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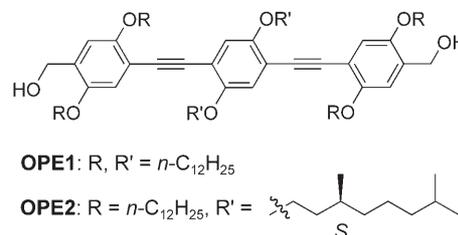
From Vesicles to Helical Nanotubes: A Sergeant-and-Soldiers Effect in the Self-Assembly of Oligo(*p*-phenyleneethynylene)s**

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The past few years have witnessed significant progress toward the design of supramolecular architectures of nano- to micrometer dimensions with intriguing properties.^[1,2] Of particular interest to chemists is the self-assembly of rigid π -conjugated molecules with controlled size and shape, as active components of organic electronic devices.^[3,4] In this context, self-assembly of oligo(*p*-phenyleneethynylene)s (OPEs) has received considerable attention.^[5] Control of the morphology of self-assembled structures requires rational design of molecular components.^[6] For example, spherical to tubular or cylindrical assemblies are obtained by structural variation of the self-assembling units,^[7] whereas nonhelical to helical transformation can be achieved by attaching chiral handles^[8–11] or by the “sergeant-and-soldiers” coassembly approach.^[12–14] However, transitions of linear π -conjugated molecules from vesicles to helical tubules or vice versa are rare.^[15] Herein we reveal a spectacular chirality-amplification effect and an unprecedented transition from vesicles to helical tubules during the sergeant-and-soldiers coassembly of chiral and achiral OPEs.

We chose **OPE1** and its chiral analogue **OPE2** for our studies. These compounds were synthesized by palladium-catalyzed Sonogashira–Hagihara cross-coupling reactions^[16] and characterized by ¹H NMR, ¹³C NMR, and FAB-MS techniques.^[17] Compound **OPE1** self-assembles in nonpolar hydrocarbon solvents to form nanoparticles, microspheres, giant superstructures, and blue-light-emitting organogels.^[18] Surprisingly, **OPE2** failed to form aggregates in nonpolar hydrocarbon solvents, as evident from absorption, emission,

and CD spectral features. This behavior of **OPE2** is different from that of an analogous chiral oligo(*p*-phenylenevinylene), OPV, for which formation of helical structures in decane leads to gelation.^[19] These observations reveal the differences in the self-organization propensities of OPEs and OPVs, which reiterate that a subtle difference in π interaction is sufficient to induce a large difference in the morphological features.



The UV/Vis absorption spectrum of **OPE1** in decane (1×10^{-5} M) at 25 °C exhibited a maximum at 384 nm with a shoulder at 420 nm. At this concentration, a decrease in the intensity of the π – π^* transition band with first-order kinetics ($k = 47.41 \text{ min}^{-1}$) is observed over 6 h (Figure 1a). Interestingly, addition of **OPE2** (5–30 mol %) to this solution at a total concentration of 1×10^{-5} M resulted in reversal of the absorption, which indicates probable destruction of the initial **OPE1** aggregates to form coassembled or molecularly dissolved species. On the other hand, addition of **OPE2** (5–30 mol %) to a fresh solution of **OPE1** in decane (without aging) at a total concentration of 0.7×10^{-5} M led to a decrease in the intensity of the aggregate band at 420 nm.^[17] After heating to 80 °C and cooling to room temperature, this solution did not show any considerable change in the absorption spectrum, that is, the time-dependent process is arrested in this case (Figure 1b).

Circular dichroism (CD) measurements on **OPE1** and **OPE2** in decane (1×10^{-5} M) did not show any detectable

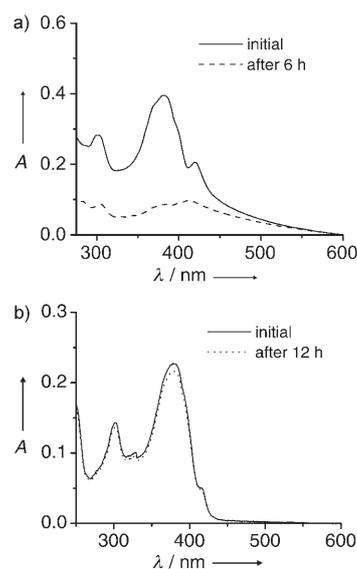


Figure 1. a) Time-dependent absorption changes of a) **OPE1** (1×10^{-5} M) and b) **OPE1** with 30 mol % of **OPE2** (0.7×10^{-5} M) in decane at 298 K.

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Cotton effect. Though this is expected for **OPE1**, the CD silence of **OPE2** was rather surprising and indicates that it is not able to form aggregates in decane. However, addition of **OPE2** (5–30 mol%) to a solution of **OPE1** (1×10^{-5} M) in decane, followed by heating and cooling, resulted in a positive Cotton signal and two negative signals (Figure 2 a). Since both individual components are CD-silent, the observed CD of the coassembly is due to the induced chirality from **OPE2** in a

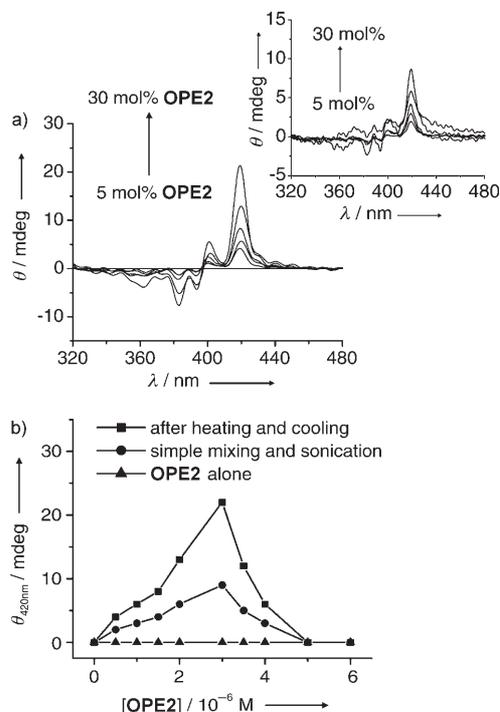


Figure 2. a) CD spectra of **OPE1** with different fractions of **OPE2** recorded after heating and cooling. The inset shows the corresponding spectra of sonicated solutions without heating and cooling. b) Plots of CD intensity at 420 nm against concentration of **OPE2**. All experiments were carried out in decane (1×10^{-5} M, $l = 10$ mm) at 298 K.

helical sense. Interestingly, simple mixing of the two components in decane followed by sonication resulted in weak CD signals (Figure 2a, inset), that is, heating and cooling are crucial to the formation of helical coassemblies. The intensity of the induced CD (ICD) signals increases with increasing fraction of **OPE2** up to 30 mol%, then decreases, and finally disappears at 50 mol%, which is clear from the plots of the ICD intensity at 420 nm against the concentration of **OPE2** (Figure 2b). The increase in the ICD intensity reveals that up to 30 mol% **OPE2** is able to induce chirality in **OPE1**. Above this concentration, coassembly is destabilized, as indicated by the decreased ICD intensity, which finally disappears at higher concentrations of **OPE2** (50 mol%).

Dynamic light scattering (DLS) experiments on the aged solution of **OPE1** in decane (1×10^{-6} M) revealed the formation of particles with sizes in the range of 50–180 nm with peak intensity at 93 nm and a polydispersity of 0.24.^[17] Tapping-mode atomic force microscopy (AFM) images of **OPE1** from decane (1×10^{-6} M) on a freshly cleaved mica surface showed characteristics of flattened spherical mor-

phology (Figure 3a).^[20] The histogram shows Lorentzian distribution ($R^2 = 0.9103$) with an average circular width of 94 nm (full width at half-maximum 34 nm) and height of 4 ± 1 nm after accounting for the tip-broadening factor.^[21] The

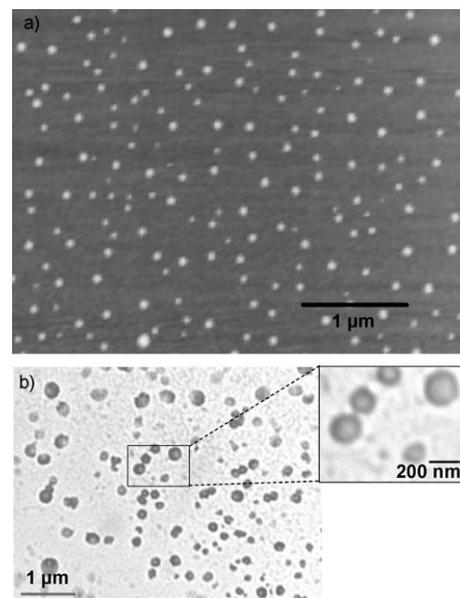


Figure 3. a) Tapping-mode AFM height (z scale = 20 nm) and b) TEM images (unstained) of **OPE1** from decane (1×10^{-6} M) under ambient conditions. The inset shows the zoomed portion of the marked area.

AFM analysis of **OPE1** from chloroform on a mica surface revealed significantly different morphology when compared to that from decane, that is, the solvent has some role in the formation of spherical aggregates.^[17] The transmission electron microscopy (TEM) images of an evaporated decane solution of **OPE1** on carbon-coated grid revealed that the particles are vesicular with contrast difference between the inner part and the periphery (Figure 3b).

Interestingly, **OPE2** does not show any specific morphology from decane.^[17] This observation is in agreement with the absorption and CD studies, which indicated that **OPE2** does not aggregate in decane. However, AFM pictures of the coassemblies of **OPE2** with **OPE1** revealed the formation of both nanoparticles and helical structures at 8 mol% of the former (Figure 4a). The width of the particles obtained under these condition varies in the range of 30–60 nm with average heights of 3–16 nm. However, at 25 mol% of **OPE2** almost all the spherical assemblies were transformed into helical structures (Figure 4b). Section analysis of the helical fibers revealed a width of 90 nm for the smallest fiber after accounting for the tip-broadening effect,^[21] with almost uniform pitch of 140 nm. The height of the fibers varies between 6 and 25 nm, and this indicates considerable flattening of the fibers. However, TEM analysis of the coassembly revealed that the helical fibers are tubular in nature with diameters of 55–90 nm (Figure 4c). The width of the inner hollow tubular space is almost uniform in all cases. Above 50 mol% of **OPE2**, an ill-defined morphology could be seen, in agreement with the complete disappearance of the CD

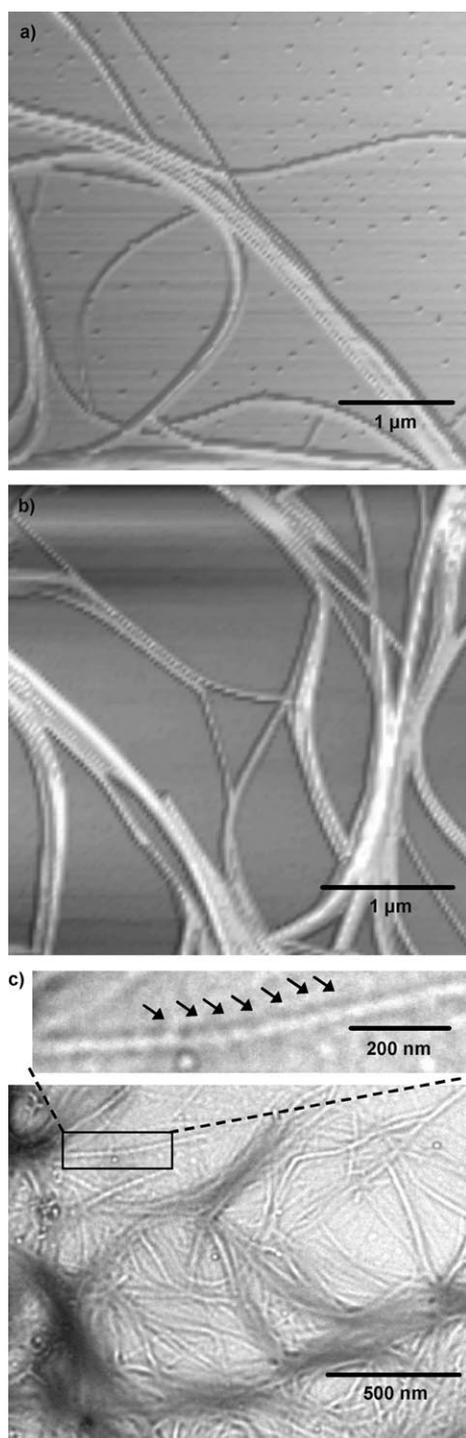


Figure 4. Tapping-mode AFM height images of the coassembly of **OPE1** with different concentrations of **OPE2** from decane (1×10^{-5} M). a) 8 mol% and b) 25 mol% under ambient conditions on freshly cleaved mica surface (z scale = 50 nm). c) TEM images (unstained) of 25 mol% **OPE2** with **OPE1** under ambient conditions. The inset is a zoomed image of the marked area showing the helical-tubular nature of the coassembly.

signal in Figure 2b.^[17] Heating and cooling of the two components resulted in significant morphological differences in the AFM images when compared to those of samples prepared by simple mixing and sonication.^[17]

A schematic representation of the coassembly processes of **OPE1** and **OPE2** is shown in Figure 5. In decane, **OPE1** forms vesicular structures, as indicated by DLS, AFM, and TEM studies. However, the coassembly of **OPE2** with **OPE1**

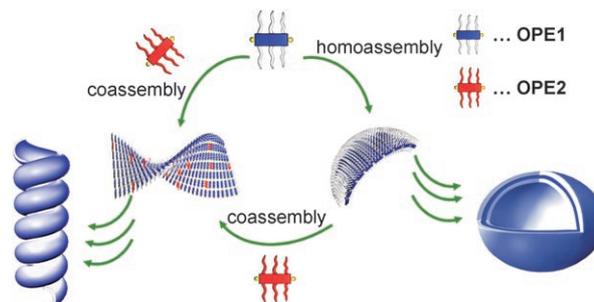


Figure 5. Self-assembly of vesicles and subsequent transformation into helical tubes in decane.

facilitates transcription of the molecular chirality of the former in a helical sense and results in transition from vesicular assemblies to helical tubular structures, as confirmed by CD, AFM, and TEM data. In summary, coassembly of **OPE1** with the chiral analogue **OPE2** retards the formation of vesicular assemblies and facilitates the evolution of helical structures. Though **OPE2** alone is unable to self-assemble, when mixed with **OPE1**, the former participates in coassembly and thereby transfers chiral information to the latter. To the best of our knowledge, this is the first report of the sergeant-and-soldiers approach to chirality-induced transformation from vesicles to helical tubules.

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