Communication

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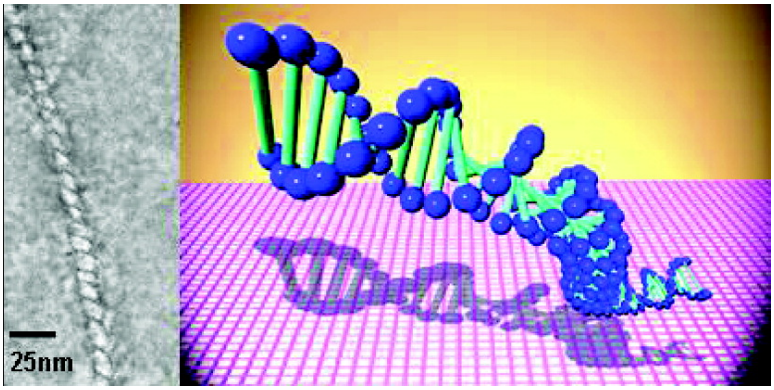

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Helical Nanofibers from Aqueous Self-Assembly of an Oligo(*p*-phenylene)-Based Molecular Dumbbell

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The self-assembly of incompatible molecular components leading to microphase separation comprises a powerful approach toward the fabrication of complex nanoarchitectures and plays an essential role in living systems, for example, in protein folding and the formation of biological membranes.[1] Extensive efforts thus have been directed toward bioinspired supramolecular systems for exploration of novel properties and functions that are difficult without specific assembly of molecular components.[2] Self-assembling molecules based on *p*-conjugated rods are receiving increased attention as building blocks for electrooptically active supramolecular structures, such as discrete bundles, ribbons, and vesicles.[3] One can envision that incorporation of a conjugated rod into an amphiphilic dumbbell-shaped molecular architecture, by grafting bulky flexible dendrons to its both ends, extends the supramolecular organization capabilities of conjugated aromatic rods. The attachment of bulky dendrons into both ends of a rod would frustrate a parallel arrangement of the rod segments commonly observed for linear rod−coil molecules,[4] in order to minimize a steric repulsion between bulky dendritic segments. Instead, the rod segments should be strongly driven to aggregate in one dimension with a regular helical arrangement through microphase separation between incompatible molecular components and $\pi-\pi$ stacking interactions between the aromatic units.

We present here the formation of helical nanofibers from the self-assembly of a dumbbell-shaped molecule based on a conjugated rod segment in aqueous solution (Figure 1). The dumbbell-shaped molecule that forms this aggregate consists of a dodeca-*p*-phenylene rod and aliphatic polyether dendrons that are covalently linked at both ends of the rod segment. The synthesis of the dumbbell-shaped molecule started with the preparation of an aromatic scaffold containing three oligoether dendrons according to the procedures described previously.[5] The final dumbbell-shaped molecule was synthesized by palladium-catalyzed homocoupling reaction of the precursor molecules. The resulting molecule was characterized by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and MALDI-TOF mass spectroscopy and shown to be in full agreement with the structures presented.

The molecular dumbbell (**1**), when dissolved in a selective solvent for one of the blocks, can self-assemble into an aggregate structure because of its amphiphilic characteristics.[6] Aggregation behavior of the molecule was subsequently studied in aqueous solution by using UV−vis, fluorescence, and circular dichroism (CD) spectra (Figure 2). The absorption spectrum of **1** in aqueous solution (0.5 wt %) exhibits a broad transition with a maximum at 351 nm, resulting from the conjugated rod block. The fluorescence spectrum of **1** in chloroform solution (0.32 wt %) exhibits a strong emission maximum at 419 nm. However, the emission maximum in aqueous solution shows to be red-shifted with respect to that observed in chloroform solution, and the fluorescence is significantly quenched, indicative of aggregation of the conjugated rod segments (Figure 2a).[7] CD spectra of the aqueous solutions of **1**

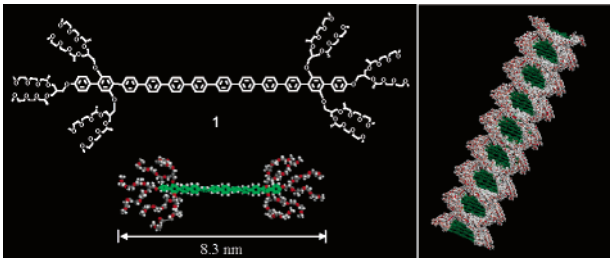

Figure 1. Molecular structure of **1** and schematic representation of a helical nanofiber.

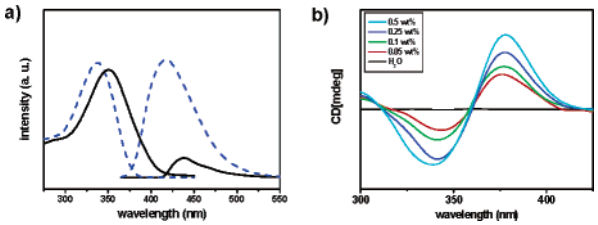

Figure 2. (a) Absorption (left) and emission (right) spectra of **1** in chloroform solution (0.32 wt %, blue dashed line). Absorption (left) and emission (right) spectra of **1** in aqueous solution (0.5 wt %, black solid line). (b) CD spectra of **1** at 25 °C.

above certain concentrations (from 0.05 wt %) show first a negative Cotton effect followed by a positive Cotton effect at higher wavelength with the CD signal passing through zero near the absorption maximum of the chromophore (Figure 2b), indicating the formation of a helical superstructure with a preferred handedness.[8]

Dynamic light scattering (DLS) experiments were performed with **1** in aqueous solution to further investigate the aggregation behavior.[9] The CONTIN analysis of the autocorrelation function shows a broad peak corresponding to an average hydrodynamic radius of approximately 270 nm. The angular dependence of the apparent diffusion coefficient (D_{app}) was measured because the slope is related to the shape of the diffusing species. The slope was observed to be 0.02, consistent with the value predicted for cylindrical micelles (0.03).[10] The formation of cylindrical micelles was further confirmed by the Kratky plot that shows a linear angular dependence over the scattering light intensity of the aggregates.[11]

The evidence for the formation of the cylindrical aggregates was also provided by transmission electron microscopy (TEM) experiments performed with the solutions of **1** (0.05 wt %) (Figure 3). The micrographs of the unstained samples show cylindrical aggregates with a left-handed helical arrangement with lengths up to several micrometers and widths of 340 and 80 nm, respectively. When the sample was negatively stained with a 2 wt % aqueous solution of uranyl acetate, the images show predominantly the smallest left-handed helical objects with a uniform diameter of about 8 nm and a pitch length of 5.6 nm. Considering the extended

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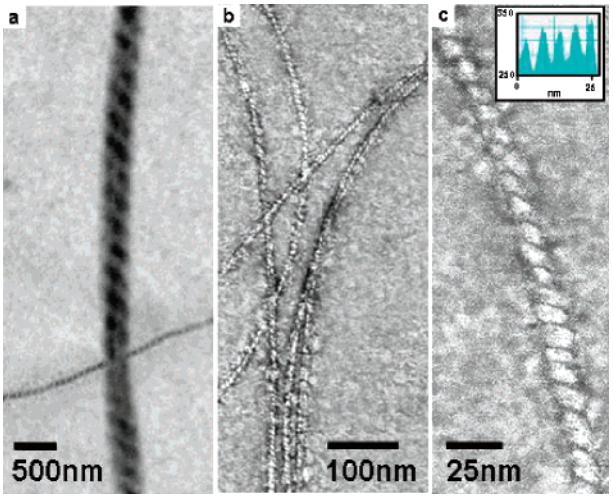

Figure 3. TEM images of **1** (a) without staining, (b) and (c) with negative staining, with density profile inset.

molecular length (8.3 nm by CPK), the image indicates that the diameter of the elementary cylindrical objects corresponds to one molecular length. The density profiles taken parallel to the long axis of a helical fiber confirmed a regular pitch to be 5.6 nm (Figure 3c).

On the basis of the results described thus far, it can be concluded that molecular dumbbell **1** self-assembles into cylindrical micelles in which the molecules are aligned perpendicularly to the cylinder axis. However, the rod segments stack on top of each other with mutual rotation in the same direction to avoid steric hindrance between the bulky dendritic wedges. Consequently, this stacking of the aromatic rod segments would lead to helical objects, consisting of hydrophobic aromatic cores surrounded by hydrophilic dendritic segments that are exposed to the aqueous environment. The observed supramolecular handedness is believed to arise from steric constraints imposed by the chiral centers in the dendritic wedges.

The formation of a helical structure is also illustrated by a computer model in which the COMPASS empirical force-field calculation is used on a small cluster of 12 molecules stacked on top of each other. Energy minimization of the cluster suggests that a helical arrangement of the rod segments is energetically favorable. The calculation revealed that the distance between two adjacent rods is 0.46 nm and the angle of rotation is close to 15 degrees, resulting in a pitch length of 5.4 nm. These single elementary fibrils are further assembled via amphiphilic interactions to give left-handed superhelical fibers. Although the origin of superhelicity is not clear at present, winding of the individual helical strands around each other seems to be responsible for the formation of a superhelical structure.

In summary, the results described here demonstrate that the molecular dumbbell based on an oligo-*p*-phenylene self-assembles into well-defined left-handed helical cylinders with a diameter of a molecular length scale and a pitch length of 5.6 nm. These elementary fibrils are further assembled to superhelical fibers with lengths up to several micrometers. The primary driving force responsible for the helical arrangement of the conjugated rods is believed to be the energy balance between repulsive interactions among the adjacent bulky dendritic segments and $\pi-\pi$ stacking interactions. Such a well-defined helical arrangement of conjugated rod building blocks may provide a new strategy for the design of one-dimensional nanostructured materials with biomimetic, electronic, and photonic functions.

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Supporting Information Available: Synthetic procedures, characterization, and DLS data. This material is available free of charge via the Internet at http://pubs.acs.org.

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