>
<td>PG</td>
<td>PG</td>
<td>P</td>
<td>S</td>
</tr>
<tr>
<td>COPV2</td>
<td>6.5</td>
<td>7.0</td>
<td>7.2</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>COPV3</td>
<td>S</td>
<td>S</td>
<td>S</td>
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\textsuperscript{a}Souble (S), precipitation (P) and partial gelation (PG).

4.2.3. Optical and Chiroptical Properties of Chiral OPVs

The absorption and emission spectra of COPV1-3 in chloroform and dodecane are shown in Figure 4.4. In the case of COPV1, the absorption spectra did not show much change in the two solvents (Figure 4.4a). However, in dodecane COPV2 developed an additional shoulder band at 470 nm (Figure 4.4c), whereas in the case of COPV3 in dodecane, the spectrum is broadened towards the long wavelength region and the shoulder band at 472 nm is predominant even at low concentration (Figure 4.4e). The emission spectra of COPV1 in chloroform and dodecane showed two maxima around 455 and 484 nm with a shoulder around 525 nm (Figure 4.4b). The spectrum in dodecane is slightly blue shifted (ca. 5 nm) without changing the intensities of the various emission bands. In the case of COPV2 and COPV3, considerable differences could be observed for the emission spectra in chloroform and dodecane. For example, for COPV2 in dodecane, the emission spectrum showed four major bands at 450, 480, 525 and 570 nm in which the intensities of the long wavelength emitting bands are relatively strong when compared to those in chloroform (Figure 4.4d). Interestingly, for COPV3 in dodecane, the emission spectrum is significantly shifted towards the long wavelength region where the bands
at 528 and 571 nm are predominant (Figure 4.4f). The change in the absorption and emission spectra of COPV2 and COPV3 in dodecane relative to chloroform indicates the self-assembly of the molecules in dodecane, which is strong for COPV3. Interestingly, despite the strong aggregation of COPV3 in dodecane, it is surprising to note that this molecule showed very weak gelation. This could probably be due to the bias of the delicate balance between the crystallization and precipitation of the molecule in favor of latter, which plays a critical role in gelation.

Temperature dependent UV/Vis and emission spectra of COPV2 and COPV3 in dodecane showed a transition from the self-assembled species to the molecularly dissolved species as the temperature is increased. In the case of COPV2, on increasing the temperature, the intensity of the absorption maximum at 406 nm was increased with a concomitant decrease in the intensity of the shoulder band at 470 nm through an isosbestic point at 433 nm (Figure 4.5a). Similarly in the fluorescence spectra ($\lambda_{ex} = 380$ nm), the intensity of the long wavelength maximum at 525 nm decreases with the simultaneous increase in the intensity of the emission bands at 450 nm and 480 nm (Figure 4.5b). Similar observations were made with the variable temperature UV/Vis and fluorescence measurements of COPV3 in dodecane, even though much higher temperatures were needed for the complete breaking of the self-assembly to molecularly dissolved phase (Figures 4.6a and b).
Figure 4.4. Normalized a) UV/Vis and b) fluorescence spectra of COPV1-3 in dodecane and chloroform.
Detailed circular dichroism experiments of COPV1-3 have been carried out in order to get better understanding on the nature of the self-assemblies. As expected, no Cotton effects were observed for COPV1-3 in chloroform solution, reiterating the molecularly dissolved state of the OPVs. Furthermore, COPV1 does not feature any Cotton effect in dodecane, as they are not aggregated even in nonpolar solvents. However, the presence of self-assembled molecules of COPV2 in dodecane ($5.3 \times 10^{-4}$ M) at room temperature was clear from the CD experiments, which showed
a strong bisignated Cotton effect at the position of the \( \pi-\pi^* \) band, with a zero crossing close to the absorption maximum (400 nm) (Figure 4.7). The exciton coupled bisignated negative couplet in the CD spectrum is a signature of the left-handed-helical assembly of OPVs.

![CD spectra of COPV2 in dodecane and chloroform (c = 5.3 x 10^{-4} M, l = 1 mm).](image)

**Figure 4.7.** CD spectra of COPV2 in dodecane and chloroform (c = 5.3 x 10^{-4} M, l = 1 mm).

Detailed concentration and temperature dependent CD measurements of COPV2 in dodecane provided insight into the hierarchical helical self-assembly and the gelation of the molecules. The CD spectral changes between 8.8 x 10^{-5} M - 5.3 x 10^{-4} M concentration range at 20 °C is shown in Figure 4.8a (with chiral anisotropic factor at 381 nm, \( g_{381\text{nm}} = 6.8 \times 10^{-4} - 5.2 \times 10^{-3} \)).\(^{19}\) Up to a concentration of 2.7 x 10^{-4} M, COPV2 in dodecane showed a bisignated CD signal with a negative first Cotton effect followed by a second positive Cotton effect with a zero crossing around 440 nm, which is not on the absorption maximum of the chromophore. During this concentration range, a linear increase is observed, on plotting the intensity of the CD signal at 391 nm against the concentration (Figure 4.8b). Surprisingly, above 3.5 x 10^{-4} M concentration, a sharp transition of the CD signal could be seen. The zero crossing of the new CD signal is now exactly at the absorption maximum (400 nm), indicating a true exciton coupled spectrum. The transition of the CD signal is
accompanied by a strong amplification of the chirality as evident from the deviation of the Cotton effects from linearity (Figure 4.8b), indicating that the observed transition is a highly cooperative process. Temperature dependent study at a concentration of $5.3 \times 10^{-4}$ M in dodecane showed a decrease in the CD signal up to a temperature of 24 °C along the zero crossing point (Figures 4.8c and d). However at 26 °C, a sharp transition of the intense exciton coupled CD signal to a weak bisignated signal with a shift of the zero crossing from 400 nm to 440 nm was noted, which continued to decrease till it reached the baseline at 35 °C.

**Figure 4.8.** a) Concentration dependent ($T = 293$ K, $l = 1$ mm) CD spectra of COPV2 in dodecane and b) the corresponding transition of CD intensity monitored at 391 nm. c) Temperature dependent ($c = 5.3 \times 10^{-4}$ M, $l = 1$ mm) CD spectra of COPV2 in dodecane and d) is the zoomed portion of the temperature dependent CD spectra of COPV2 between 24-35 °C.
Moreover the melting transition curves obtained by plotting the fraction of aggregate molecules versus temperature, as inferred from the temperature dependent CD and UV/Vis studies clearly showed two transitions during the temperature dependent denaturation of the helical assembly (Figure 4.9). It is interesting to note that both concentration and temperature dependent transition of the CD signals are complementary to each other, which indicate a similar pathway involving same chiral intermediate during the formation and breaking of the supramolecular assembly.

Figure 4.9. Plot of the fraction of aggregate versus the temperature of COPV2 in dodecane.

CD measurements of COPV3 in dodecane showed an entirely different CD spectrum, when compared to that of COPV2. In this case, a first weak positive Cotton effect with maximum at 474 nm and an intense negative second Cotton effect with a maximum at 384 nm are observed followed by another positive Cotton effect with maximum at 313 nm (Figure 4.10). The zero crossing of the bisignated signal occurs at 432 and 343 nm. Even though the CD spectrum is consistent with an exciton model, in which the OPV molecules aggregate in a chiral supramolecular stack, the complex nature of the CD signal with double pseudo bisignated curves makes the prediction of the helical bias of the aggregate difficult.
Concentration dependent CD experiments have shown that even up to $10^{-7}$ M concentration, the COPV3 self-assembly is stable and most of the molecules remain as the part of the helical assembly (Figure 4.10a). Upon increasing the concentration, the intensity of the CD signal is increased through the isodichroic points at 432 and 343 nm. However, the plot of CD intensities at 385 and 312 nm versus concentration show a linear behavior indicating the absence of a cooperative chiral amplification which is contrast to the behavior of COPV2 (Figure 4.10b).

The temperature dependent CD experiments of COPV3 in dodecane showed a transition from the aggregated phase to molecularly dissolved species with increase in temperature (Figure 4.11a). When the fraction of self-assembled molecules (obtained from UV/Vis, fluorescence and CD experiments) was plotted against temperature, good correlations were obtained as shown in Figure 4.11b. In all cases, similar first order transitions were found. The transition temperature of the COPV3 self-assembly is found to be 42 °C, which is 16 °C higher when compared to that of COPV2 (26 °C) assemblies.
4.2.4. Optical Polarizing Microscopic (OPM) Studies

OPM studies of the neat COPV2-3 showed the formation of spherulite like textures. When COPV3 is cooled at a rate of 20 °Cmin⁻¹ from the isotropic melt, spherulite textures appeared at 67 °C, which was stable up to room temperature (Figure 4.12a). It is interesting to note that, the structurally related achiral BH-OPV1 derivatives described in Chapter 2 showed long fibers when cooled from the isotropic melt and hence the spherulite textures obtained for COPV3 could be attributed to the chirality of the molecule. Similar observation was made with neat COPV2 (Figure 4.12b).Interestingly, when COPV2 and COPV3 were rapidly cooled from isotropic melt, by quenching with ice, transparent organic glasses were formed, showing birefringent textures (Figures 4.12c-d). OPM studies of the dodecane gels of COPV2 revealed birefringent four-arm brush textures emanating from several nucleation centers, when cooled from the isotropic solution at a rate of 5 °Cmin⁻¹ (Figure 4.13). From the OPM studies it can be concluded that, the spherulite and four-arm brush textures of chiral OPVs in their neat and gel phases, could be the indication of the
helical ordering of the molecules. In order to confirm this speculation detailed microscopic investigation of the gel samples were performed.

Figure 4.12. Optical polarizing microscopic pictures of a) spherulite crystalline textures of COPV3 and b) COPV2, c) organic glasses formed by COPV3 and d) COPV2.

Figure 4.13. Optical polarizing microscopic pictures of dodecane gels of COPV2 (c = 9 mg/mL). magnification is a) 100x and b) 400x.

4.2.5. Morphological Characterization of Chiral OPV Nanostructures

Field emission scanning electron microscope (FE-SEM) images of COPV2 from a dilute solution in dodecane (9 x 10^{-4} M) showed left-handed helical fibers of 20-50 nm in diameter and a few micrometers in length with a uniform helical pitch of
approximately 200 nm (Figures 4.14a and b). This is in agreement with the CD studies, in which a negative exciton coupled CD signal indicated a left-handed organization of the chromophores. However, the FE-SEM image of COPV2 (partially gelled) from a more concentrated solution in dodecane (5 x 10^-4 M) showed the formation of left-handed coiled-coil rope-like structures of 50-100 nm in diameter with an average pitch of 330 nm. These rope-like structures are formed by the twisting together of several helical fibers (Figure 4.14c).

Figure 4.14. Helical morphology of COPV2 self-assembly from a dodecane solution: FE-SEM images of a) left-handed helical fibers, b) isolated single helical fibers and c) formation of coiled-coil ropes (5 x 10^-4 M).

AFM analysis of the COPV2 gel from dodecane (6.5 x 10^-3 M) indicates the formation of entangled left-handed helical coiled-coil fibers of 50-100 nm in diameter.
Careful analysis of a single fiber showed the morphology of a left-handed coiled-coil rope of approximately 90 nm in width and 11 nm in height in which the pitch of each helix has an angle of about 40° with respect to the main fiber axis (Figure 4.15c). These observations point towards a hierarchical self-organization of COPV2 into coiled-coil gel nanostructures.

**Figure 4.15.** a) and b) AFM images of the dense coiled network of COPV2 gel fibers (6 x 10^{-3} M) and c) AFM image of a single left-handed coiled-coil rope.

SEM pictures of a drop casted dodecane solution of COPV3 (3 x 10^{-5} M) showed, bundles of ‘leaf-like’ structures emanating from several randomly arranged nucleation points (Figure 4.16a) which are entirely different from the morphology of COPV2. Each bundle is composed of several leaves having diameter ca. 1-2 μm and length around 15-20 μm (Figure 4.16b) with relatively low aspect ratio when compared to that of COPV2 structures.
4.3. Gelation Induced Hierarchical Growth of Helical Coiled-Coil Gel Nanostructures

The concentration and temperature dependent CD signal transition of COPV2 is a unique observation associated with the gelation of chiral OPVs. During the gelation of COPV2, several hierarchical levels of supramolecular assemblies could be possible. In the initial levels, the molecules organize to form left-handed chiral aggregates, which are helical as indicated by the weak bisignated CD signal. At higher concentrations, these initial chiral assemblies grow further into helical fibers and coiled-coil ropes, thus resulting in a strong exciton coupled CD signal. It is interesting to note that the CD transition and the chiral amplification are accompanied by the gelation. A plausible helical packing of COPV2 to form the left-handed coiled-coil rope, is represented along with the observed AFM image in Figure 4.17. As we have postulated earlier in the case of the molecular packing of the achiral OPVs, the cooperative interaction of H-bonding and π-stacking facilitate the lamellar organization of the chromophores to form a supramolecular tape-like morphology. The remote chiral handles present in the molecules will induce a long range twisting of the tapes, thereby forming twisted tapes as evidenced by the FE-SEM analysis. In the next level of assembly, several of the twisted tapes will join together to evolve
coiled-coil rope-like structures of an average of 90-100 nm in width and several micrometers in length as evidenced by the AFM image shown in Figure 4.17b. Interestingly, when the results of the CD and microscopic analyses are considered together, it is evident that the coiled-coil structures evolve through two distinct chiral assemblies. At higher temperatures, denaturing of the coiled-coil gel assemblies occurs via intermediate chiral states, and the helical self-assembly ultimately collapses into isotropic single molecules for which no CD signals are observed.

![Schematic representation of the hierarchical self-assembly of COPV2 into helical coiled-coil gel nanostructures](image)

**Figure 4.17.** Schematic representation of the hierarchical self-assembly of COPV2 into helical coiled-coil gel nanostructures. A magnified AFM picture of the coiled-coil rope is shown on the right hand side.

### 4.4. ‘Sergeants and Soldiers’ Approach to Supramolecular Chirality Amplification

Green and coworkers have introduced the idea of ‘Sergeant and Soldiers’ principle and ‘Majority Rules’ to induce helicity in poly(isocyanate)s with the help of
a chiral guest. These rules illustrate that, to favor one of the helical conformations, either P or M of poly(\(n\)-alkylisocyanate)s, it is only required to add a small portion of the chiral monomer units (sergeants) to the achiral monomers (soldiers) or have a slight majority of 'R' over 'S' (Majority Rule). The ability of poly(isocyanate)s to bias the helicity is explained on the basis of its highly cooperative helical folding. Recently, Meijer and coworkers have successfully applied the 'sergeant and soldiers' principle in a variety of supramolecular discotic systems. The co-assembly of \(C_3\)-symmetric discotic chiral and achiral molecules results in the amplification of chirality, with one chiral molecule capable of organizing as much as 80 achiral ones in either a right- or a left-handed helical stack. Except in discotic systems, chiral amplification via the 'sergeants and soldiers' approach to form helical supramolecular architectures remains elusive and challenging. This is particularly true in the case of rigid \(\pi\)-conjugated molecules which self-organize via supramolecular lamellar fashion. This has prompted us to explore the possibilities of chiral induction and amplification of a helical bias using co-assembly behavior of the chiral OPVs (COPV1-3) with the achiral OPVs, BH-OPV1a and BH-OPV1b (Chart 4.2).

![Chart 4.2](image)

A series of co-assembled OPV gels of the achiral OPV derivatives BH-OPV1b, carrying dodecyl side chains, with varying amounts of structurally related chiral COPV2 (0-50%) were prepared in dodecane, by heating the mixed OPV
solution to 90 °C and the subsequent cooling to 5 °C at a cooling rate of 20 °Cmin⁻¹. In all cases stable, transparent and fluorescent gels were obtained indicating the co-assembly of both achiral and chiral OPVs. The ‘sergeant and soldiers’ experiment of BH-OPV1b/ COPV2 dodecane gels were conducted at 5 °C by monitoring the CD spectra as a function of the mol% of COPV2 (sergeant) (Figure 4.18a). As expected, the dodecane gel of pure BH-OPV1b does not show any Cotton effect. However, the BH-OPV1b/ COPV2 dodecane gels showed pseudo-bisignated Cotton effects at the OPV absorption, the intensity of which increases with the mole fraction of the COPV2. Up to 25% of COPV2, the co-assembled OPV gel showed a weak pseudo-bisignated CD signal with the negative maxima at 456, 380 and 317 nm and the positive maximum at 406 nm, whose intensity increases linearly with COPV2 concentration. This is further evident from the plot of the CD intensity at 406 and 317 nm, versus the percentage of COPV2 in the co-assembled gels as shown in Figure 4.18b. However, when the percentage of the COPV2 is increased beyond 25%, a strong amplification of chirality is observed, which is clear from the deviation of the plot of the CD intensity from linearity. The CD signals grow in intensity through the isodichroic points at 436 nm and 388 nm. Even though, the strong pseudo-bisignated Cotton effect with positive maximum at 406 nm and the negative maximum at 380 nm with a zero crossing at 388 nm obtained with 50% COPV2 co-assembled gels can be attributed to a helical arrangement of the OPV chromophores, the appearance of an additional negative Cotton effect at 460 nm, makes it difficult to assign the exact handedness from the CD signal.
Interestingly, when a pre-heated dodecane solution of BH-OPV1b containing 50% COPV2, is allowed to gel by slow cooling at room temperature, a strong amplification of chirality is observed, resulting in an intense exciton coupled bisignated CD signal with a first positive Cotton effect having a maximum at 415 nm and a second negative Cotton effect with a maximum at 380 nm, through a zero crossing at 392 nm (Figure 4.19a). This CD signal is nearly three times more intense than that of the fast cooled gel. However, the slow cooled BH-OPV1b/COPV2 dodecane gel showed the opposite sign of Cotton effect when compared to the CD signal of the pure COPV2 dodecane gel (5.3 × 10⁻⁴ M) (Figure 4.19b). Although, the two CD spectra are not the exact mirror images, the inversion of Cotton effect indicates that, the OPV chromophores in the BH-OPV1b/COPV2 dodecane gels are arranged in a different helical sense in the co-aggregate, when compared to that of the pure COPV2 assembly.
Figure 4.19. a) CD spectra of the fast cooled (20 °C/min) and slow cooled (room temperature cooling) BH-OPV1b/COPV2 co-assembled dodecane gels (T = 278 K, l = 1 mm) containing 50% of COPV2 and b) comparison of the slow cooled BH-OPV1b/COPV2 co-assembled dodecane gels with the CD spectrum of pure COPV2 dodecane gels (5.3 x 10^{-4} M).

Figure 4.20 shows the plots of the CD signal intensities of the BH-OPV1b, COPV2 and the BH-OPV1b/COPV2 co-assembled dodecane gels. It is interesting to note that at same concentrations of COPV2, the CD signal intensity of the co-assembled gels of BH-OPV1b/COPV2 is larger than that of COPV2 dodecane gel which is a clear indication of the ‘sergeants and soldiers’ effect in chirality amplification. In the co-assembled gel state, the chiral OPV molecules can efficiently bias the packing of the achiral OPV molecules resulting in the amplification of chirality, indicating the cooperative nature of the self-assembly.
Figure 4.20. Plots of the concentration dependent CD intensity at 391 nm of the pure COPV2, co-assembled BH-OPV1b/COPV2 and pure BH-OPV1b dodecane gels.

The temperature dependence of the Cotton effect of the co-assembled BH-OPV1b/COPV2 gels has been investigated to get insight into the cooperativity of the self-assembly process. Figure 4.21 shows the temperature dependent CD spectra of the slow cooled dodecane BH-OPV1b/COPV2 gel doped with 50% COPV2. The inset of the Figure 4.21 shows the corresponding self-assembly transition curve obtained by plotting the fraction of the aggregates versus temperature. From the temperature dependent CD curves, it is evident that the co-aggregated OPV helices have intense CD signal up to 50 °C, and the denaturation of the helix took place over a small temperature range, as is indicated by the complete loss of the CD signal at 63 °C. The lack of isodichroic point during the temperature dependent breaking of the helical OPV stacks supports the involvement of intermediate chiral states during the hierarchical evolution of the helical assembly. The difference in the CD spectrum of the fast cooled co-assembled gels can be attributed to that of a kinetically controlled assembly, whereas a thermodynamically more stable self-assembly is resulted upon slow cooling, as evident from the appearance of the intense exciton coupled CD
signal. It is interesting to note that the stability of the chiral OPV gels have been considerably increased, by co-assembling with achiral OPVs. The pure COPV2 \((5.3 \times 10^{-4} \text{ M})\) gels are stable only up to 30 °C, while the co-assembled BH-OPV1b/COPV2 gel containing \(2 \times 10^{-4} \text{ M}\) of COPV2 is stable up to 63 °C as observed from the temperature dependent studies.

**Figure 4.21.** Temperature dependent CD spectra of slow cooled dodecane BH-OPV1b/COPV2 gel doped with 50% COPV2. The inset shows the aggregate stability curve obtained by plotting the fraction of self-assembled molecules versus temperature.

Results of the CD spectral studies of the co-assembly between the achiral BH-OPV1a and the chiral COPV3 are shown in Figure 4.22. Even though, COPV3 could not form gels despite its strong aggregation ability, co-assembly of COPV3 with BH-OPV1a in dodecane resulted in the formation of stable gels. When BH-OPV1a is doped with different concentrations of COPV3, rapid formation of stable and transparent co-assembled gels could be observed.
Figure 4.22. a) and b) CD spectra of BH-OPV1a/COPV3 co-assembled dodecane gels ($T = 278\, K$, $l = 1\, \text{mm}$) at various mol% of COPV3 and c) the corresponding changes in the CD intensity monitored at 415 and 370 nm, as a function of the concentration of COPV3 in the co-assembled gels. d) Comparison of the CD spectra of BH-OPV1a/COPV3 co-assembled dodecane gels with that of pure COPV2 dodecane gels ($5.3 \times 10^{-4}\, \text{M}$).

Up to 25% of COPV3, the co-assembled OPV gels showed a weak exciton coupled CD signal with a positive maximum at 406 nm and negative maximum at 314 nm through a zero crossing at 380 nm (Figure 4.22a). At a concentration of 24% of COPV3, a sudden transition to a new exciton coupled bisignated signal with positive and negative maxima at 433 and 378 nm, respectively was observed, which is accompanied by a shift in the zero crossing to 390 nm (Figure 4.22b). The observed shift in the CD signal accompanied by the significant increase in the intensity is an
indication of the reorganization of the initial co-assembly to a more stable packing of the chromophores. The plot of CD signal intensities at 415 nm and 370 nm, against the mol% of COPV3 showed a sharp increase above 20 mol% indicating a strong chiral induction from COPV3 to BH-OPV1a in the co-assembly (Figure 4.22c). Comparison of the CD signals of pure COPV2 with BH-OPV1a/COPV3 co-assembly showed a near mirror image relationship indicating apposite helical sense between the two supramolecular assemblies (Figure 4.22d).

The presence of the intermediate chiral states is further evident from the temperature dependent CD studies of the BH-OPV1a/COPV3 dodecane gels. When the temperature was increased up to 55 °C, a sudden transition of the strongly exciton coupled CD signal to a weak CD signal was observed, which is similar in shape to the one observed during the initial stages of the growth of the co-assembled gels (Figure 4.23a). This could be easily observed in the corresponding stability curve (Figure 4.23b). The intensity of the CD signal continued to decrease with increase in temperature until it reached the baseline at 70 °C.

Figure 4.23. a) Temperature dependent CD spectra of the dodecane BH-OPV1a/COPV3 gel doped with 50% COPV3 and b) the corresponding melting transition plot obtained by plotting the fraction of self-assembled molecules versus temperature.
From the detailed CD studies, it is clear that supramolecular chirality can be induced into achiral OPV gels by co-assembling with structurally related chiral self-assembling OPV derivatives. However, in the present case for the efficient induction of the supramolecular chirality more than 25% of the chiral oligomers are needed. This is in contrast to the amplification of chirality observed for the helical columnar discotic molecules, for which even 2.5% of chiral 'sergeant’ molecules are sufficient for a full bias of the helicity.\(^5\) This may be due to the difference in the stacking interaction of the OPV chromophores in a lamellar assembly leading to a three-dimensional supramolecular structure in contrast to the one-dimensional columnar stacks of the discotic molecules. In such situations, the chirality of the ‘sergeant’ molecules would not be strongly recognized by the achiral ‘soldiers’. However, to the best of our knowledge, this induction of chirality using ‘sergeant and soldiers’ principles in achiral OPV gels by co-assembling with chiral OPVs, furnishes the first example of its kind for the design of helical OPV nanostructures. The most remarkable observation during the chiral induction experiments is the unusual bias of the supramolecular chirality towards right-handedness in the co-assembly. The ‘S’-chiral center present in the side chains of chiral OPVs are expected to direct the self-assembly of achiral OPVs in a left-handed direction, as observed in the case of pure chiral COPV2 gels. Recently, Jonkheim et al. have also observed such an inversion of supramolecular chirality during the helical rosette formation of homochiral triazine substituted OPVs.\(^1\) Detailed studies have shown that, the right-handed OPV rosette helical assembly is only a kinetically controlled metastable state, which changed into the thermodynamically favored left-handed helical assembly very quickly with first-order kinetics. However, in the present co-assembled gel systems, the induced right-handed helicity is preserved even after two weeks. These results indicate that, the
intact arrangement of the OPV chromophores in the co-assembled network enabled
the locking of the induced right-handed supramolecular chirality and to memorize it
for several weeks.

We have carried out detailed optical polarizing and scanning electron
microscopic studies in order to confirm the induction of chirality in the co-assembled
OPV gels. The optical polarizing microscopic studies of the co-assembled dodecane
gels of BH-OPV1b/COPV2 showed considerable differences from that of the
individual chiral and achiral OPVs. For example, the achiral OPV gels have long
birefringent fibrous textures (Figure 4.24a), whereas the chiral OPV gels (Figure
4.24b) exhibit four-arm brush textures characteristic of the helical packing of the
molecules. Interestingly, when the co-assembled BH-OPV1b/COPV2 dodecane gels
are cooled from the isotropic solution, a texture which is different from the individual
molecules could be observed (Figure 4.24c). This observation is an indication of the
co-assembly of COPV2 with BH-OPV1b which is responsible for the supramolecular
chirality and the helical bias.

Figure 4.24. Optical polarizing micrographs of a) BH-OPV1b, b) COPV2 and c) co-assembled BH-
OPV1b/COPV2 dodecane gels (magnification is 100x).

Scanning electron micrographs of BH-OPV1b/COPV2 co-assembly showed
the presence of long entangled twisted tapes of 50-200 nm diameters and several
micrometers length (Figure 4.25). Careful analysis revealed that all fibers have left-
handed twist. However, the positive bisignated CD signal of co-assembled gels suggest a right-handed helical arrangement of the OPV chromophores. These observations point towards the possibility of having several hierarchical structures of organization in the co-assembled OPV gels. At the primary level, the OPV chromophores are directed to assemble in a right-handed helical manner by the remote chiral side chains, which is responsible for the positive bisignated CD signal. However, at the secondary level of the self-assembly, the right-handed primary structures organize into left-handed tape-like assemblies, as observed through SEM images.

Figure 4.25. Scanning electron microscopic pictures of BH-OPV1b/COPV2 dodecane gels.

4.5. Conclusions

Three different oligo(p-phenylenevinylene)s, COPV1-3 having remote chiral handles have been designed and synthesized. Among the three derivatives, only COPV2 forms gel in apolar hydrocarbon solvents, which indicates that the nature of the side chain is crucial in the gelation of chiral OPVs. While COPV1 failed to form gel, COPV2 provided stable gel in dodecane whereas COPV3 forms strong aggregates with weak gelation property. Optical polarizing microscopy showed birefringent fibrous four-arm brushes revealing strong molecular anisotropy. FE-SEM pictures of
COPV2 revealed concentration dependent hierarchical self-assembly leading to the formation of left-handed helical fibers of 20-50 nm and coiled-coil ropes of ca. 150 nm in width. AFM analysis of the gel fibers showed the characteristics of left-handed coiled-coil ropes. Concentration and temperature dependent CD spectral studies of COPV2 revealed a helix transition during the hierarchical growth of the self-assembly indicating the presence of different chiral intermediates. Helical bias through an amplified chiral induction could be achieved to achiral OPV gels by co-assembling with the chiral OPVs which showed a right-handed supramolecular chirality in the initial levels of the co-assembly and a left-handed helicity at the higher levels of the co-assembly as evidenced from the SEM images. This is the first report of a gelation assisted chiral amplification and helical bias in the supramolecular co-assembly of extended \( \pi \)-conjugated system.

4.6. Experimental Section

4.6.1. Synthesis and Characterization of COPV1-3

Solvents and the reagents used were purified and dried by usual methods. All starting materials were obtained from commercial suppliers and used as received. All melting points were determined with a Mel-Temp-II melting point apparatus and are uncorrected. \(^1\)H and \(^{13}\)C NMR were measured on a 300 MHz Bruker Avance DPX spectrometer or on a Varian Gemini 300 MHz spectrophotometer. IR spectra were recorded on a Nicolet Impact 400D Infrared spectrophotometer. Matrix assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry was conducted on a perspective Biosystems Voyager DE-Pro MALDI-TOF mass spectrometer. Chiral side chains were prepared according to previous report.\(^{5a}\) The compounds
COPV1-3 were synthesized using similar procedures used for the synthesis of corresponding achiral derivatives (see Chapter 2 for details).

**COPV1.** Yield 95%. mp 75-76 °C. FT-IR (KBr) $\nu_{\text{max}} = 865, 912, 1051, 1124, 1201, 1253, 1382, 1418, 1470, 1506, 2918, 2955, 3348 \text{ cm}^{-1}$. $^1$H NMR (300 MHz, CDCl$_3$, TMS) $\delta$ 0.75-1.8 (m, 114H, –CH$_3$ and –CH$_2$), 3.95-4.03 (m, 12H, –OCH$_2$), 4.6-4.62 (d, 4H, –CH$_2$OH), 6.8 (s, 2H, aromatic), 7.06 (s, 2H, aromatic), 7.08 (s, 4H, aromatic), 7.38 (s, 4H, vinylic) ppm. $^{13}$C NMR (300 MHz, CDCl$_3$, TMS) $\delta$ 14.09, 22.64, 25.93, 29.34, 29.68, 31.37, 62.30, 69.52, 69.73, 108.49, 114.26, 115.91, 126.76, 128.47, 128.60, 129.73, 151.12, 151.51 ppm. MALDI-TOF MS (MW = 1280.02): $m/z = 1279.64$ [M]$^+$.  

**COPV2.** Yield 94%. mp 83-84 °C. FT-IR (KBr) $\nu_{\text{max}} = 865, 968, 1046, 1206, 1258, 1387, 1424, 1465, 1506, 2846, 2924, 3348 \text{ cm}^{-1}$. $^1$H NMR (300 MHz, CDCl$_3$, TMS) $\delta$ 0.75-1.8 (m, 130H, –CH$_3$ and –CH$_2$), 4.02-4.16 (m, 12H, –OCH$_2$), 4.72-4.74 (d, 4H, –CH$_2$OH), 6.92 (s, 2H, aromatic), 7.17 (s, 2H, aromatic), 7.21(s, 4H, aromatic), 7.51(s, 4H, vinylic) ppm. $^{13}$C NMR (300 MHz, CDCl$_3$, TMS) $\delta$ 14.04, 19.25, 24.45, 25.62, 27.60, 28.70, 28.93, 29.37, 29.19, 29.80, 31.68, 62.43, 68.21, 69.10, 69.51, 110.54, 114.12, 123.56, 126.76, 127.21, 127.76, 129.46, 150.67, 151.07 ppm. MALDI-TOF MS (MW = 1391.2): $m/z = 1392.15$ [M]$^+$.  

**COPV3.** Yield 96%. mp 90-91 °C. FT-IR (KBr) $\nu_{\text{max}} = 725, 860, 979, 1046, 1124, 1253, 1346, 1418, 1470, 1506, 2851, 2918, 3327 \text{ cm}^{-1}$. $^1$H NMR (300 MHz, CDCl$_3$, TMS) $\delta$ 0.75-1.76 (m, 162H, –CH$_3$ and –CH$_2$), 3.91-4.01 (m, 12H, –OCH$_2$), 4.61-4.62 (d, 4H, –CH$_2$OH), 6.79 (s, 2H, aromatic), 7.05 (s, 2H, aromatic), 7.08 (s, 4H, aromatic), 7.38(s, 4H, vinylic) ppm. $^{13}$C NMR (300 MHz, CDCl$_3$, TMS) $\delta$ 14.54,
19.34, 22.34, 24.40, 25.56, 27.69, 28.45, 28.90, 29.23, 29.45, 29.75, 31.61, 62.45,
68.34, 69.15, 69.54, 110.43, 114.01, 123.43, 126.65, 127.21, 127.45, 129.73, 150.97,
151.14.

4.6.2. General Procedure for Gelation Studies

A weighed amount of the compound in an appropriate solvent (6-8 mM) 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 gel mixture to flow by inverting the glass vial. The
thermo reversibility of the gelation was confirmed by repeated heating and cooling.

4.6.3. General Procedure for ‘Sergeant and Soldiers’ Experiments

The co-assembled OPV dodecane gels of the achiral BH-OPV1a/b, and chiral
COPV2/3 OPV derivatives were prepared by heating the mixed OPV solution to
90 °C and the subsequent cooling either at a cooling rate of 20 °Cmin⁻¹ or by slow
cooling at room temperature. In all cases stable, transparent and fluorescent gels were
obtained indicating the co-assembly of both achiral and chiral OPVs and the
measurements were carried out 5 °C, in a 1 mm cuvette.

4.6.4. Description on Experimental Techniques

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).

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.

**Field-Emission Scanning Electron Microscopy.** FE-SEM studies were carried out on a CARL Zeiss LEO GEMINI 1550. The SEM samples were prepared by transferring the dodecane solution of COPV1 onto a 400 mesh carbon-coated Formvar copper grid. The samples were allowed to dry and then coated with platinum prior to imaging.

**Optical and Chiroptical Measurements.** Electronic absorption spectra were recorded on a Shimadzu UV-3101 PC NIR scanning spectrophotometer and the emission spectra were recorded on a SPEX-Fluorolog F112X spectrofluorimeter. Temperature dependent studies were carried out either in a 0.1cm or 1 cm quartz cuvette with a thermistor directly attached to the wall of the cuvette holder. CD spectra were recorded either on JASCO-J-600 or JASCO-J-810 spectropolarimeters equipped with a JASCO PTC-348WI or JASCO PTC-423S Peltier type temperature control system.

**4.7. References**


19. A measure of for the induced chirality is given by the chiral anisotropy factor ‘g’. \[ g = \frac{\Delta \varepsilon}{\varepsilon}, \] in which \( \Delta \varepsilon \) can be calculated as follows: \( \Delta \varepsilon = \text{CD-effect}/(32980cI) \), where ‘CD-effect’ is the intensity of Cotton effect in mdeg, ‘c’ is the molar concentration and ‘I’ is the path length in cm.