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Mirror Image Nanostructures

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Supramolecular organic nanostructures are formed through concerted weak interactions among self-assembling molecules. Hydrogen-bonding, $\pi-\pi$ stacking, and metal−ligand interactions play central roles in controlling the form and function of these nanostructures,[1] including one-dimensional assemblies with columnar,[2] ribbon,[3−5] and cylindrical[6] architectures. Several groups have incorporated chiral moieties in self-assembling organic molecules with the objective of forming chiral supramolecular assemblies.[7,8] In one case, a chiral assembly was mineralized with silica, transcribing the chirality of the molecule onto the inorganic nanostructure to create a catalyst that showed high enantioselectivity.[9] Supramolecular nanostructures with appropriately sized cavities[10] and well-defined chiral structure on the scale of their constituent molecules will enable the rational design of enantioselective catalysts. We report here the use of enantiomerically enriched self-assembling molecules to create such one-dimensional nanostructures with well-defined chiral structure.

Previously, our laboratory has developed triblock molecules known as dendron rodcoils (DRCs) that self-assemble in organic solvents to form high aspect ratio ribbonlike nanostructures that are 10 nm wide and μm long.[3,4] Self-assembly of this class of molecules is driven by head-to-head hydrogen-bonding interactions among their dendritic segments and also by $\pi-\pi$ stacking interactions among their rodlike segments. We showed previously that the coil segment in DRC molecules imparts solubility to these high aspect ratio, self-assembling nanostructures; however, thus far, only achiral or racemic coil segments have been explored for this purpose.

The DRC molecules synthesized and studied in this work have a triblock structure consisting of a generation one 3,5-dihydroxybenzoic ester dendron, a ter(biphenyl ester) rod, and a 3,7-dimethyloctyl coil (Figure 1). The stereocenter at carbon 3 of the dimethyloctyl coil is enantiomerically enriched.[11] The structures were synthesized by carbodiimide esterifications[12] using tertiary butyl[13] and benzyl ester[14] protection/deprotection chemistry similar to that described previously by our laboratory[3] (details can be found in the Supporting Information). The macroscopic indicator of self-assembly is an increase in solution viscosity and ultimately gelation due to formation of an interconnected network of high aspect ratio ribbonlike nanostructures. All three compounds, *R*-, *S*-, and racemic DRC, were found to form birefringent gels in acetonitrile at 0.25 wt %, indicative of molecular assembly.[3,4,15,16] Gelation was found to be solvent dependent and did not occur in tetrahydrofuran (THF) (NMR spectra of *R*-, *S*-, and racemic DRC show well-resolved peaks in deuterated THF). In deuterated acetonitrile, however, aromatic peaks are unresolved, while aliphatic peaks are broadened (see Supporting Information). This behavior is consistent with the ribbonlike packing of DRC molecules observed previously.[3,4]

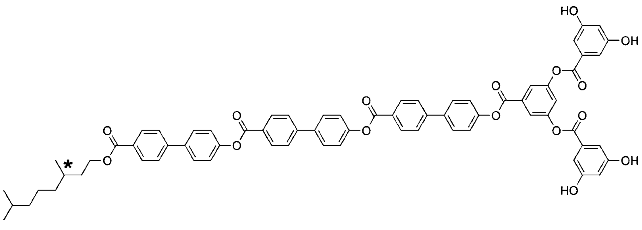

Figure 1. Chemical structures of *R*-, *S*- and racemic DRCs. Chirality located at the indicated stereocenter.

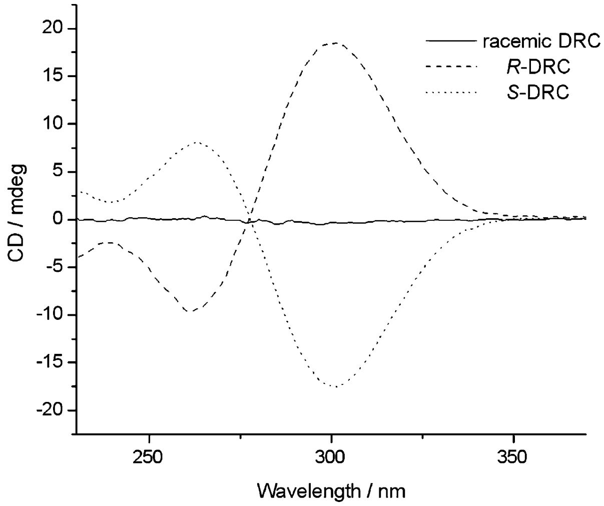

Figure 2. Circular dichroism spectra of *R*-, *S*-, and racemic DRC.

We used circular dichroism (CD) spectroscopy as a tool to probe handedness of the self-assembled nanostructures.[17] Preformed gels (20.0 μL at 0.25 wt %) of *R*-, *S*-, and racemic DRC were dispersed in 0.50 mL of acetonitrile and analyzed by CD. The CD spectra of self-assembled *R*- and *S*-DRC each show Cotton effects in the biphenyl group absorbance due to exciton coupling of the chromophore (Figure 2). The differences in the two spectra demonstrate the influence of the chiral coil segment on handedness of the $\pi-\pi$ stacked biphenyl rod segments of the molecule. As expected, similarly prepared samples in THF do not show any exciton coupling in the CD spectrum, thus linking the source of the observed handedness to self-assembly (see Supporting Information). Furthermore, racemic DRC does not have a CD signal (Figure 2), despite the ability of these molecules to form a self-supporting gel.

DRC nanostructures cast from dilute solution onto freshly cleaved mica were imaged by AFM. Images reveal collections of micron-long, one-dimensional nanostructures with a height that varies periodically from 6 to 9.3 nm above the mica surface and with a regular pitch of 28 ± 3 nm along their length. Images of isolated nanostructures formed by *R*- and *S*-DRC molecules are clearly mirror images of each other (Figure 3), forming left- and right-handed helices, respectively. Interestingly, AFM studies of self-assembled racemic DRC molecules show similar helical features with left- and right-handed ribbonlike structures with the same

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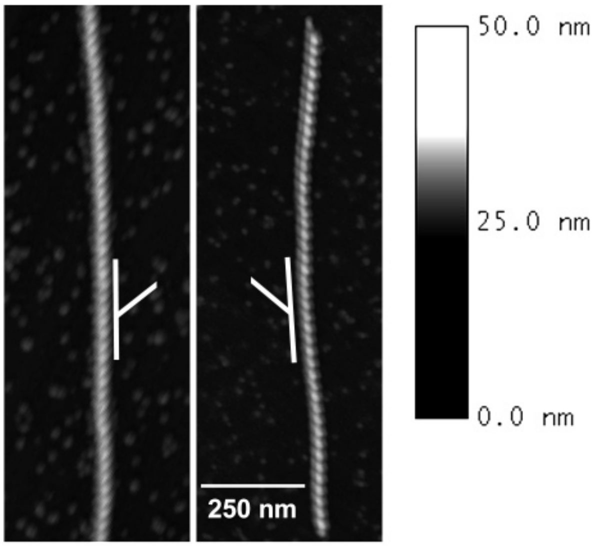

Figure 3. Atomic force microscopy images of *R*-DRC (left) and *S*-DRC (right). The horizontal and vertical scale bars are identical for both images. The white lines indicate handedness.

periodicity (see Supporting Information), and no flat ribbons are observed. The AFM images and CD spectra of the racemate could indicate that *R*- and *S*-DRC molecules self-sort into *R* and *S* nanostructures through homochiral recognition of molecules during self-assembly.[7,18]

We have reported on three DRC molecules that show helical supramolecular assembly, inducing gelation at low concentrations. We propose that interactions among chiral coil segments of *R*- and *S*-DRC molecules control the handedness of the helical pitch. We believe this control is rooted in steric constraints imposed by the chiral centers in the coil segment, hence, the supramolecular handedness we observe. The formation of the well-defined, molecular scale, mirror image nanostructures may result from the significant separation between the stereocenter and hydrogen-bonding dendron (more than 4 nm). We propose when stereocenters and intermolecular bond-forming functional groups are in proximity, supramolecular structures might be more prone to organize into large, hierarchical chiral structures than to form well-defined objects on the molecular scale. Structural control of supramolecular chirality on the scale of molecules could have implications in design of nanoscale catalysts or for nonlinear optical materials.

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Supporting Information Available: Full synthetic details, absorbance spectra, control CD in THF, and additional AFM. This material is available free of charge via the Internet at http://pubs.acs.org.

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