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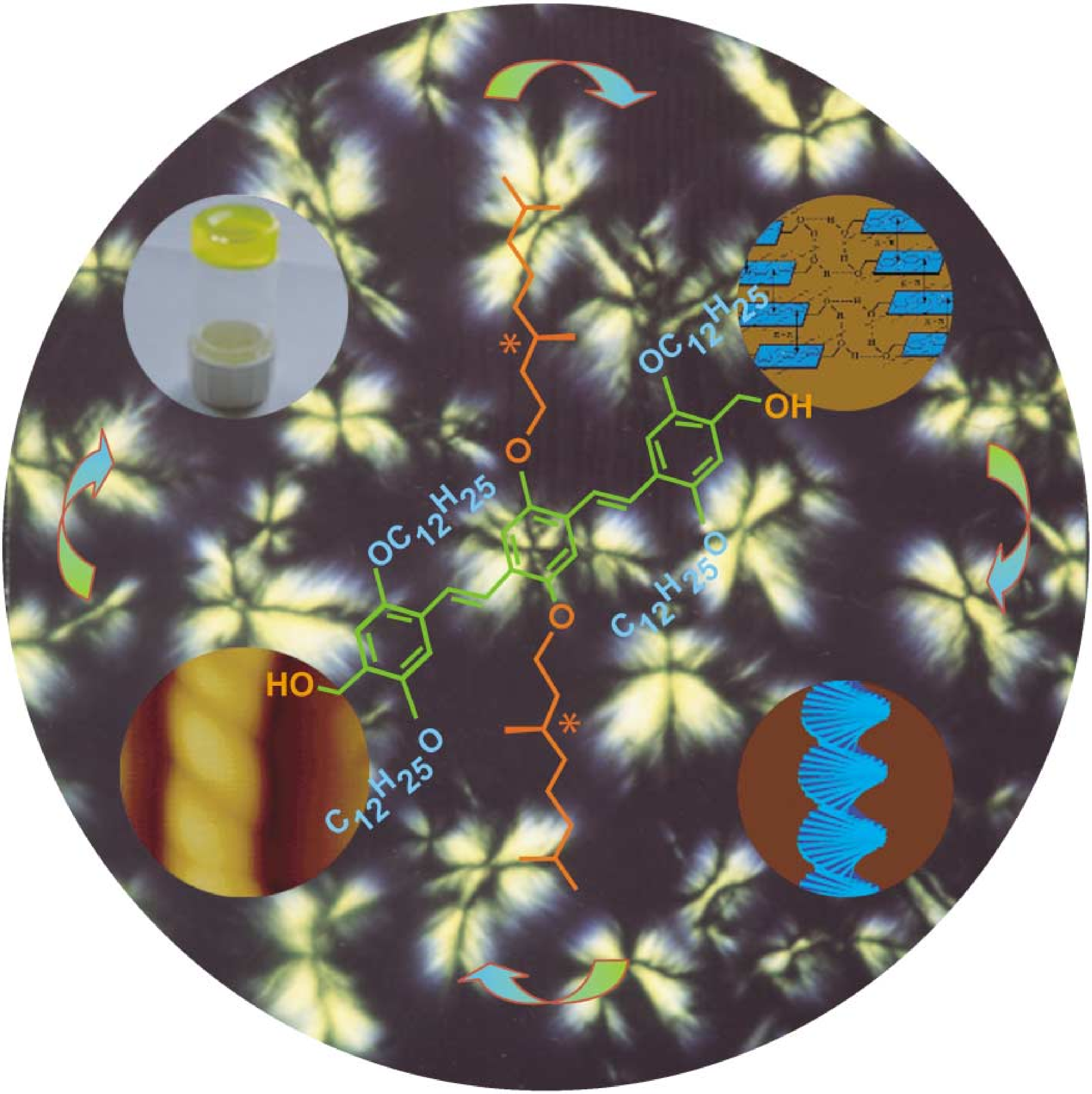

Im folgenden Beitrag beschreiben A. Ajayaghosh et al. das hierarchische Wachstum linksgängig helicaler Nanostrukturen chiraler Oligo(*p*-phenylenvinylene) (OPVs) und die damit verbundenen Änderungen im CD-Spektrum. Im Hintergrund sind die doppelbrechenden vierarmigen Faserstrukturen eines Gels aus einem fluoreszierenden chiralen OPV zu sehen.

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Helical Nanostructures

Coiled-Coil Gel Nanostructures of Oligo(*p*-phenylenevinylene)s: Gelation-Induced Helix Transition in a Higher-Order Supramolecular Self-Assembly of a Rigid π-Conjugated System**

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Dedicated to Professor C. N. R. Rao
on the occasion of his 70th birthday

The intriguing phenomenon of the supramolecular assembly of biological molecules into helical nanostructures, such as the DNA double helix, the collagen triple helix, and the α coiled-coil of myosin, has always fascinated scientists. With the help of noncovalent forces, such as hydrogen bonding, π stacking, and van der Waals interactions, chemists have been able to design a variety of aesthetically appealing helical supramolecular assemblies.[1,2] In this context, the control of the supramolecular organization of π-conjugated systems into helices of nanoscopic dimensions is of the utmost importance, as the resulting structures could find application in the emerging area of supramolecular electronics because of their unique optical and electronic properties.[3]

The spontaneous self-assembly of organic molecules to form gels is a method for creating nanoscopic and mesoscopic structures.[4] In particular, the gelation of chiral molecules to form helical morphologies has received considerable attention.[5–8] Recently, through a serendipitous observation, we showed the gelation of functionalized oligo(*p*-phenylenevinylene)s (OPVs) and their application in light harvesting.[9] Herein we report an interesting case of a gelation-assisted helix transition during the hierarchical self-assembly of a rigid π-conjugated system to form coiled-coil helical ropes. The gelation-induced helix formation in the present case is promoted by a pair of remote chiral handles and assisted by weak hydrogen-bonding motifs and long hydrocarbon chains, thus allowing the molecules sufficient freedom to undergo self-assembly.

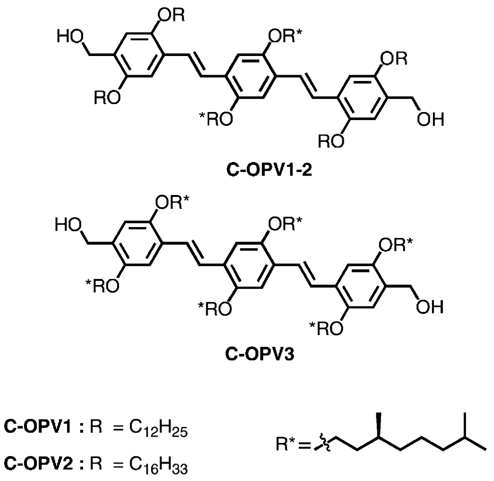

Figure 1. Structures of chiral OPV derivatives.

Three different OPVs with remote chiral handles, **C-OPV1**, **C-OPV2**, and **C-OPV3** (Figure 1), were prepared by a reported procedure and fully characterized.[9,10] **C-OPV2**, with hexadecyl side chains, was most able to form stable aggregates in solution (as evident from optical studies).[10] **C-OPV1**, with dodecyl side chains, was found to be a better gelator than **C-OPV2**, and formed a yellow fluorescent gel in nonpolar solvents, such as dodecane, heptane, and cyclohexane (critical gelator concentration in dodecane: 6.4×10^{-3} M). However, **C-OPV3**, which is substituted with six chiral side chains, failed to form a gel in any of the solvents. Optical polarizing microscopy (OPM) revealed that **C-OPV1** forms birefringent fibrous four-arm brushes when cooled from the isotropic dodecane solution, whereas neat **C-OPV1** and **C-OPV2** crystallize into spherulite textures when cooled from the isotropic melt.[10] Field emission scanning electron microscope (FESEM) images of **C-OPV1** from a dilute solution in dodecane (9×10^{-5} 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 150 nm (Figure 2a).[11] However, the FESEM image of **C-OPV1** (partially gelled) from a more concentrated solution in dodecane (5×10^{-4} M) showed the formation of left-handed coiled-coil ropelike structures of 50–100 nm in diameter with an average pitch of 330 nm. These ropelike structures are formed by the twisting together of several helical fibers (Figure 2b). AFM analysis of the **C-OPV1** gel from dodecane (6.5×10^{-3} M) clearly showed the formation of entangled left-handed-helical coiled-coil fibers of 50–100 nm in diameter (Figure 3b). 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 3c). These observations point towards a hierarchical self-organization of

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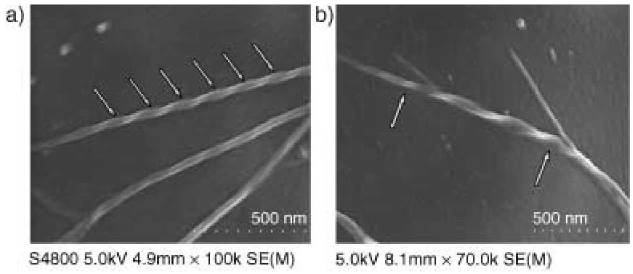

Figure 2. Helical morphology of **C-OPV1** self-assembly from a solution in dodecane: a) FESEM image of left-handed-helical fibers (9×10^{-5} M) and b) FESEM image showing the formation of a coiled-coil rope (5×10^{-4} M).

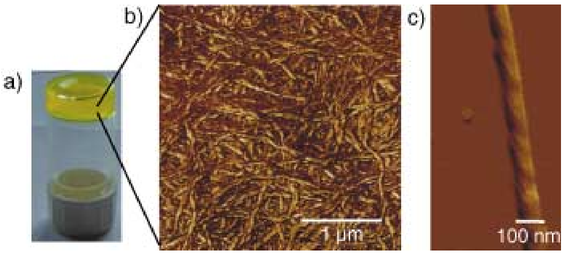

Figure 3. Physical appearance and AFM images of the **C-OPV1** gel from a solution in dodecane (6×10^{-3} M): a) photograph of the gel; b) dense network of helical fibers; c) single left-handed coiled-coil rope.

the **C-OPV1** into coiled-coil aggregates of nanometer dimensions.

UV/Vis absorption, fluorescence emission, and circular dichroism (CD) experiments were performed on **C-OPV1** to obtain better insight into the self-assembly of chiral OPVs. The absorption and emission properties of **C-OPV1** in chloroform are typical of molecularly dissolved OPVs.[10] The absence of a CD signal in chloroform suggests that **C-OPV1** is not aggregated in chloroform (Figure 4a, inset). However, the CD spectrum of **C-OPV1** in dodecane (5.3×10^{-4} M) showed a vibronic shoulder at 470 nm and 25 °C. The fluorescence spectrum of **C-OPV1** in dodecane (5.3×10^{-4} M, 1-mm cuvette, with front-face geometry to minimize the inner filter effect) at 25 °C showed peaks at 450 nm and 480 nm, and a shoulder at 525 nm. Upon cooling, the intensity of these bands decreased and their relative ratios changed with the formation of an additional red-shifted peak at 570 nm. These changes are characteristic of the formation of aggregates of OPVs as a result of cooperative hydrogen-bonding and π-stacking interactions. CD experiments in dodecane (**C-OPV1**: 5.3×10^{-4} M) revealed a strong bisignated Cotton effect at the position of the π–π* band, with a zero crossing close to the absorption maximum (400 nm), thus indicating the transfer of chiral information to the self-assembled chromophores in a helical sense (Figure 4a). The exciton-coupled bisignated negative couplet in the CD spectra is a signature of the left-handed-helical assembly of OPVs. Thus, these results are in agreement with those of the FESEM and AFM analyses, in which left-handed helicity was also found.

Concentration- and temperature-dependent CD measurements of **C-OPV1** in dodecane have provided insight into the hierarchical helical self-assembly and helix transition during the gelation of the molecules. The changes in the CD spectrum in the concentration range 8.8×10^{-5} M–5.3×10^{-4} M at 20 °C are shown in Figure 4a ($g_{381\text{nm}}=6.8\times10^{-4}$–$5.2\times10^{-3}$). Up to a concentration of 2.7×10^{-4} M, the CD spectrum of C-

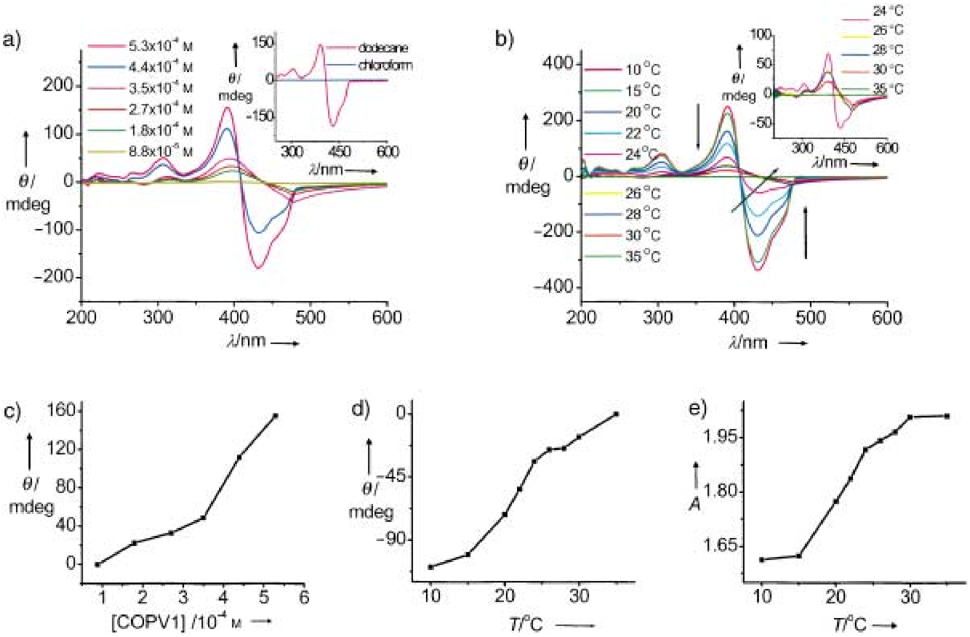

Figure 4. Concentration and temperature dependence of the CD spectrum of **C-OPV1** in dodecane: CD spectra of **C-OPV1** at different a) concentrations ($T=293$ K, $l=1$ mm) and b) temperatures ($c=5.3\times10^{-4}$ M, $l=1$ mm). c) Concentration-dependent transition of the intensity of the CD signal of **C-OPV1** monitored at 391 nm; d) melting-transition plot of CD intensity at 470 nm; e) melting-transition curve of the absorbance of **C-OPV1** at 405 nm. The inset in (a) shows the CD spectra of **C-OPV1** in dodecane and chloroform ($c=5.3\times10^{-4}$ M, $l=1$ mm); the inset in (b) shows the same CD spectra as in the main plot at different temperatures, but just within the range 24–35 °C.

OPV1 in dodecane showed a bisignated signal with a negative first Cotton effect followed by a second positive Cotton effect, with a zero crossing at about 440 nm; this value does not correspond to the absorption maximum of the chromophore. Surprisingly, above a concentration of 3.5×10^{-4} M, a sharp transition was observed in the CD spectrum from one bisignated signal to a different bisignated signal.[12] The zero crossing of the new CD signal now occurred exactly at the absorption maximum (400 nm), which is indicative of a true exciton-coupled spectrum. A study of temperature dependence at a concentration of 5.3×10^{-4} M in dodecane revealed a decrease in the intensity of the CD signal up to a temperature of 24 °C, but the zero-crossing point remained the same (Figure 4b). 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 observed (Figure 4b, inset). The intensity of the signal continued to decrease until it reached the baseline at 35 °C. The plots in Figure 4c–e clearly show two transitions during the concentration- and temperature-dependent changes in circular dichroism and UV/Vis absorption. The occurrence of a two-stage transition was further supported by temperature-dependent fluorescence measurements, which showed a higher melting transition of 27 °C for a sample that was 40 times more dilute (1.24×10^{-5} M).[10] The complementary nature of the concentration- and temperature-dependent transitions of the CD signals indicates that a similar pathway via same chiral intermediate is involved during the formation and breaking down of the supramolecular assembly.

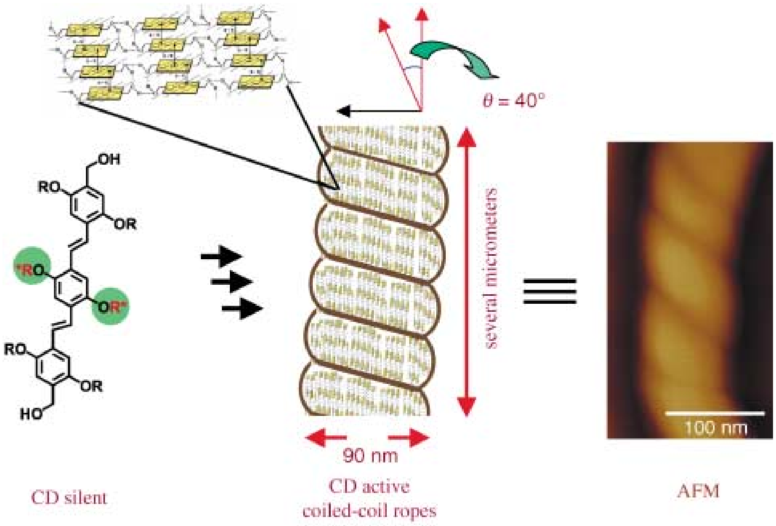

Figure 5. Schematic representation of the hierarchical self-assembly of **C-OPV1** into helical coiled-coil gel nanostructures. A magnified AFM image of the coiled-coil rope is shown on the right.

The characteristic transition described above for the CD, UV/Vis absorption, and fluorescence signals of **C-OPV1** is a unique observation associated with the gelation of chiral OPVs. During the gelation of **C-OPV1**, 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. The helical packing of **C-OPV1** to form the left-handed coiled-coil rope, in which it is postulated that hydrogen-bonding and π-stacking interactions play an important role, is represented with the observed AFM image in Figure 5.[13] When the results of the CD and microscopic analyses are considered together, it is evident that the hierarchical growth of the coiled-coil structures evolves 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.

In conclusion, we have shown the hierarchical helical growth of coiled-coil nanostructures during the gelation of rigid π-conjugated systems. Although a few reports on helical self-assemblies of OPVs have appeared,[14] to the best of our knowledge this is the first example of a gelation-induced CD-signal change. The unusual transition observed in the CD signal is indicative of a helix transition during the hierarchical evolution of ropelike nanostructures via intermediate chiral assemblies and is reminiscent of the multistate folding and unfolding of the helical assemblies of biological macromolecules.

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Keywords: helical structures · nanostructures · organogels self-assembly · supramolecular chemistry

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[10] See Supporting Information.

[11] Exposure of the **C-OPV1** self-assembly to high-magnification FESEM conditions causes deformation of the helical fibers. The disappearance of the helicity of some of the fibers in Figure 2 a is a result of this problem. However, a low-magnification image of the densely populated fibers showed uniform left-handed helicity in all fibers.

[12] The minimum concentration required for gelation in a 1-mm cuvette is much lower than that in a 1-cm cuvette or vial. Thus, the CD spectra recorded at concentrations above 3.5×10^{-4} M at 293 K correspond to the gel state. The contribution from linear dichroism (LD) in the gel state is negligibly small, as turning of the sample had no effect on the type of Cotton effect observed.

[13] The postulated chromophore arrangement in Figure 5 is based on a fluorescence polarization experiment on an OPV gel, which showed packing of the OPV units perpendicular to the fiber axis.

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