Molecular Monolayer Nanotubes Having 7–9 nm Inner Diameters Covered with Different Inner and Outer Surfaces

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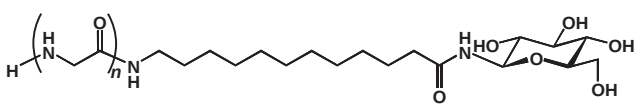
Novel unsymmetrical bolaamphiphile, bearing glucose- and triglycine-headgroups at both ends, exclusively self-assembled into nanotubes with 7–9-nm inner diameters, which consist of a single monolayer lined by polyglycine-II-type hydrogen-bond networks among the triglycine moieties.

Lipid nanotubes self-assembled from amphiphilic molecules have been becoming attractive nanoarchitectures[1,2] since the hydrophilic hollow cylinder can act as vessels for nanomaterials,[3] templates for metal nanowire formation,[4] nanochannels for nanofluidic devices,[5] and carriers for drug delivery.[6] Rational functionalization of their surfaces and control of their inner diameters are currently big issues to achieve effective and selective encapsulation of target guest substances into the hollow cylinders.[7,8] Unsymmetrical bolaamphiphiles, in which two hydrophilic headgroups of different sizes are connected to a hydrophobic spacer at each end, often form nanotubes having different inner and outer surfaces depending on their parallel molecular packing within the monolayer lipid membranes.[7–10] However, the control of the molecular packing during the self-assembly procedure has been difficult since the bolaamphiphiles also packed in favorable antiparallel fashion.[7–9,11] Although we succeeded in the formation of such nanotubes, the obtained nanotubes actually involved a mixture of parallel and antiparallel molecular packing.[7] The preorganization of the molecular packing before self-assembly was also indispensable for the control of polymorphism.[8] In those studies, we have also found that the inner diameter of such nanotubes decreases with shorting the length of the oligomethylene spacer in the bolaamphiphiles. However, the bolaamphiphiles having short oligomethylene spacers tended to form nanotubes with antiparallel molecular packing as well as tape-like structures.[7,11] Therefore, the down sizing of the inner diameter into single nm has been impossible until now, although we and some groups have reported the nanotubes with inner diameters below 10 nm consisting of bilayer membrane type.[1]

Here, we describe novel unsymmetrical bolaamphiphiles, **1(*n*)** (Scheme 1), having both glucose and oligoglycine-headgroups connected to a short oligomethylene spacer at each end,[12] which exclusively give nanotubes with controlled molecular packing. The number of glycine residues in **1(*n*)** influences not only the morphologies of the resultant self-assemblies but also the stabilization of the parallel molecular packing based on hydrogen-bond networks among the glycine moieties.



Scheme 1. Unsymmetrical bolaamphiphiles **1(*n*)** ($n = 1$, 2, and 3).

The self-assembly experiment was carried out as follows: The synthetic **1(*n*)** (1 mg) was dispersed in water (1 mL) at pH 7–10 under reflux conditions. The resultant hot aqueous solutions were gradually cooled to room temperature. Transmission electron microscopic (TEM) observation revealed that the self-assembled morphologies strongly depend on the number of glycine residues (Figure 1). Self-assembly of **1(1)** and **1(2)** gave helical nanofibers with 10–25-nm width, while **1(3)** formed nanotubes with 7–9-nm inner diameters and 3–4-nm thickness. The nanotubes are distinguishable from the nanofibers, since the penetration of the negative staining reagent, phosphotungstate, into the hollow cylinder allows visualization of the tubular structure.

IR measurements[13] were performed to clarify the difference

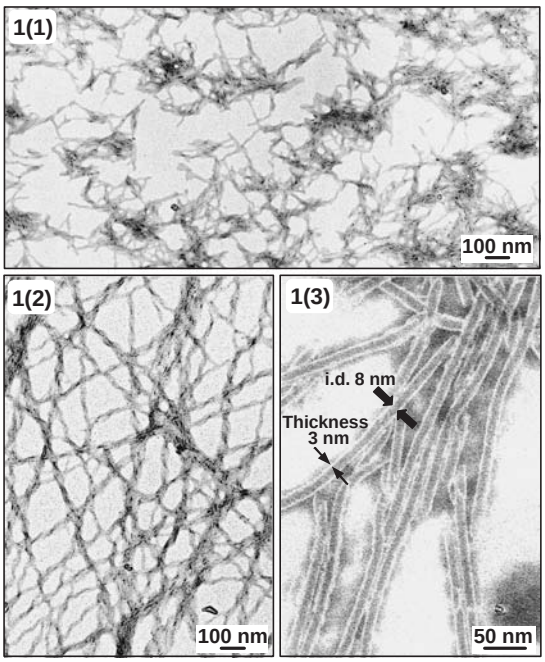


Figure 1. TEM images of the self-assemblies formed from **1(*n*)** negatively stained with phosphotungstate. The hollow cylinder space of the nanotubes for **1(3)** can be visualized by relatively darker image than surrounding.

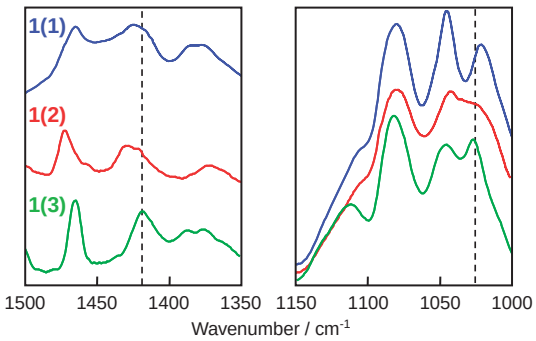


Figure 2. The CH deformation and skeletal vibration IR bands for the oligoglycine moieties in the self-assembled **1(*n*)**.

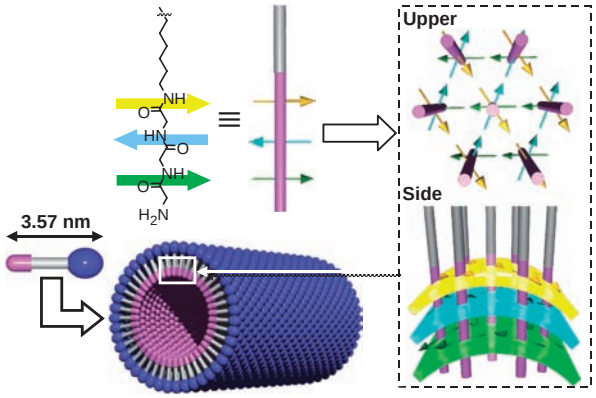


Figure 3. A schematic model for the nanotube consisting of the single monolayer lined by pseudo polyglycine-II-type hydrogen-bond networks among triglycine in **1(3)**.

in the molecular packing between the nanotubes and the nanofibers. The nanotube from **1(3)** indicates two peaks at 1420 and 1026 cm^{-1}, whereas the nanofibers from **1(1)** and **1(2)** have one of them (Figure 2). The two bands are observable in the CH deformation and skeletal vibration bands of polyglycine,[14] showing that the triglycine of **1(3)** in the nanotube form the intermolecular hydrogen bonding similar to the polyglycine-II-type hydrogen-bond networks of polyglycine.[15] Pseudo hexagonal-type hydrogen-bond networks[16,17] should induce the parallel molecular packing in the nanotube from **1(3)** having triglycine moieties (Figure 3). On the other hand, the nanofibers from **1(1)** and **1(2)** will allow the coexistence of the antiparallel packing partly due to the incomplete hydrogen-bond networks among the mono- or di-glycine moieties. Actually, the frequencies of the C=O stretching (amide I), N–H deformation (amide II), and N–H stretching vibration bands support the view that the amide hydrogen bond of the nanotube was stronger than that of the nanofibers (Table 1).

The $\delta(CH_2)$ scissoring and $r(CH_2)$ rocking vibration bands reflecting the lateral chain packing of the oligomethylene spacer in **1(*n*)**, the so-called "subcell structure," support the difference in the molecular packing between the nanotube and nanofibers (Table 1).[18] A single sharp peak of each band for the nanotubes indicates a triclinic parallel ($T_{//}$) structure. A single broad peak of each for the nanofibers is compatible with a distorted hexagonal (Hex) structure. These results are in good accord with our previous nanotubes with parallel molecular packing.[11] The

Table 1. IR absorption band for the self-assemblies from **1(*n*)**

	1(*n*)		
	$n = 1$ nanofiber	$n = 2$ nanofiber	$n = 3$ nanotube
NH str./cm^{-1}	3288	3298	3290
Amide I/cm^{-1}	1655	1653	1642
Amide II/cm^{-1}	1548	1548	1561
ν_s (CH_2)/cm^{-1}	2850	2849	2850
δ (CH_2)/cm^{-1}	1465 (13.4)[1]	1473 (10.1)[1]	1465 (8.3)[1]
r (CH_2)/cm^{-1}	718	717	719

[1]Full width half-maximum.

$\nu_s(CH_2)$ stretching vibration band is sensitive for the gauche/trans conformation in the oligomethylene spacer.[11] The oligomethylene spacer in the nanotube and nanofibers takes an all-trans conformation since the band frequencies appear at less than 2850 cm^{-1} (Table 1). The membrane thickness (3–4 nm) of the nanotubes estimated from TEM image is similar to the extended molecular length (3.57 nm) of **1(3)**, indicating the nanotube consists of a single monolayer. Powder X-ray diffraction measurement for the nanotubes showed no information about *d* spacing because of the thin layer. All results suggest that **1(3)** forms single monolayer with parallel molecular packing and produces nanotubes with spontaneous membrane curvature based on the size difference of the hydrophilic headgroups (Figure 3).

Self-assembly of unsymmetrical bolaamphiphile **1(*n*)** proved to give separately nanotubes and nanofibers depending on the number of the glycine residues. Especially, the specific hydrogen-bond networks among the triglycine in **1(3)** allowed the nanotubes to bring not only different inner and outer surfaces but also the inner diameters below 10 nm.

References and Notes

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