

Supramolecular Nanomaterials Derived from Self-Assembly of Dendritic Building Blocks

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Introduction

Recent advances in self-assembly of dendrimers or dendrons provide a unique methodology to create supramolecular nanomaterials.^[1-12] In particular, self-organization of dendron building blocks into ordered suprastructures has been demonstrated in several conditions. In our laboratory, we have reported on the formation of thermoreversible supramolecular gels through self-organization of some amide dendrons in organic media, and the formation of lamella or columnar hexagonal arrays in dry state depending on the structures of the dendron building blocks.^[7-12] The key structural elements in the self-assembly of the amide dendron, for example, dendron A in Figure 1, were amide branches for hydrogen bonding, carboxyl functionality at the focal point, and alkyl tails for the stabilization of assembled structures via van der Waals interactions. The TEM and XRD study showed that the dimeric form of dendron A, induced by hydrogen bonding at the focal carboxyl groups of two dendron units, is the primary building block in the self-aggregation process. Therefore, it was suggested that dendron dimers which are covalently bridged at the focal point should be able to form similar self-assembled supramolecular structures. This type of supramolecular assembly of the amide dendrons is expected to be very effective for the construction of nanomaterials which have functional elements in the core of the nano-size cylinders or lamellar layers. Therefore, it is important to understand the self-assembly characteristics of dimeric dendrons with diverse bridge units (dendron B). In this work, aromatic junctions such as biphenyl, naphthoxy, and isopropylidenediphenoxy groups are introduced as the bridge unit of the amide dendrons to investigate the self-assembly characteristics of these dimeric dendrons not only in organic media but also at the solid-liquid interface. In addition, transformation of the supramolecular self-assembled structure by using inclusion complex formation is discussed.

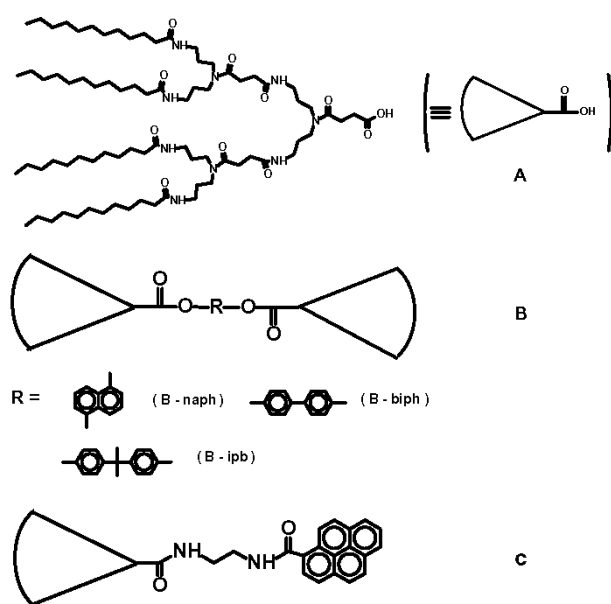


Figure 1. General structure of amide dendrons.

Results and discussion

The self-organization characteristics of the dendrons in various environments were investigated by using TEM, SAXS, AFM, SEM, and dynamic light scattering (DLS) techniques. Dimeric dendrons with aromatic core bridges formed thermoreversible gels in methylene chloride, THF, n-octanol, and n-decanol. The dry gel obtained by self-organization of the dendron dimer with naphthoxy core unit (B-naph) in n-octanol exhibited well-defined and continuous ribbons (Figure 2), while the other two gels of B-biph and (B-ippb) from n-octanol revealed relatively short stands of fibrils. The X-ray diffractogram of B-naph gel shown in Figure 2 revealed a lamellar structure with interlamellar spacing of 70 Å. Therefore the TEM images of B-naph gel in Figure 1 together with the XRD result suggest that B-naph forms lamella nanoribbons. In contrast, B-biph exhibited the hexagonal columnar structure with the column diameter of 63 Å. However, the dendron dimer with the isopropylidenediphenyl central bridging unit, B-ippb, did not form gels in n-octanol and n-decanol. This can be attributed to the steric crowded kink structure of the central isopropylidenediphenyl group which could hinder the packing process of the dendritic building blocks. These results obviously indicate that the core bridging units are critical not only for the formation of supramolecular assemblies of the dendritic dimers but also for determination of the nature of the supramolecular structure.

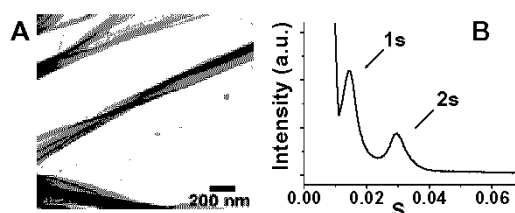


Figure 2. TEM and X-ray results of B-naph gel.

One of the unique aspects of these dimeric dendrons is their self-assembly characteristics at the solid-liquid interface when the solid surface is exposed to the dilute organic solution of the dimeric dendrons. A dilute (0.1 wt %) solution of B-biph in n-octanol did not form any gel. However, dimeric dendron B-biph can self-assemble on the surface of carbon-coated copper grid or silicon wafer which was immersed in a dilute (0.1 wt %) n-octanol solution of B-biph. Figure 3 (A) shows a TEM image of the self-assembled structure of B-biph. It is notable that the width of each nanostack ranging from ~10 nm to ~40 nm is uniform through out the entire length of the assembled structure. The AFM images in Figure 3 (B) also confirmed that each nanostack is uniform in width with a length spanning several micrometers. The height of the nanostack is 7 nm in Figure 3 (B). Considering the dimension of B-biph (84 Å) in the direction of long molecular axis, B-biph building blocks are lying parallel on the solid surface and a uniform number of dimer building blocks are stacked in the vertical and the transverse direction. These results suggest that DD1 forms self-assembled lamellar structure on the surface with a uniform number of lamellar layers in in-plane direction, and the building blocks are assembled together to form a lamellar stack with a uniform width and a length of several microns.

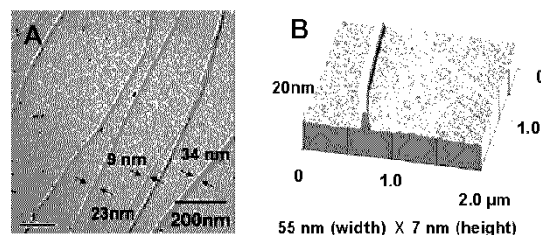


Figure 3. TEM and AFM images of self-assembled nanoribbons of B-naph at the solid-liquid interface.

The amide dendrons have a capability of enforcing various focal moieties into organized states in aqueous phase. In this work, we present a unique methodology for the control and the transformation of the supramolecular structures in aqueous phase by using the nature

of the focal moiety of the dendritic building blocks.

The self-assembly characteristics of the amide dendron **C** with focal pyrene units were investigated in aqueous phase (Fig. 4). The inclusion of pyrene moiety into CD can make a drastic change in the nature of the focal moiety of the dendron from hydrophobic pyrene to hydrophilic exterior of CD. Therefore, we reasoned that the CD-inclusion would trigger the transformation of supramolecular structures induced by self-assembly of the dendrons with focal pyrene unit. In addition, removal of CDs from the focal inclusion complex moiety by using CD-poly(propylene glycol) pseudorotaxane motif would provide a unique route to the reversal of the supramolecular structure. In addition, pyrene has unique fluorescence characteristics depending on the environmental condition, which is very useful for monitoring the transformation of the organized structures.

The amide dendron with pyrene focal unit were prepared by coupling of amide dendron **A** with pyrene derivative. Dendron **C** with pyrene unit at the focal moiety formed very stable vesicular organization. The typical vesicle images were obtained by using transmission electron microscopy (TEM), scanning electron microscopy (SEM). The gel filtration experiment coupled with dynamic light scattering measurement (DLS) confirmed the existence of water entrapped in the interior of the spherical supramolecular assembly. The average diameter of the vesicle from dendron **C** measured by using DLS was 253 nm.

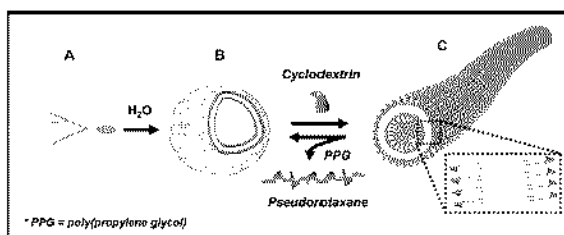


Figure 4. Schematic route to organic nanotubes and the reversible transformation of supramolecular assemblies of dendrons triggered by the motifs of cyclodextrin inclusion and pseudorotaxane formation. (A) Amphiphilic dendron-pyrene conjugate. (B) Vesicular organization of dendron-pyrene conjugates in water. (C) The CD-covered nanotubes obtained by the supramolecular transformation after addition of cyclodextrins to the vesicular solution. The reverse transformation from nanotube to vesicle can be accomplished by removal of CDs on the surface of the nanotube by using PPG.

The organized state of the focal pyrene units in the vesicle was investigated by using fluorescence techniques. The aqueous vesicular solution revealed a broad emission of pyrene excimer (E) at 420 ~ 550 nm with an excitation at 345 nm, which suggests that the focal pyrene units are pre-organized to form excimers. The vesicular solution of dendron **C** showed only broad excimer emission band at 485 nm and 479 nm, respectively without emission of monomeric pyrene (M).

The supramolecular transformation of vesicle into nanotube was induced by introducing the focal pyrene units included into the cavity of CD, which makes the focal moiety very hydrophilic due to the hydroxyl groups of the CD exterior. Indeed, addition of γ -CD to the aqueous vesicular solution of dendron **C** with sonication for 1 min caused disappearance of the excimer band of pyrene (420 ~ 550 nm), and the emission bands of monomeric pyrene (370 ~ 410 nm). This result shows that the inclusion of the focal pyrene moiety into the cavity of γ -CD interrupts the formation of pyrene excimer.

The dramatic transformation of the supramolecular structures from vesicle to nanotube after addition of γ -CD to the vesicular solution of dendron **C** was confirmed by using TEM, SEM. From the TEM image, a clear tubular structure is observed. SEM analysis showed an open end of the tubular structure. Based on the TEM analysis, the outer and inner diameters of the nanotube were about 45 nm and 22 nm, respectively, and the wall thickness was 11.5 nm. Considering the dimension of the fully-stretched structure of dendron **C** (53.5 Å), the wall thickness of the nanotube must be associated with the unilamellar bilayer of dendron **C** with the focal pyrene moiety included into the cavity of γ -CD. It is suggested that the hydrophilic exterior of the CD-pyrene inclusion complex at the focal moiety is exposed to the aqueous phase, and the hydrophobic alkyl peripheries

are located in the middle of the wall membrane of the nanotube. Therefore, the surface of both the exterior and interior of the nanotube is covered with CDs. This result also indicates that the surface functionality of the nanotube can conveniently be controlled by the modification of the functionality of CD.^[13] To the best of our knowledge, this is the first example of the organic nanotubes that possess CD-inclusion complex on the tubular surface.^[14]

The reversal of the supramolecular structure from nanotube to vesicle was accomplished by removal of focal CD by using a motif of pseudorotaxane formation. Addition of poly(propylene glycol) (Mn = 1000, PPG1000) to the aqueous solution of the nanotube derived from dendron **C** and γ -CD induces reversal of emission spectra from monomeric to excimeric pyrene. These results indicate that focal γ -CD is removed from the nanotube and taken up by PPG to form pseudorotaxane. TEM and SEM images exhibit the image of vesicles.

The modification of the CD structure and the alkyl periphery would provide an opportunity to construct a new class of functional nanotubes.^[15] Also, we expect that our findings will lead to unprecedented supramolecular materials with a variety of applications based on CDs.^[16]

Conclusions

Unique characteristics of self-assembly of the amide dendrons are described. Particular emphasis is placed on the formation of cyclodextrin-covered organic nanotubes derived from self-assembly of amide dendrons and their supramolecular transformation. Finally, unique biosensory characteristics of the self-assembled nanotubes will be discussed.

Acknowledgement

This work was supported by Korea Research Foundation (2005-041-D00238).

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