

# Tubular assembly of amphiphilic rigid macrocycle with flexible dendrons†

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An amphiphilic rigid macrocycle was shown to self-assemble into tubular aggregates that can solubilize SWNTs in aqueous solution through significant  $\pi$ - $\pi$  interactions.

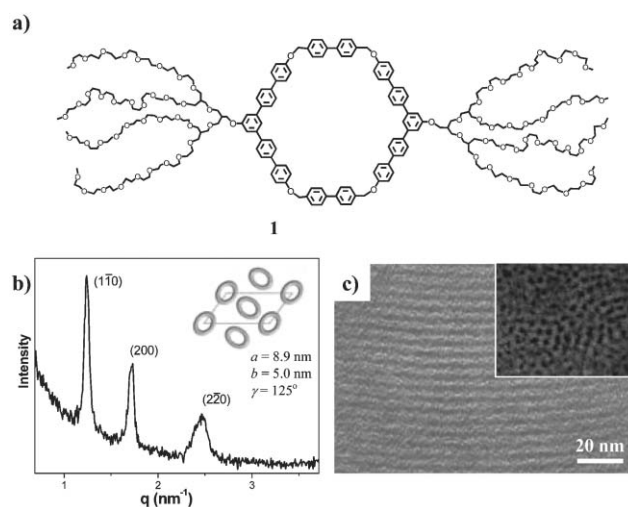
The self-assembly of incompatible molecular components leading to microphase separation comprises a powerful approach toward the fabrication of complex supramolecular architectures and new materials.<sup>1</sup> Rigid-flexible block molecules represent a unique class of self-assembly systems, in which the anisotropic orientation of the rigid segments and repulsion between the covalently connected segments lead to self-organization into a wide variety of aggregation structures.<sup>2</sup> In the same context, the incorporation of a rigid macrocyclic component into a rigid-flexible system would lead to another class of self-assembling systems that self-assemble into hollow tubular aggregates arising from the microphase separation between the rigid and flexible segments and  $\pi$ - $\pi$  stacking interactions.<sup>3</sup> Thus, this design concept may offer an opportunity to reversibly encapsulate giant guest molecules within the internal cavity of a tubular superstructure.

We present here a unique example of 2D organized columns in the liquid crystalline state and tubules in aqueous solution based on the self-assembly of amphiphilic rigid macrocycles driven by noncovalent interactions. In particular, the supramolecular tubules solubilize single-walled carbon nanotubes (SWNTs) in aqueous solution. The amphiphilic macrocyclic molecule that forms these aggregates consists of a rigid aromatic macrocycle and oligo(ethylene oxide) dendrons in its periphery (Fig. 1a). The molecule was obtained in a multiple step synthesis from readily available starting materials.<sup>4</sup> The resulting macrocyclic molecule with oligo(ethylene oxide) dendrons was characterized by <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy, elemental analysis and MALDI-TOF mass spectroscopy, and shown to be in full agreement with the structure presented. The polydispersity of the macrocyclic molecule measured by gel permeation chromatography (GPC) with the use of polystyrene standards appeared to be less than 1.05.

Macrocyclic molecule **1** was observed to have a stable liquid crystalline structure as confirmed by differential scanning calorimetry (DSC), polarized optical microscopy, X-ray scatterings and transmission electron microscopy (TEM). After the crystal melting transition at 34 °C, **1** exhibited a birefringent liquid crystalline state, followed by an isotropic phase at 86 °C. The small-angle X-ray scattering (SAXS) of **1** in the melt state displayed several

sharp reflections that correspond to a 2D oblique columnar structure with lattice constants  $a = 8.9$  nm and  $b = 5.0$  nm, and a characteristic angle of 125° (Fig. 1b).<sup>5</sup> While the wide-angle X-ray scattering (WAXS) showed only a broad halo, indicative of a liquid crystalline order of the rigid macrocyclic segments within domains. On the basis of the X-ray results, molecule **1** self-assembles into an oblique columnar structure in which the rigid macrocyclic segments stack on top of each other. The columnar structure was further confirmed by transmission electron microscopy (TEM) which shows organized dark, more stained 1D aromatic domains with a thickness of 2.0 nm that corresponds to the diameter of an aromatic macrocycle (1.9 nm by Corey-Pauling-Koltun (CPK) molecular model) (Fig. 1c). Compared to the system reported previously,<sup>6</sup> the bulky dendritic geometry of the flexible segments relative to a linear chain is likely to prohibit the 2D growth of a self-assembled structure. Instead, the aromatic macrocyclic segments are strongly driven to aggregate in one dimension with a columnar stack through microphase separation between the rigid and flexible segments, and  $\pi$ - $\pi$  stacking interactions between aromatic units.<sup>7</sup>

Self-assembly of the rigid macrocyclic molecules into a columnar structure with a hydrophilic exterior in bulk suggests that they may also assemble into a similar structure in aqueous solution. Toward this direction, the aggregation behavior in aqueous solution was



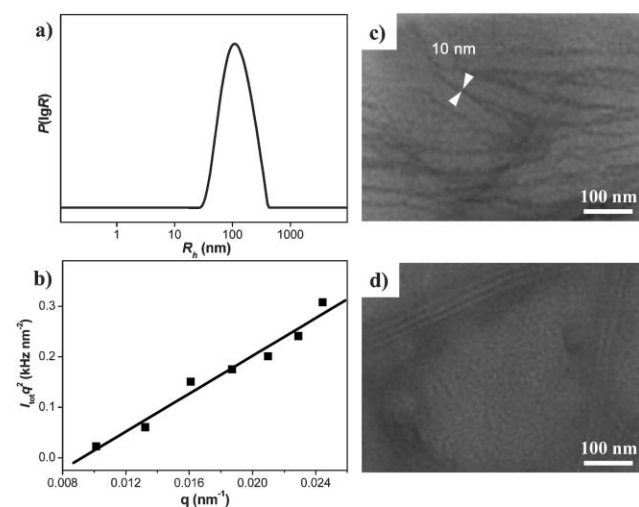
**Fig. 1** (a) Molecular structure, (b) small-angle X-ray diffraction data at 40 °C and (c) TEM images of ultramicrotomed films of polymer **1** stained with RuO<sub>4</sub> revealing columnar array of alternating light-colored dendritic, and dark aromatic layers. The inset image at perpendicular beam incidence shows an oblique columnar array of aromatic core.

† Electronic supplementary information (ESI) available: detailed synthetic procedures, characterization, GPC, MALDI-TOF mass, WAXS, DSC, DLS and UV-Vis spectra. See <http://www.rsc.org/suppdata/cc/b4/b419213c/>

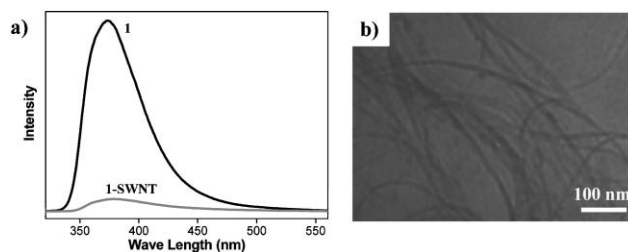
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investigated by using dynamic light scattering (DLS). DLS studies of aqueous solutions showed that **1** self-assembles into discrete aggregates with an average hydrodynamic radius of approximately 119 nm (Fig. 2a). The Kratky plot showed a linear angular dependence over the scattering light intensity of the aggregates, suggesting the presence of cylindrical micelles (Fig. 2b).<sup>8</sup> Further evidence for the formation of the cylindrical aggregates was provided by TEM experiments (Fig. 2c). The micrograph showed long cylindrical aggregates with a diameter of about 10 nm. This dimension of the aggregate is approximately consistent with the molecular dimension (8.7 nm in molecular length by CPK), suggesting that the rigid macrocyclic segments stack directly on top of each other to form a 1D superstructure. Based on these results, the amphiphilic molecule can be considered to self-assemble into a tubular superstructure that is composed of a hydrophobic, stiff interior and a hydrophilic, flexible exterior.

The formation of a tubular structure with a hydrophobic interior stimulated us to investigate if the supramolecular tubules solubilize SWNTs in aqueous solution through hydrophobic interactions and  $\pi$ - $\pi$  stacking interactions between aromatic units.<sup>9</sup> With this consideration in mind, solubilization capability was evaluated by using fluorescence spectroscopy. SWNTs were observed to be solubilized in water by mixing with **1** along with sonication (solubility of about 0.85 mg mL<sup>-1</sup>). The emission spectrum of the aqueous solution, in the absence of SWNTs, displayed a strong fluorescence with a maximum at 372 nm (Fig. 3a). In great contrast, the fluorescence intensity of the solution containing SWNTs was significantly suppressed because of fluorescence quenching, indicative of significant  $\pi$ - $\pi$  interactions between the macrocycles and the SWNTs.<sup>9,10</sup> The solubilization of the SWNTs by the supramolecular tubules was further confirmed by TEM (Fig. 3b). The image shows well-separated cylindrical objects with a uniform diameter of about 10 nm, approximately corresponding to a molecular dimension, suggesting that the aromatic macrocycles wrap the individual SWNTs.



**Fig. 2** (a) Size distribution graph of **1** in aqueous solution (0.05 wt%) at a scattering angle of 90° (from CONTIN analysis of the autocorrelation function), (b) Kratky plot (■) and linear fit (—) and (c) TEM images by freeze drying an aqueous solution without staining and (d) with negative staining.



**Fig. 3** (a) Fluorescence spectra of the aqueous solution of **1** and of **1**-SWNTs (excitation wavelength; 290 nm), (b) TEM image of the aqueous solution of **1** containing SWNTs.

To confirm the effect of tubular aggregation on the solubility of SWNTs, a THF solution of **1** without aggregation behavior was investigated using UV-vis spectroscopy. As opposed to an aqueous solution of **1**, the THF solution showed negligibly low solubility of SWNTs (see ESI†). This result strongly supports that the formation of tubular structure in solution plays a crucial role in the solubilization of SWNTs.

In conclusion, we have demonstrated that the amphiphilic macrocycle consisting of a rigid aromatic macrocycle and oligo(ethylene oxide) dendrons self-assembles into a stable 2D oblique columnar liquid crystalline structure in bulk. In aqueous solution, the macrocycles assemble into a tubular structure with a hydrophobic internal cavity. Notably, the tubules in aqueous solution can solubilize SWNTs through  $\pi$ - $\pi$  interactions. These results demonstrate that rational design of self-assembling molecules based on a rigid cyclic building block allows 1D nanostructures to be produced, which potentially have a number of applications including nanocarriers and nanodevices.

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