

π -Organogels of Self-Assembled *p*-Phenylenevinylenes: Soft Materials with Distinct Size, Shape, and Functions

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ABSTRACT

This Account is focused on the self-assembly of *p*-phenylenevinylenes, a linear π -system, which has been extensively studied over the years due to both fundamental and technological importance. A serendipitous observation of the gelation of an oligo(*p*-phenylenevinylene) (OPV) derivative in nonpolar hydrocarbon solvents that led to a new class of functional materials, namely, π -organogels, is described. Strategies to control the size, shape, and functions of the supramolecular architectures of OPV self-assemblies are highlighted. Formation of nano- to micro-sized helical architectures, control on chromophore packing, self-assembly induced modulation of optical properties, and application as light-harvesting assemblies are the important features of this novel class of photonically and electronically active soft materials.

1. Introduction

Nature does wonders by crafting complex molecular and supramolecular architectures, which are vital for sustaining life. Both covalent and noncovalent chemistry play important roles in this creativity. A few examples include nanoscopic DNA and proteins to macroscopic virus and bacteria. Chemists try to mimic the molecular architectures of such functional assemblies using weak interactions such as hydrogen bonding, π -stacking, dipolar, and van der Waals forces. These efforts have succeeded in the

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design of a variety of artificial supramolecular architectures of different sizes, shapes, and functions.¹

An interesting property of molecular self-assemblies, in certain cases, is the formation of extended structures leading to the gelation of the solvent in which the molecule is dissolved.^{2–5} Most of the early findings on molecular gels were serendipitous. However, over the years, insights gained on the self-assembly of molecules facilitated the design of a variety of molecules that form strong gels with intriguing properties useful for wide-ranging applications in food, cosmetics, medicine, tissue engineering, biomineralization, catalysis, controlled release, and advanced materials.^{2–5} Among the different class of molecules, self-assembly of linear π -systems is at center stage due to favorable optical and electronic properties, useful to the design of organic electronic devices.^{6–8} From this view point, oligo(*p*-phenylenevinylene)s (OPVs) are one of the preferred classes of molecules. The optical and electronic properties of these molecules strongly depend upon structural features and hence can be modulated by variations in conjugation length^{8–10} and donor–acceptor strengths.^{8a,10b,11} An alternate approach to the modulation of the optoelectronic properties is by inducing intermolecular interactions using weak noncovalent forces.⁶ Among these interactions hydrogen-bonding and π -stacking are widely exploited for the self-assembly of OPVs.

2. OPV Self-Assemblies

Hydrogen-bond mediated self-assembly of OPV derivatives has been extensively studied by Meijer and coworkers.^{12,13} These studies have unraveled many interesting properties of OPV aggregates, particularly their morphological and optical properties. For example, OPV when functionalized with a ureidopyrimidinone moiety (**M-OPVUP**, Chart 1) is shown to form self-assembled dimers whereas the bifunctional derivative **B-OPVUP** forms a supramolecular polymer through quadruple hydrogen bonding in nonpolar solvents.^{12a,12b} Monofunctional OPVs containing uriedo-*s*-triazine units (**M-OPVUTs**) in dodecane self-assemble to form left-handed helical columns as evidenced from the bisignate circular dichroism (CD) signal.^{12c,12d} Detailed temperature and concentration dependent optical studies have shown that the stability of these self-assembled stacks increases with conjugation length due to the favorable π - π interactions. However, the bifunctional OPV derivatives (**B-OPVUTs**) organize into frustrated polymeric stacks due to the competition between favorable π - π interactions and restricted conformational freedom, due to the alkyl spacer between the hydrogen-bonding motifs. Recently, Meijer and coworkers have made a significant contribution to the understanding of the mechanistic details of the self-assembly processes in uriedo-*s*-triazine functionalized OPVs (**M-OPVUTs**).^{12e} Based on spectroscopic data a nucleation–growth pathway

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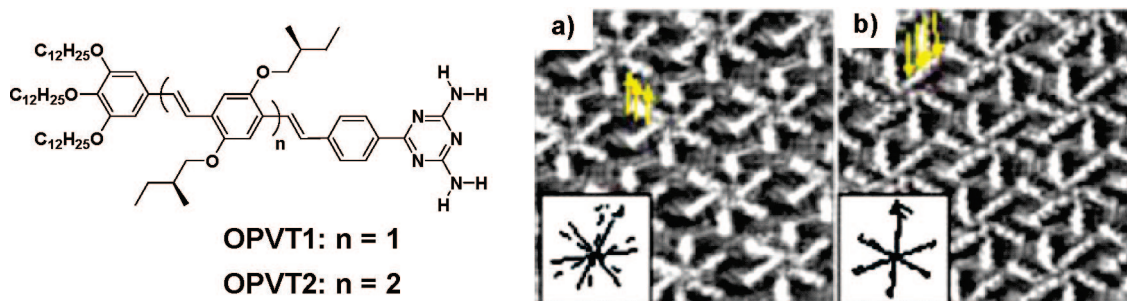
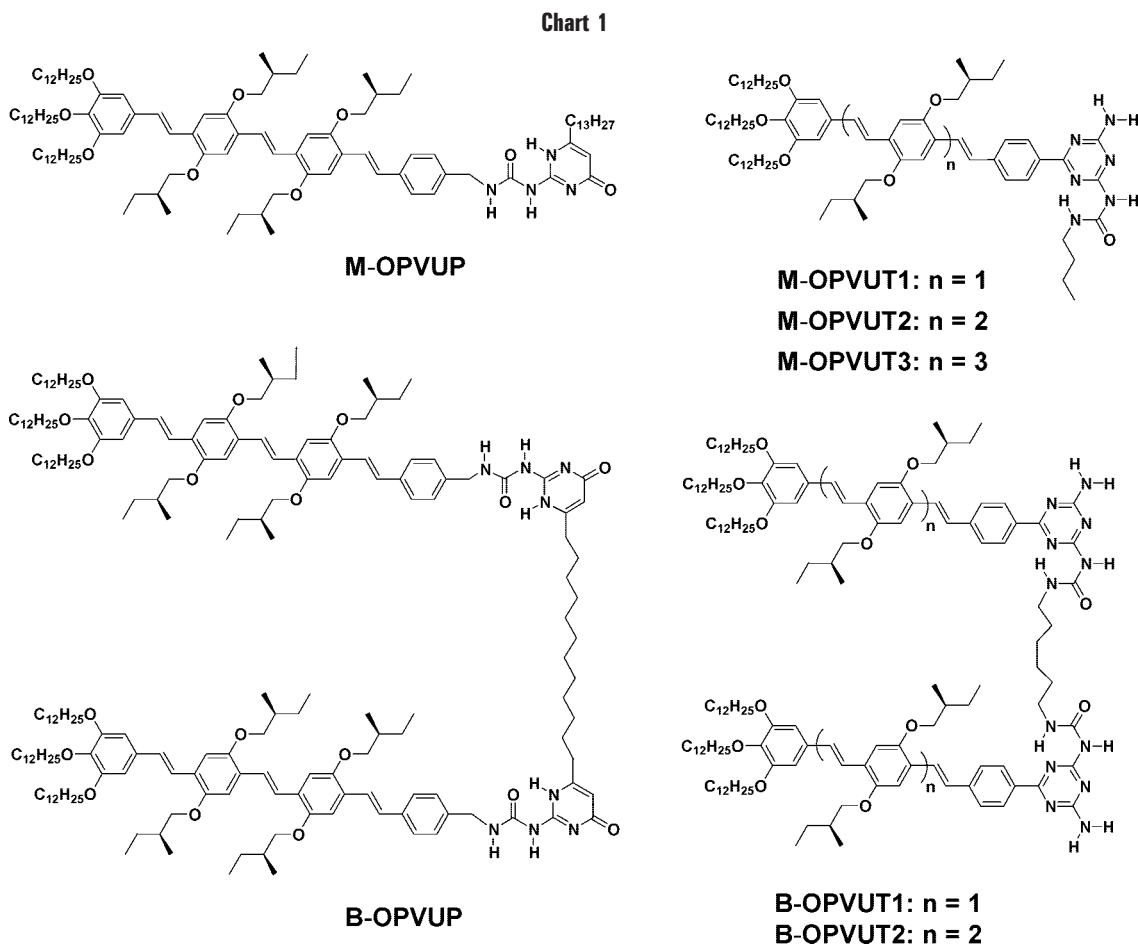


FIGURE 1. Molecular structures of diamino triazine unit functionalized OPV derivatives (**OPVT1** and **OPVT2**) that form hexameric rosettes and STM images of (a) **OPVT1** and (b) **OPVT2** monolayers at the solid–liquid interface using graphite as the substrate and 1-phenyloctane as the solvent. Reprinted from ref 13a with permission. Copyright 2004 Wiley-VCH.



that suggests a remarkable degree of cooperativity has been proposed that may be applicable to the self-assembly of similar systems.

OPVs upon functionalization with diamino triazine moieties (**OPVT1** and **OPVT2**) self-assemble to hexameric π -conjugated rosette structures and subsequently grow into chiral tubular objects (Figure 1).^{13a} Scanning tunneling microscopy (STM) images showed chiral hexameric rosette structures lying flat on the surface with the diamino triazine moieties pointing to the center, forming a hydrogen-bonded cavity. Atomic force microscopy (AFM) and CD studies have shown that in nonpolar solvents these rosette structures stack on each other through π - π interactions to form tubular self-assemblies. Recently, it has been demonstrated that functionalization of OPVs with nucleotides allows the comple-

mentary interaction of single-stranded oligodeoxyadenylic acid in aqueous solutions resulting in right-handed helical structures.^{13b}

3. *p*-Phenylenevinylene: A Versatile Building Block for π -Organogels

In the year 2001, we reported the first π -organogel based on a short linear π -system.¹⁴ We accidentally found that the oligo(*p*-phenylenevinylene) derivative **OPV1** having two hydroxymethyl groups and six dodecyloxy side chains forms a self-supporting soft solid from aliphatic hydrocarbon solvents such as hexane, cyclohexane, decane, dodecane, petrol, diesel, and kerosene, when dissolved in small quantities (<2 mM) at room temperature (Figure

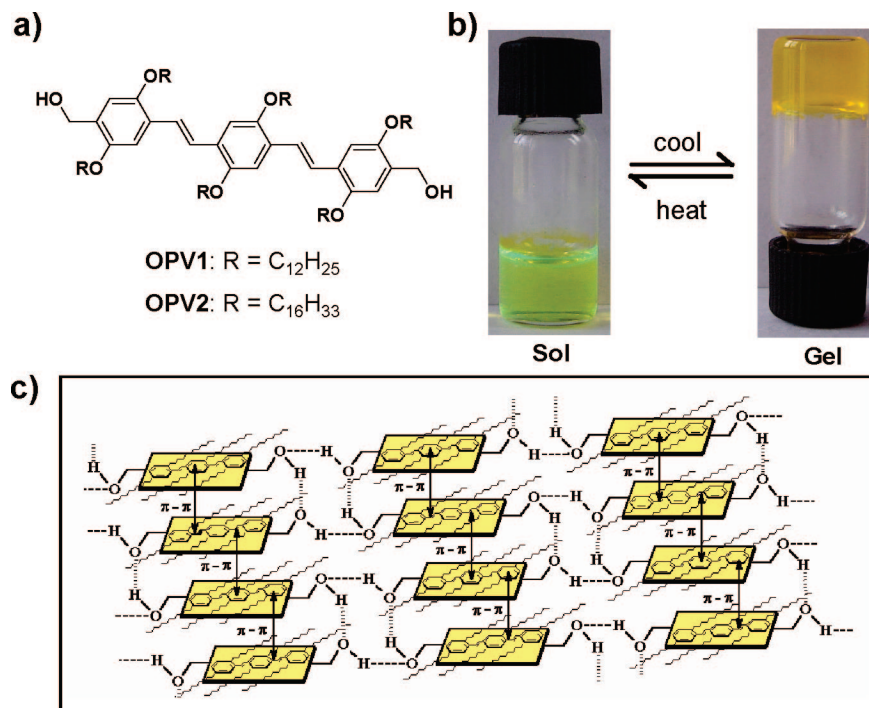


FIGURE 2. (a) Structures of the gel-forming OPVs. (b) Photograph of **OPV1** in cyclohexane before and after gelation (critical gelator concentration, CGC = 1.1 mM). (c) Probable self-assembly of OPVs, depicting the H-bond and π -stack induced three dimensional network formations.

2).^{14–16} This observation attracted our immediate attention revealing the interesting chemistry of a variety of tailor-made OPVs.^{14–16} In the absence of the hydroxymethyl groups or long hydrocarbon side chains, OPVs failed to form gels although they indicate the formation of aggregates as evidenced by the absorption and emission studies. This could be because the extended self-assembly of the aggregates to hierarchical supramolecular architectures may not be favored in the absence of hydrogen bonding groups. Moreover, the presence of long hydrocarbon chains, which favor van der Waals interaction and prevent crystallization, are essential for the gel formation. Thus, gelation is a delicate balance between crystallization and precipitation of the molecules, leading to the formation of extended supramolecular networks with the aid of cooperative hydrogen bonding, π -stacking, and van der Waals interactions. The hydroxymethyl groups facilitate linear hydrogen-bonded polymeric structures, which undergo π -stacking to form arrays of supramolecular polymeric structures (Figure 2c). Hierarchical self-assembly of these structures will result in the formation of entangled networks that hold large volumes of solvents eventually resulting in the gelation of the solvents.

Morphological features of the gels were revealed by optical polarizing microscopy (OPM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), and X-ray diffraction (XRD) studies.^{14–16} The OPM textures of the **OPV2** gel of decane (0.9 mM) showed birefringent fibrous textures indicating molecular anisotropy of the self-assembly (Figure 3a). An SEM picture of the **OPV2** toluene gel (2.8 mM) exhibited an entangled supramolecular tape-like morphology having a width of 50–100 nm, which is

several micrometers in length (Figure 3b). TEM images of a dilute solution of **OPV2** (1×10^{-4} M) evaporated from toluene on a carbon grid showed the formation of tapes of 20–200 nm widths and micrometers in length (Figure 3c). The height and width of the tapes vary with concentration of the gelator. At higher concentrations, bundles of tapes were formed leading to micrometer-sized superstructures. These tapes are twisted at several places indicating their tendency to form coiled structures. AFM studies of dried **OPV2** toluene gels on mica surface (Figure 3d) support the morphological features observed in SEM and TEM images. Cross-section analysis of the tapes revealed heights of 12–20 nm, which correspond to four to six layers of the molecules over the mica surface.

X-ray diffraction patterns of a dried film of **OPV1** gel on a glass plate showed peaks at 23.2 Å corresponding to the molecular length of 21.2 Å, lamellar packing distance of 35.2 Å, and π -stacking distance of 3.8 Å.¹⁵ From these data, we proposed that the molecules are packed to have multilayer lamellar assemblies through hydrogen bonding and π -stacking in which each chromophore is arranged perpendicular to the long axis of the fiber (Figure 4).

Subsequent to our report, a dendron rod-coil molecule that contained a conjugated segment of OPV (**DRC-OPV**) was shown to form gels in toluene/THF (30:1).^{17a} The absorption and emission studies indicated the formation of H-type aggregates during the gelation of this molecule. Morphological studies indicated the formation of high-aspect-ratio ribbon-like nanostructures consisting of two molecules held together by hydrogen-bond interactions of the hydroxyl-rich dendrons that further self-assemble by π - π stacking. The amphiphilic molecules, **A-OPVn**

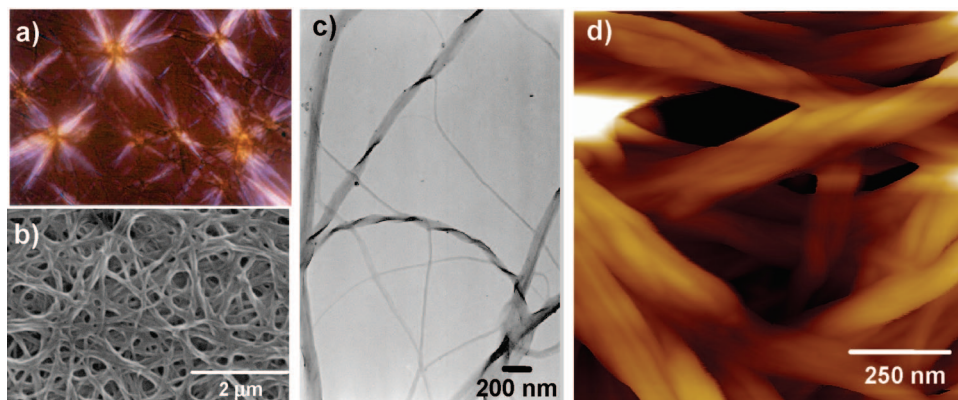


FIGURE 3. Morphological features of self-assembled **OPV2**: (a) OPM picture ($400\times$ magnifications) of the decane gel (0.9 mM); (b) SEM image of a toluene gel (2.8 mM); (c) TEM image of a toluene solution (1×10^{-4} M) evaporated on a carbon grid; (d) AFM tapping mode height images of a toluene gel.

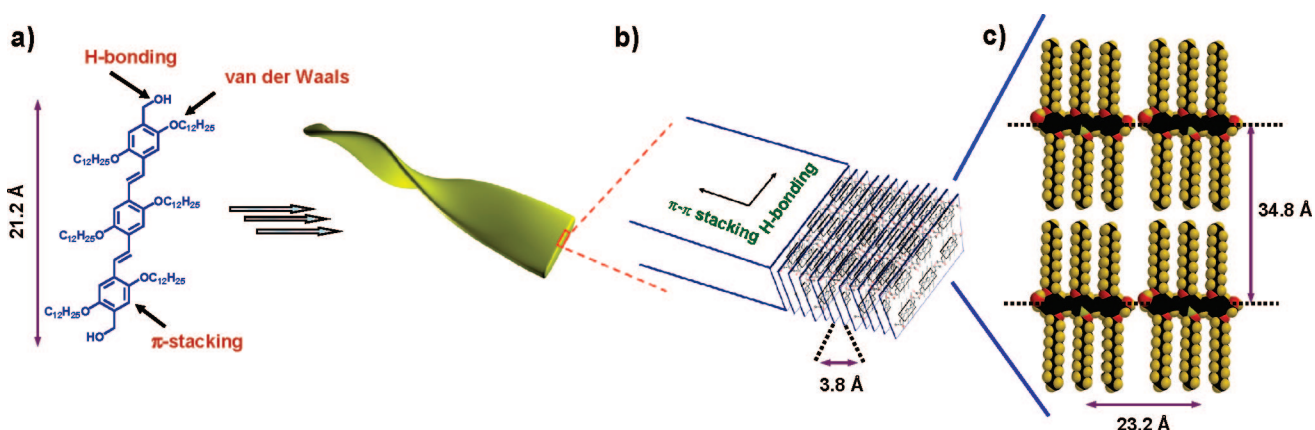
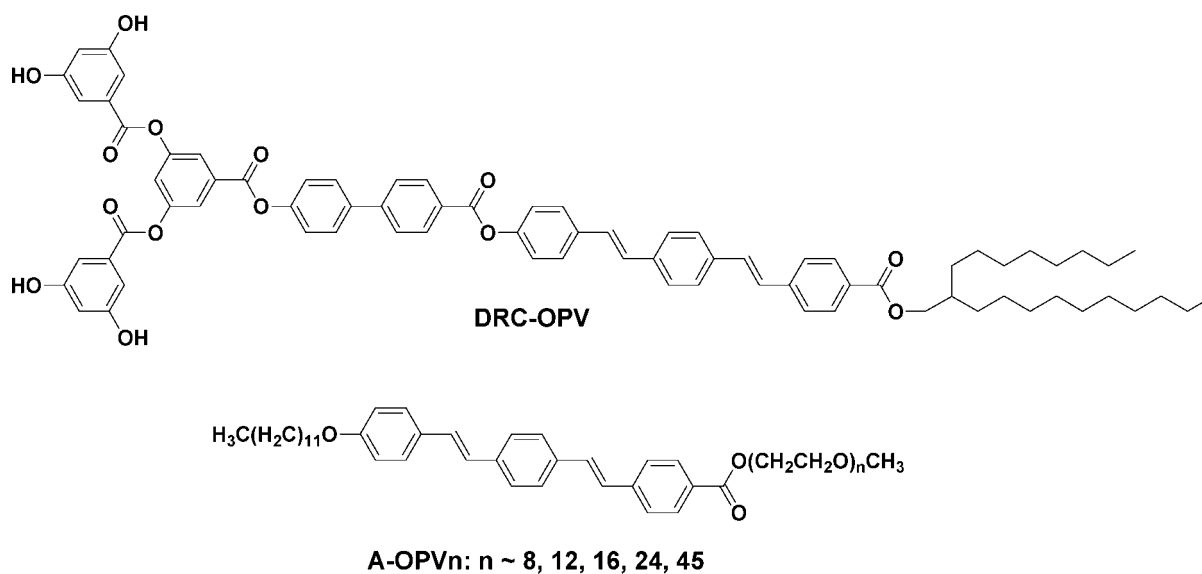


FIGURE 4. Schematic view of the lamellar packing of **OPV1** in the gel state: (a) structure of **OPV1**; (b) side view of the lamellar packing of the OPVs in a self-assembled tape; (c) top view of the molecular model of OPVs on a layer.

Chart 2



(Chart 2), which are asymmetrically end-substituted with hydrophilic poly(ethylene glycol) moieties and hydrophobic alkyl chains, self-assemble in water and polar organic solvents resulting in strongly fluorescent gels.^{17b} Detailed

temperature-dependent emission studies revealed enhanced emission in the gel state even at high concentrations of OPVs (>30 wt %), which is due to the lyotropic LC order in the gel state.

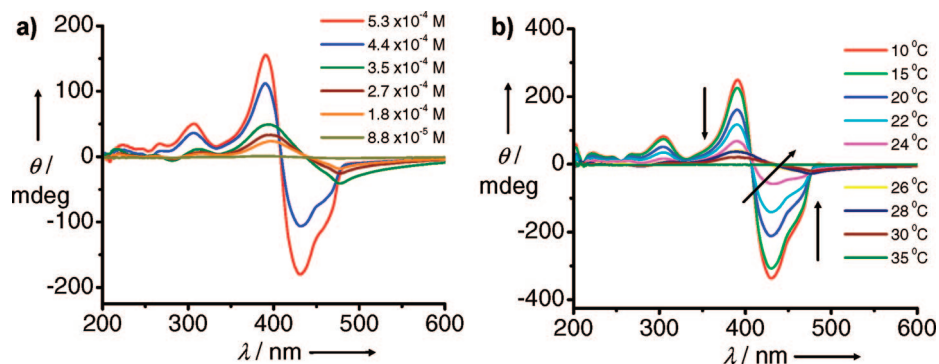


FIGURE 5. (a) Concentration- and (b) temperature-dependent CD spectra of **OPV3** (5.3×10^{-4} M) in dodecane.

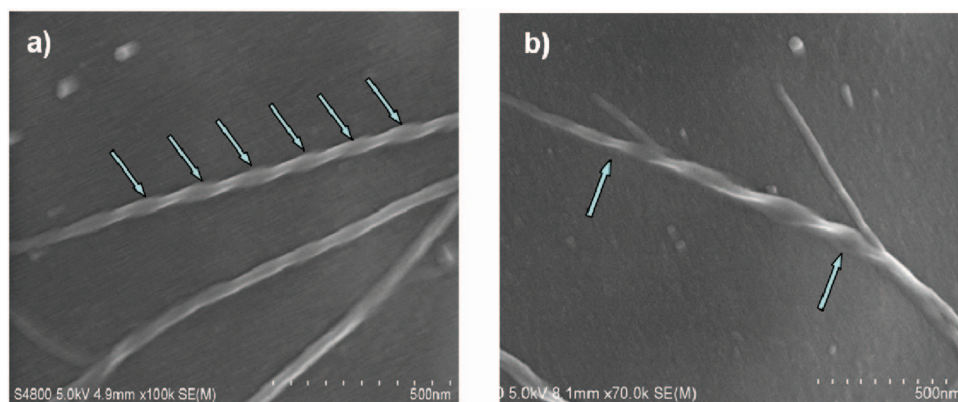


FIGURE 6. FE-SEM images of (a) left-handed helical fibers (9×10^{-5} M) and (b) coiled-coil ropes (5×10^{-4} M) of **OPV3** self-assembly in dodecane.

4. Gelation-Induced Helix Formation in Chiral OPV Self-Assembly

Self-assembly of **OPV3**, a chiral analogue of **OPV1**, resulted in yellow fluorescent gels in dodecane ($\text{CGC} = 6.4 \times 10^{-3}$ M).¹⁸ The ability to form gel is significantly reduced with introduction of the chiral side chains. However, the presence of the chiral handle in **OPV3** is expected to bias the self-assembly in a helical sense depending upon the chirality of the asymmetric carbon. CD spectra of **OPV3** in dodecane (5.3×10^{-4} M) exhibited a strong bisignate Cotton effect corresponding to the π - π^* transition. Change of the first negative Cotton signal to the second positive signal through the absorption maximum (400 nm) indicates a helical bias of the chromophore packing. Concentration- and temperature-dependent CD studies in dodecane have revealed an interesting case of the CD signal transition as shown in Figure 5a. Up to a concentration of 2.7×10^{-4} M, the CD spectrum showed a bisignate signal with a negative first Cotton effect and a zero crossing at about 440 nm, which does not correspond to the absorption maximum. On the other hand, above 3.5×10^{-4} M concentration, a sharp transition of the CD signal could be observed resulting in a bisignate Cotton effect in which the zero crossing of the sign of the signals occurs exactly at the absorption maximum. A similar transition of the CD signals and the zero crossing is observed during the heating and cooling cycles (Figure

5b). Plots of the concentration or temperature against the intensity of the CD signals revealed a two-stage transition indicating the involvement of at least two different kinds of helical aggregates.

The above observations indicate that different hierarchical levels of self-assembly are involved during the helical bias of the overall supramolecular architectures, eventually resulting in gel formation. At low concentration and under higher temperatures, the molecules self-assemble to form randomly organized helical aggregates as indicated by the weak non-bisignate CD signals. However, at higher concentrations, well-organized helical architectures are formed leading to the gelation of the solvent as indicated by the CD and morphological data. Field emission scanning electron microscope (FE-SEM) images of a dilute dodecane solution (9×10^{-5} M) of the chiral OPV revealed left-handed helical fibers of 20–50 nm in width and a few micrometers in length with uniform helical pitch of ~ 150 nm. On the other hand, FE-SEM images of the weak gel (5×10^{-4} M in dodecane) revealed coiled-coil rope-like structures with size varying from 50–100 nm in width as a result of the helical twisting of the individual fibers (Figure 6). The AFM image of a single fiber shows a double helical structure that is ~ 90 nm in width and several micrometers in length. A cartoon version of the self-organization of the chiral OPVs to a left-handed double helical rope-like structure is shown in Figure 7.

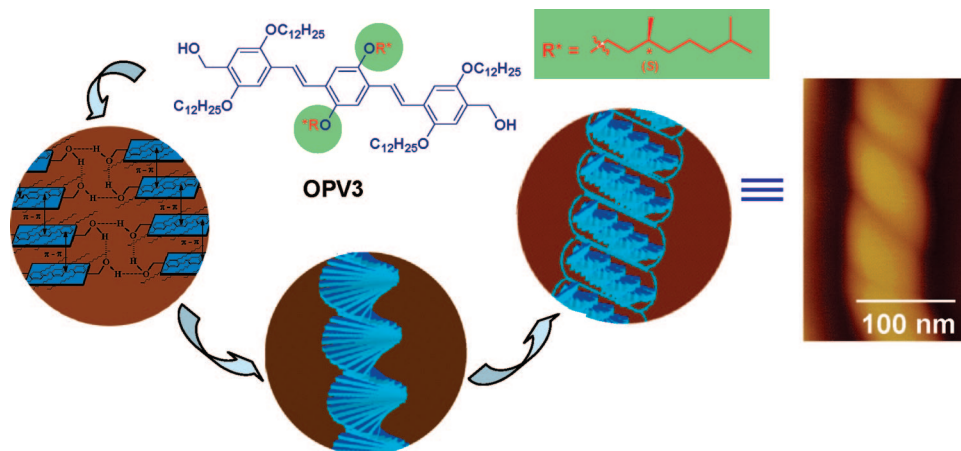


FIGURE 7. Schematic representation of the hierarchical self-assembly of **OPV3** into helical coiled-coil supramolecular structures. A magnified AFM image of the coiled-coil rope is shown on the right.

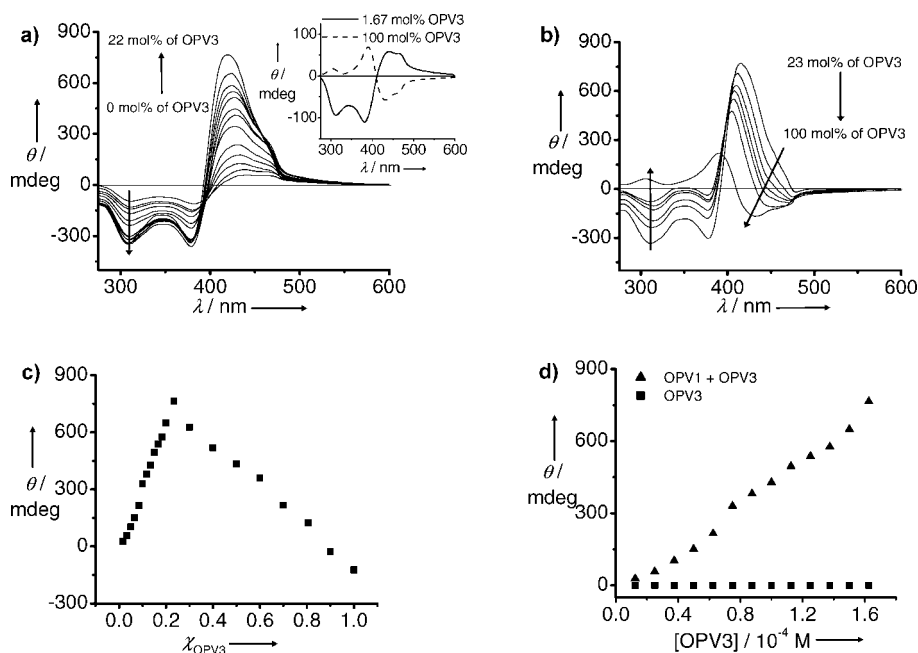


FIGURE 8. CD spectra of the coassembly of **OPV1** and **OPV3** in dodecane (7.5×10^{-4} M) at different compositions: (a) 0–22 mol % of **OPV3**; the inset shows the mirror-image relationship of the CD spectra of **OPV3** and the **OPV1–OPV3** coassembly at 1.67 mol %; (b) 23–100 mol % **OPV3**; (c) variation of CD intensity at 420 nm with increasing mole fraction (χ) of **OPV3** at a total concentration of 7.5×10^{-4} M in dodecane; (d) plots of CD intensity at 420 nm against the concentrations of **OPV3** in the homoassembly and coassembly.

5. Helicity via Chirality Induction: The “Sergeant and Soldiers” Effect

Induction and amplification of molecular chirality in dynamic hydrogen-bonded assemblies have been a subject of considerable interest. Co-assembly of achiral molecules with a small amount of chiral molecules may bias the overall organization of the molecular assemblies resulting in helical supramolecular structures with a preferred handedness. This is known as the “sergeant and soldiers” effect.¹⁹ In this approach, the helicity of the majority of the soldiers (achiral molecules) is decided by the chiral features of the minority sergeants (chiral molecules). Contrary to this general observation, we found that the gel-forming chiral **OPV3** with achiral **OPV1** results in the inversion of helicity during coassembly.²⁰ This is followed by a reversal of the original helicity when the

concentration of the chiral OPV is increased, which is clear from the CD signal changes during the coassembly of the two components at different compositions (Figure 8a,b). Under very low concentrations of **OPV3** (as low as 1.67 mol %), a near mirror image relationship could be seen to that of the original CD of **OPV3** (Figure 8a, inset). The intensity of the inverted CD signal kept on increasing until the composition of the chiral OPV reached 22 mol %. Further addition decreases the CD intensity, eventually regaining the native CD of the chiral molecule (Figure 8b). This is clear from the plot of the CD intensity against the mol fraction of **OPV3** (Figure 8c). The chirality transfer and amplification in the coassembly are clear from the comparison of the CD intensities of **OPV3** alone with those of the co-assemblies up to a concentration of 1.6×10^{-4} M (Figure 8d).

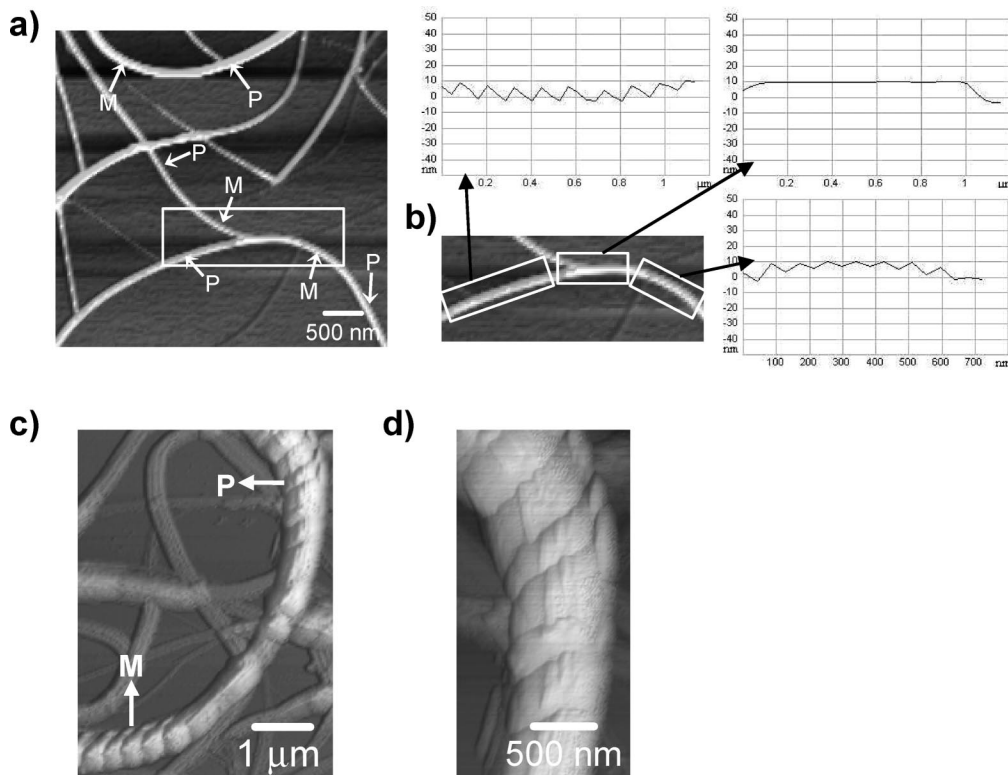


FIGURE 9. (a) AFM images of fused helices at 20 mol % **OPV3**, (b) cross-sectional analysis of *P*-, *M*-, and nonhelical zones, (c) an enlarged image of the coassembly showing the *M*- and *P*-supercoiled segments, and (d) a right-handed coiled-coil super structure formed from left-handed coiled tapes.

The AFM height image of **OPV3** homoassembly showed left-handed helical tapes, in agreement with the observed CD spectrum. However, the coassembly of **OPV1** with 9 mol % **OPV3** resulted in the formation of *P*-helical tapes along with a few oppositely biased *M*-helical tapes. The number of *M*-helices is increased as the mole percent of **OPV3** in the coassembly is increased. The AFM image of the coassembly of **OPV1** with 60 mol % **OPV3** showed the presence of mainly *M*-helices and a few *P*-helices. Surprisingly, in addition to the individual helices, longitudinally fused *M*- and *P*-helices were also observed at certain compositions. These unusual structures are formed in large numbers at around 20 mol % of **OPV3** (Figure 9a). This observation supports the formation of nonhelical stacks of **OPV1**, left-handed stacks of **OPV3**, and the right-handed coassembly of **OPV1** and **OPV3**, which at a later stage self-associates, thus resulting in fused superstructures. Since a theoretical description or modeling is rather difficult with the self-assembly of the present system, we had to rely upon the CD and the morphological data for a plausible explanation of the observed phenomena. Cross-sectional analysis of a fused assembly showed a uniform corrugated height profile for the *P*- and *M*-helical portions. The nonhelicity of the fused zone is clear from the linear profile of the AFM tip movement (Figure 9b). AFM analysis of the dried gels of the coassembly formed in dodecane (20 mol % of **OPV3**) showed micrometer-sized fused helices (Figure 9c). The enlarged image of the *P*-helical zone shows right-handed coiled-coil superstructures formed from the winding of the left-handed helical tapes in the opposite screw sense (Figure 9d).

6. Supramolecular Control over Molecular Packing

Functionalization of **OPV1** with cholesterol moieties resulted in an unprecedented control on the arrangements of chromophores in the supramolecular assembly.²¹ For example, the monocholesterol functionalized OPV (**OPV4**) showed broad absorption and emission spectra upon self-assembly, whereas the bis-cholesterol functionalized OPV (**OPV5**) exhibited structured absorption and emission (Figure 10a,b). In addition, the CD spectrum of the latter is bisignate in nature with a first negative Cotton signal followed by a positive one. Surprisingly, the CD spectrum of the former is nonbisignate and the sign of the signal is reversed (Figure 10c,d).

A striking difference between the two molecules is the disparity in the gelation behavior. Although both compounds induce the gelation of a variety of hydrocarbon solvents, the monocholesterol OPV forms stronger gel when compared with the bischolesterol derivative. This is clear from the plots of the melting transition of the gel (T_{gel}) against the OPV concentration (Figure 11a). The OPM textures of a decane gel of **OPV4** (CGC = 3.4 mM) showed the characteristic four-arm brush texture similar to **OPV1** gel, whereas **OPV5** (CGC = 7.0 mM) exhibited strongly birefringent streak-like morphology (Figure 11b,c). AFM images of **OPV4** reveal ribbon-like structures that are flat, aligned, and coiled to form superstructures (Figure 12a), whereas **OPV5** showed branched and entangled helical fibers of different sizes (Figure 12b).

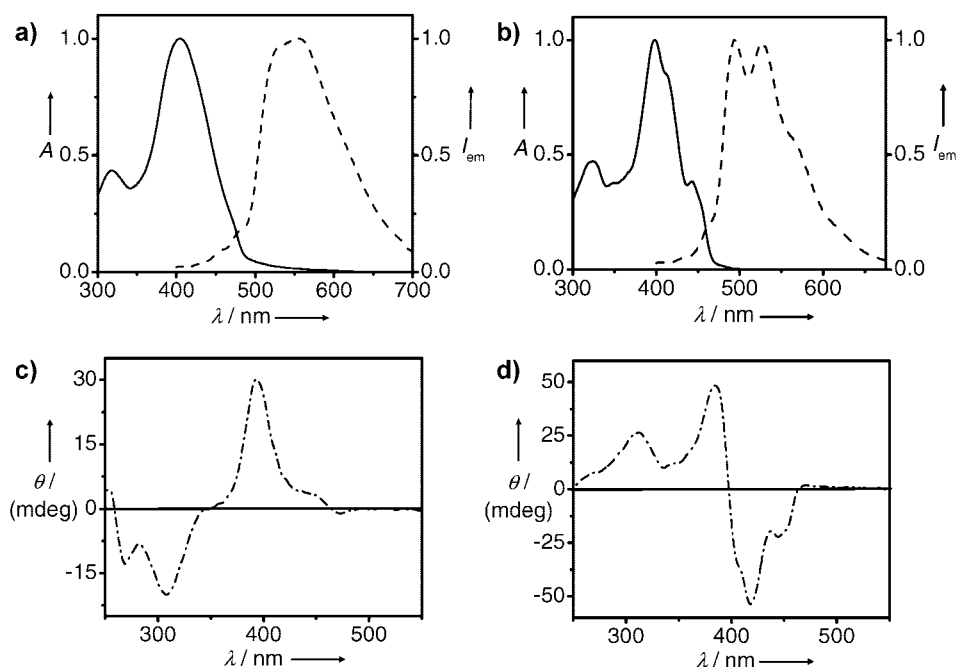
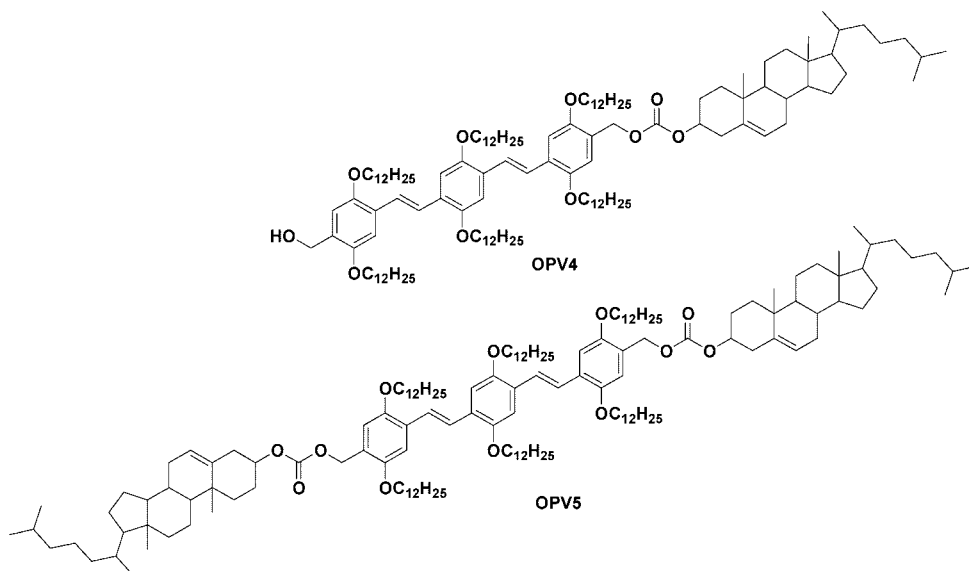


FIGURE 10. Absorption (—), and emission (---, $\lambda_{\text{ex}} = 370$ nm) spectral features of (a) **OPV4** and (b) **OPV5** and CD spectra of (c) **OPV4** and (d) **OPV5**. Concentration = 3×10^{-4} M in decane.

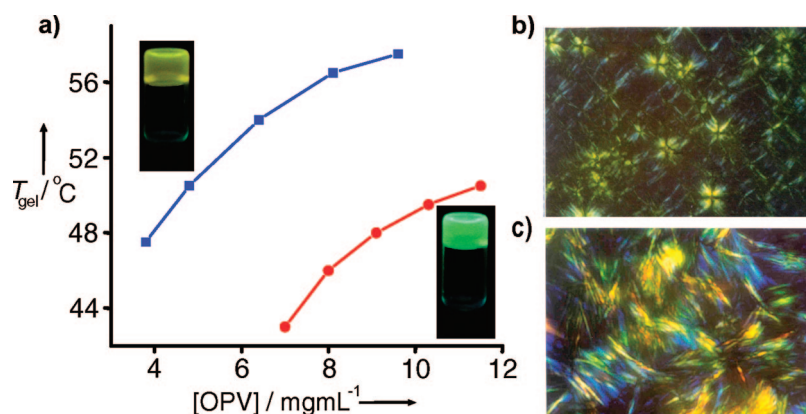


FIGURE 11. (a) Plots of T_{gel} versus concentration of **OPV4** (blue) and **OPV5** (red) in decane. Insets: Photographs of the corresponding gels under illumination with 365 nm light. OPM pictures (400 \times magnifications) of decane gels of (b) **OPV4** (3.4 mM) and (c) **OPV5** (7.0 mM).

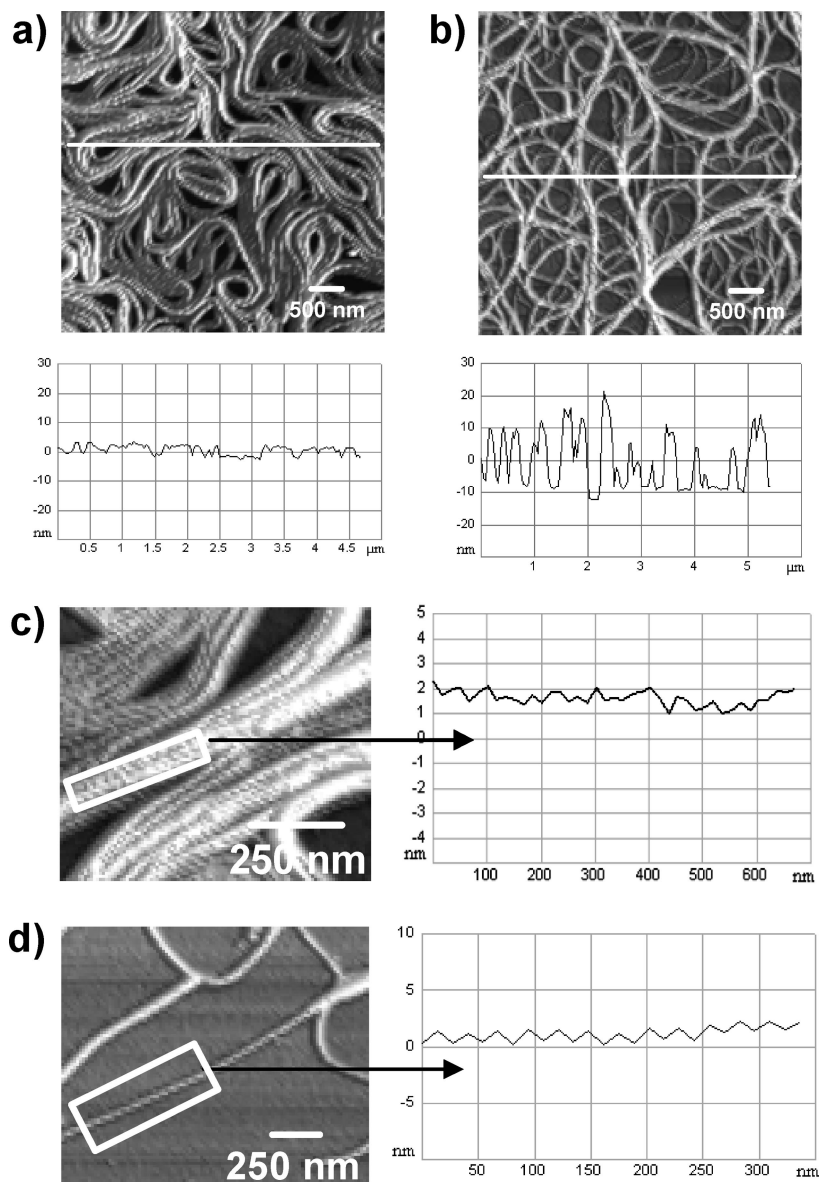


FIGURE 12. AFM images of (a) **OPV4** and (b) **OPV5** with the corresponding height profiles and zoomed region of the assembly (c) **OPV4** and (d) **OPV5** with the corresponding section analyses. Samples were prepared from solutions in decane (1×10^{-5} M) and transferred to a freshly cleaved mica sheet by drop-casting.

On the basis of the differences in the optical, chiroptical, gelation, and morphological properties, it is clear that the packing of the individual molecules in their respective supramolecular assemblies is different. The features of the absorption, emission, and CD spectra strongly support a well-organized twisted helical arrangement of the molecules in the bischolesterol derivative and a hydrogen-bond assisted tilted arrangement in the monocholesterol derivative (Figure 13). The extended supramolecular assembly of the twisted packing (pseudo-H aggregates) leads to twisted helical assemblies, whereas the tilted packing (pseudo-J aggregates) results in a coiled helical assembly.

7. Self-Assembly Induced Modulation of Optical Properties

The most important consequent of the gelation of OPVs is the self-assembly induced modulation of optical

properties.^{14–16} The absorption and emission spectra of **OPV2** in chloroform (1×10^{-5} M) at 25 °C exhibited strong bands with maxima at 407 and 463 nm, respectively. However, these bands are considerably shifted towards the long wavelength region in dodecane (1×10^{-5} M) solution at 25 °C. These shifts are strongly dependent upon the solvents, variation in temperature, and concentrations. Variable temperature UV/vis and fluorescence spectra of **OPV2** in dodecane showed a transition from the self-assembled species to the molecularly dissolved species as the temperature is increased from 15–65 °C (Figure 14). For example, the intensity of the absorption maximum at 404 nm was increased upon increasing the temperature, with concomitant decrease in the intensity of the shoulder band at 467 nm through an isosbestic point at 428 nm (Figure 14a). Similarly, in the fluorescence spectra ($\lambda_{\text{ex}} = 380$ nm), the intensity of the long wave-

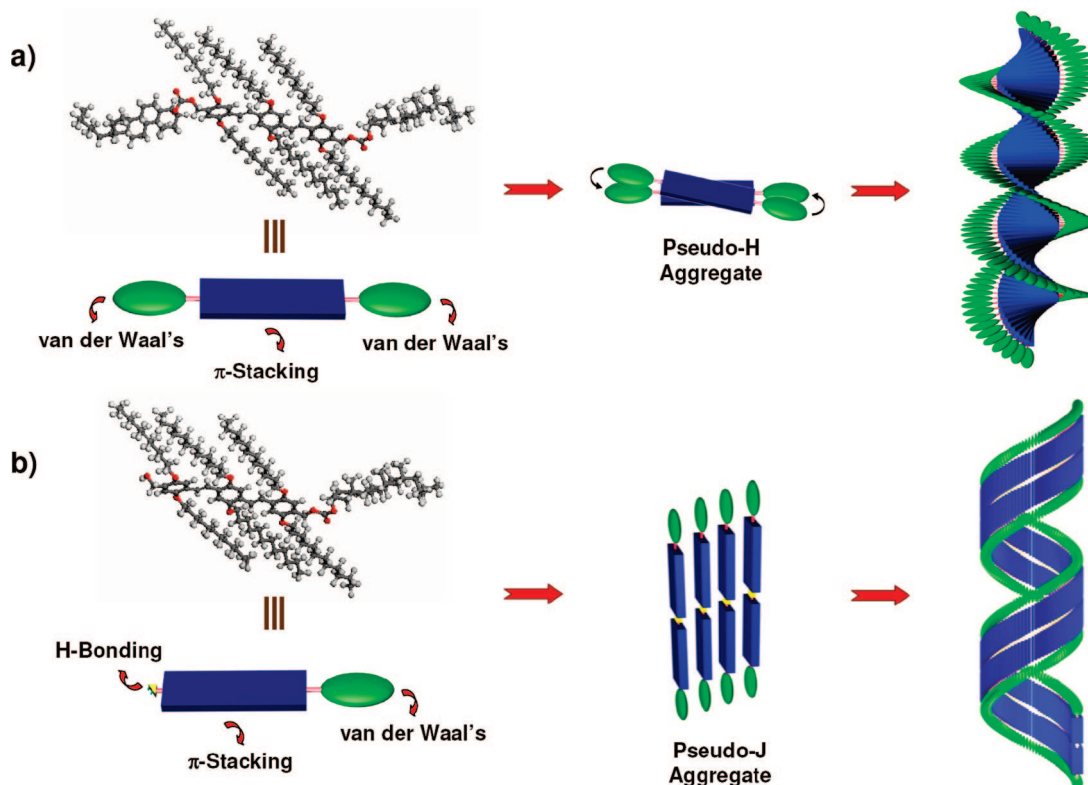


FIGURE 13. Probable mode of chromophore packing in the self-assembly of cholesterol appended OPV derivatives in decane: (a) **OPV5** and (b) **OPV4**.

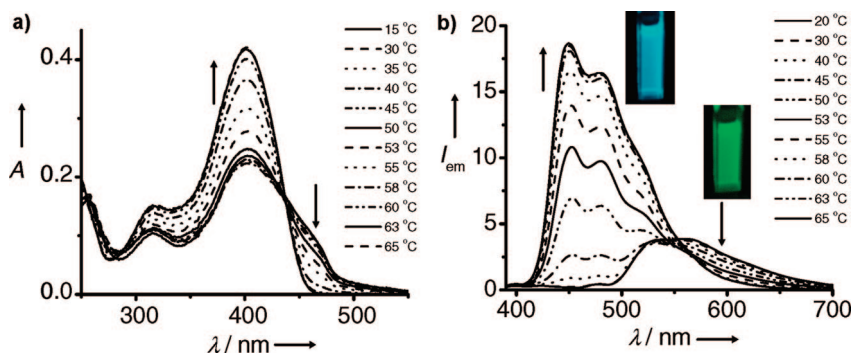


FIGURE 14. Temperature-dependent (a) absorption and (b) fluorescence spectra ($\lambda_{\text{ex}} = 380 \text{ nm}$) of **OPV2** in dodecane ($1 \times 10^{-5} \text{ M}$). Inset shows the emission colors of the molecularly dissolved (blue) and the self-assembled (green) **OPV2** molecules in dodecane.

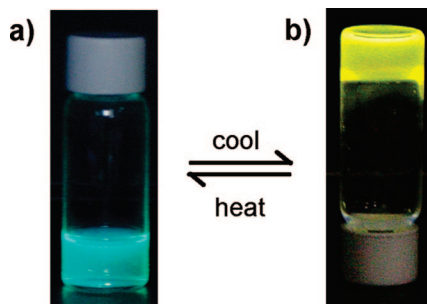


FIGURE 15. Photograph of **OPV2** in decane (CGC = 0.9 mM) under illumination at 365 nm (a) before and (b) after gelation.

length maxima at 537 and 567 nm decreases with the simultaneous increase in the intensity of the emission bands at 452 and 459 nm (Figure 14b) when the temperature is increased from 20–65 °C. These observations indicate the reversible co-existence of different self-

assembled species in dodecane at room temperature. The reversible emission color change of **OPV2** during the sol–gel transition is shown in Figure 15.

As discussed above, the appearance of the lower energy band in the absorption spectrum could be due to the

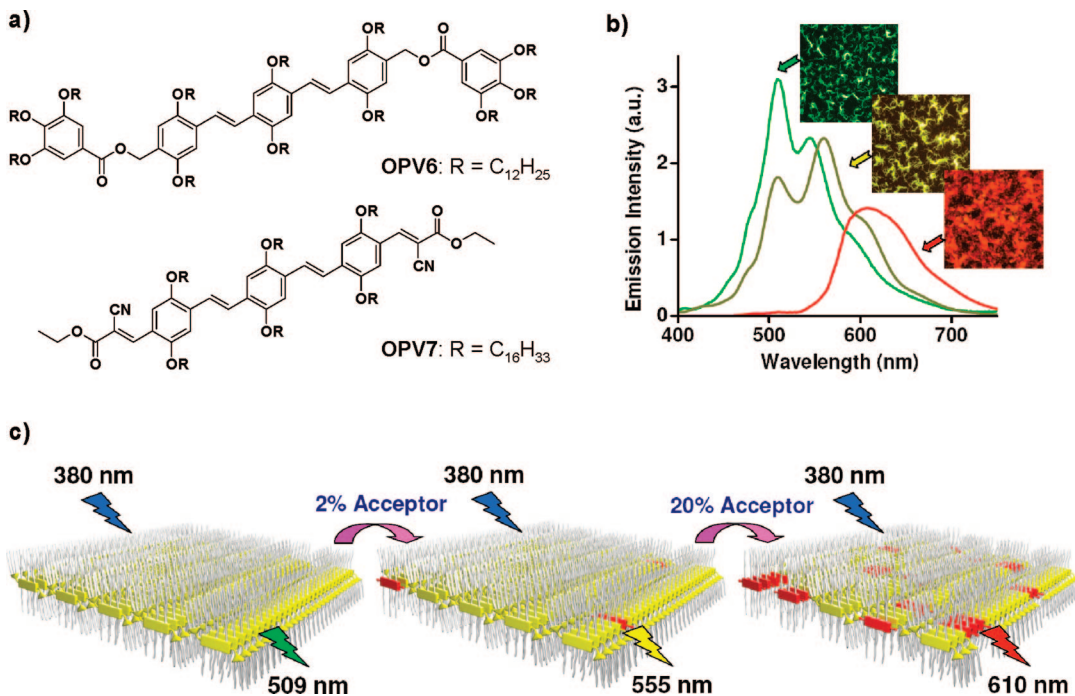


FIGURE 16. (a) Molecular structure of energy transfer donor (**OPV6**) and acceptor (**OPV7**), (b) emission spectra ($\lambda_{\text{ex}} = 380 \text{ nm}$) and corresponding fluorescence microscopy images of **OPV6** in the presence of 0, 2, and 20 mol % **OPV7**, and (c) schematic representation of the FRET process within the coassemblies of **OPV6** (yellow) and **OPV7** (red) under different donor–acceptor compositions.

formation of aggregates. The exact nature of the self-assembled aggregates as H- or J-type is difficult to establish unambiguously though the likely chance is to form J-type as indicated by the red-shifted shoulder in the absorption spectrum. However, in a few cases, H-type aggregates are proposed, which is explained on the basis of the long lifetime of the aggregates when compared with the monomers. These studies indicate that the identity of the aggregates depends upon the structure of the OPVs and the nature of the solvents. The large red shift in the emission spectra during the self-assembly of OPVs indicates the delocalization of the exciton across the self-assembled aggregates.^{12d,15,22,23} Due to efficient exciton migration within the aggregates of different HOMO–LUMO levels, emission occurs mainly from aggregates of lower energy resulting in a red shift in the wavelength. This has been experimentally proven by time-resolved emission spectroscopy (TRES) and wavelength-dependent fluorescence decay profiles. This property of OPV gels is advantageous for their use as energy donor scaffolds to suitable acceptors. This has been illustrated by entrapping rhodamine B within the self-assembled OPV donor scaffolds, which facilitate fluorescence resonance energy transfer (FRET).^{24,25} Detailed energy-transfer studies revealed that the efficiency of FRET is considerably influenced by the ability of the OPVs to form self-assembled aggregates and hence could be controlled by structural variation of donor molecules, solvent, and temperature.

The major limitation of the OPV–rhodamine B system is the incompatibility of the cationic dye with the OPV self-assembly in nonpolar solvents. In order to design a supramolecular light-harvesting system, it is necessary to have an acceptor that is compatible with the donor self-assembly, which can efficiently trap the excitation ener-

gy.^{26,27} This has been addressed using an energy transfer system comprising OPV-based donor (**OPV6**) and acceptor (**OPV7**) (Figure 16a).²⁶ The formation of co-assembly between donor and acceptor OPVs is studied by XRD and AFM techniques. XRD studies revealed a lamellar packing for **OPV6**, which gets disrupted upon intercalation of **OPV7** (20 mol %) as indicated by the broadening of the diffraction pattern as well as the shift of the π -stacking distance from 3.78 to 4.07 Å. AFM studies of **OPV6** and **OPV7** self-assemblies revealed the formation of micrometer sized extended structures with distinct morphological features. Interestingly, the co-assembly of **OPV6** with 20 mol % **OPV7** showed morphological features of both the compounds. These observations confirmed the coassembly of the acceptor within the donor scaffold.

The present supramolecular light-harvesting systems showed a wavelength-tunable FRET emission (Figure 16b).²⁶ Excitation of the decane gel of **OPV6** at 380 nm in the presence of 0–2 mol % acceptor molecules resulted in the quenching of the donor emission at 509 nm with a concomitant formation of the monomer emission of the acceptor at 555 nm (Figure 16b). This observation indicates that under this condition the acceptor molecules exist as an isolated energy trap. Upon further addition of **OPV7** (2–20 mol %), the emission was continuously red-shifted to 610 nm, which corresponds to the aggregate emission of **OPV7**. Consequently a 98% quenching of the donor emission at 509 nm was observed. Fluorescence microscopic studies of the coassembled gels of **OPV6** and **OPV7** under different composition provided visual evidence for the wavelength-tunable FRET emission. Thus efficient trapping of excitons by “isolated” or “aggregated” acceptors through control of the self-assembly and the photophysical properties of the donor–acceptor building

blocks allowed a continuous shifting of the emission color anywhere between green and red (λ_{max} 509–610 nm) in a supramolecular light-harvesting system (Figure 16c).

8. Conclusion and Outlook

Tailoring of OPVs with different noncovalently interacting functional groups allows the design of a new class of photonically and electronically active supramolecular architectures of different sizes, shapes, and functions. The use of weak nondirectional hydrogen bonding or dipolar end groups and long hydrocarbon side chains (preferably dodecyl or hexadecyl) on each phenyl ring of OPVs induce hierarchical self-assembly leading to the gelation of non-polar solvents. The packing of the molecules could be biased using chiral handles leading to helical structures of a preferred handedness. Chirality transfer and amplification is possible from chiral to achiral OPVs using the “sergeant and soldiers” approach. The emission properties of the molecules undergo remarkable modulation as a result of gelation due to efficient exciton migration between the self-assembled aggregates. This property of the OPV gels allows their use as excitation energy donor scaffolds and facilitates efficient energy transfer to encapsulated acceptors. The ultimate aim could be to design multicolor emitting π -organogels and eventually white light emitting soft materials. Moreover the insights generated could be utilized for the design of bioinspired supramolecular light-harvesting materials and photovoltaic devices. The chemistry described here is applicable as a general method to create soft self-assemblies of a variety of electronically and photonically active linear π -systems, which may have applications in organic electronic devices.^{28,29}

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