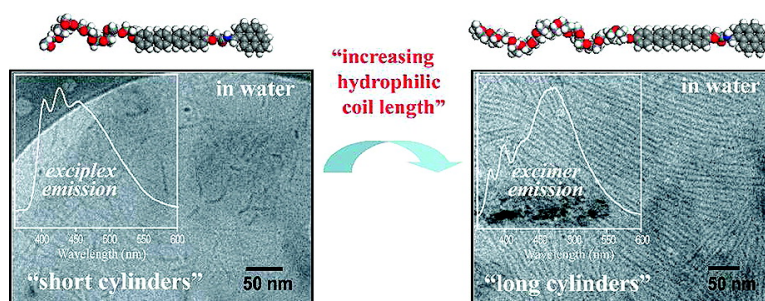


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An Extraordinary Cylinder-to-Cylinder Transition in the Aqueous Assemblies of Fluorescently Labeled Rod–Coil Amphiphiles

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Self-assembly of block molecules toward well-defined architectures has been one of the major research areas of materials science and nano and biochemistry because of its tremendous potential to produce materials with specific functions.¹ Of the variety of self-assembling block molecules, rod–coils have particularly stimulated researchers' interest because of their unique organizing power by employing conformationally distinct blocks, that is, rigid rods and flexible coils. Along with the intensive bulk studies of the rod–coil system,² several research groups have studied the self-assembling behavior of the rod–coil system in solution.³ Any such efforts have demonstrated that a variety of assembled morphologies such as spheres, vesicles, cylinders, twisted ribbons, barrels, and toroids form in solution states.

As a fluorescent probe, pyrene has been utilized in conjunction with DNA, polymers, peptide, and dendritic molecules because its emission property of pyrene is sensitive to its local environment.⁴ Depending on the relative proximity between pyrene moieties, unique monomer and excimer emissions are observed at considerably different wavelengths, through which structural information can be analyzed.

In this context, it would be interesting to attempt monitoring the self-assembling behavior of amphiphilic rod–coils in the solution, particularly in a water environment, by tagging them with a pyrenyl moiety. To this end, we designed a series of amphiphilic rod–coils labeled with a pyrenyl moiety (Scheme 1). Synthesis of the rod–coils was performed using a previously reported procedure.⁵ The final rod–coils were characterized using ¹H and ¹³C NMR spectroscopy, gel permeation chromatography, MALDI-TOF mass, and elemental analysis (Figure S1). All experimental data are in full agreement with the designed molecular structures.

To investigate the aggregation behavior of rod–coils 1–4 in water, dynamic light scattering (DLS) experiments were performed at a fixed concentration of 5×10^{-4} M over a scattering angular range of 30–150°. The angular dependence of the apparent diffusion coefficient (D_{app}) associated with the shape of the diffusion species was measured. The slopes were found to be 0.020–0.027, suggesting that the aggregations have an anisotropic rodlike shape rather than a spherical shape (Figure S2).⁷

To elucidate the morphologies of the aggregates in water, we carried out transmission electron microscopy (TEM) experiments. In Figure 1a, the TEM image of rod–coil 1 displays fibrillar aggregates with lengths up to several hundred nanometers, while the aggregates formed by rod-coil 2 were shown to be mostly truncated fibers with less than 100 nm in length (Figure 1b). This reduced length of cylindrical fibers can be interpreted by relieving the increased steric repulsion between neighboring PEO coils as

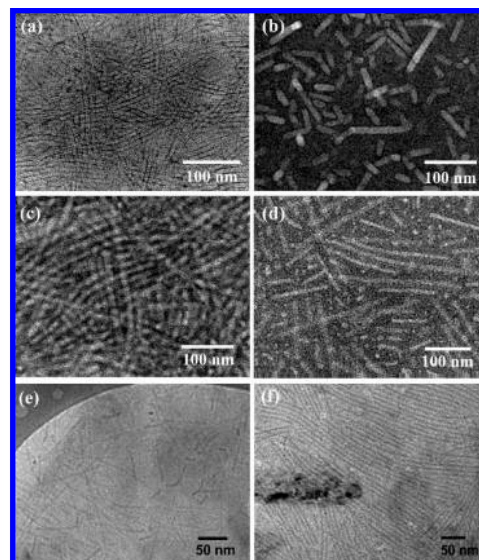
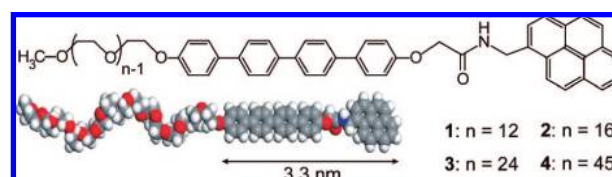


Figure 1. TEM images of cylindrical fibers self-assembled by (a) 1, (b,e) 2, (c,f) 3, and (d) 4. The images (a–d) were obtained from the solution cast samples negatively stained with uranyl acetate; (e, f) the cryo-TEM image of the aqueous solutions.

Scheme 1. Molecular Structures and Schematic Model of Rod–Coils 1–4



the length of PEO coil increases. Generally, in a given morphology in a solution a further increase in corona coil length induces more discrete morphologies.⁸ From this point of view, the morphological behavior observed in rod–coil 3 is quite surprising. In Figure 1c, the TEM image displays the re-entering elongated fibrillar aggregates with lengths up to several hundred nanometers. Similar to the morphological change in the cylindrical fibers of rod–coils from 1 to 2, the further increase of the PEO coil length from 3 to 4 was shown to shorten the lengths of cylindrical fibers (Figure 1d).

To corroborate this extraordinary morphological transition, we implemented cryo-TEM experiments with the aqueous solutions of 2 and 3. Consistent with the TEM images from the solution cast samples, the cryo-images exhibit the transition from shorter to longer cylinders (Figure 1e and 1f). On the basis of the observed morphological transformation as a function of PEO coil length, we speculated that there must be a fundamental rod packing transition

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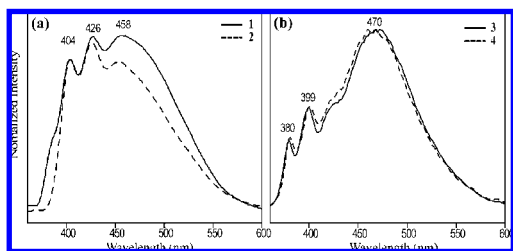


Figure 2. Emission spectra of the aqueous solutions (5×10^{-4} M) excited at 346 nm for (a) **1** and **2**, and (b) **3** and **4** at 25 °C.

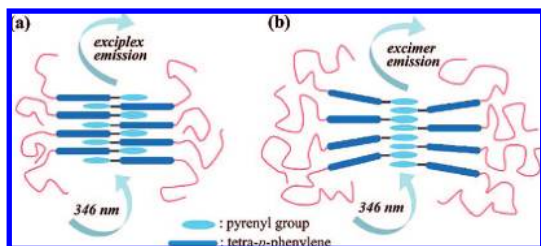


Figure 3. Schematics of (a) the antiparallel rod packing of **1** and **2**, and (b) the interdigitated rod packing of **3** and **4** in the cylinder cross-section. For reasons of clarity, water molecules are omitted.

in the core between the former (**1** and **2**) and latter (**3** and **4**) cylindrical assemblies.

In an effort to understand the difference in rod packings, we investigated the steady-state emission spectra of the solutions of **1–4** using an excitation at 346 nm. The solution emission spectra of **1** and **2**, which reveal several peaks in the range of 380–500 nm, are similar to those of their pyrene-free rod-coils, except for the broad emission band near 460 nm (Figures 2a and S3a). The extra band in the pyrene excimer region suggests that the pyrene groups are either interacting with each other to produce excimer, or with the tetra-*p*-phenylene units resulting in exciplex emission.⁹ To identify the extra band, we examined the emission spectral change of the pyrene-free rod-coil solutions of 5×10^{-4} M excited at 346 nm, upon adding different amounts of the pyrenyl moiety (Figure S4). In these aqueous solutions, it is expected that the pyrenyl molecules tend to be intercalated between tetra-*p*-phenylene rods in the cylindrical assemblies, resulting in the exciplex formation (Figure S3b–e). The obtained emission data of the mixture solutions exhibited nearly identical patterns to those observed in the emission spectra of **1** and **2**; furthermore, the emission band near 460 nm was observed to intensify with increasing pyrenyl molecules. From these data, the broadband near 460 nm in the spectra of **1** and **2** corresponds to the exciplex emission which is a consequence of the interaction between the pyrene and tetra-*p*-phenylene rod groups. In addition to the emission data, the comparison of the cylinder thickness of about 4–5 nm in the cryo-TEM image with the rod length of 3.3 nm suggests that an antiparallel rod packing with the phenylene rods and pyrenyl groups facing with each other is the most probable packing structure in the cylindrical core (Figure 3a).¹⁰

Meanwhile, the emission spectra of **3** and **4** were shown to have a considerably different fluorescence pattern from those of **1** and **2**. In Figure 2b, the spectra display an intense pyrene excimer band at 470 nm with a weak monomer emission in 380–400 nm. The formation of the excimer indicates a close packing of the pyrenyl groups. Although we are not aware of the exact arrangement of phenylene rods in the cylindrical core at present, rod interdigitation is considered to be a packing mode satisfying the cylinder thickness of ~6 nm in the cryo-TEM and the excimer emission (Figure 3b).

Because the coil conformational entropy becomes dominant upon increasing the corona coil length, the rod packing mode of **3** and **4** has to alleviate the PEO coil repulsion more than that of **1** and **2**. The interdigitation may provide a large interfacial area at the rod/coil interface, which is able to relieve the PEO coil repulsion.¹¹ Consequently, considering the excimer formation and the minimization of coil repulsive force, the interdigitated arrangement with a central close stack of pyrenyl groups can be suggested as a plausible model for the rod packing structure in the cylindrical aggregates from **3** and **4**.

For cylindrical assemblies the increase of the coil length in the corona relative to the coil length in the core has been known to induce more discrete morphologies such as shorter cylindrical or spherical micelles in solutions.¹² In this context, the cylinder-to-cylinder transformation observed in this study is a unique assembling feature of our rod-coil system. Another remarkable aspect is the role of the pyrenyl group. The employment of the pyrenyl group as a molecular probe makes it possible to obtain insight into the “unusual rod packing transformation” via simple emission spectroscopic measurements.

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Supporting Information Available: Synthesis, experimental details, GPC and mass data, DLS data, emission data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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