Supramolecular Self-assembly of Dimeric Dendrons with Aromatic Bridge Units

Hae Seung Ko,[†] Chiyoung Park,[†] Sang Man Lee,[‡] Hyun Hoon Song,[‡] and Chulhee Kim*,[†]

Department of Polymer Science and Engineering, Hyperstructured Organic Materials Research Center, Inha University, Incheon 402-751, Korea, and Department of Polymer Science and Engineering, Hannam University, Daejon 300-791, Korea

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The dimeric dendrons with amide branch units, alkyl periphery, and the aromatic bridging units such as naphthyl, biphenyl, or isopropylidenebiphenyl were synthesized via a convergent method. The self-assembly characteristics of these dimeric dendrons were investigated not only in organic media but also at the solid−liquid interface. The gel formation behavior of the dimeric dendrons in organic media and their nanostructures were highly dependent on the bridging moiety. The dendrons with naphthyl and biphenyl bridges form immobile gel in organic media such as *n*-octanol, while those with isopropylidenebiphenyl unit did not form gel. The dry gel obtained via self-assembly formed either lamellae or columnar hexagonal arrays depending on the structure of the bridge moiety. The dendron dimer with the 1,5-naphthoxy bridging unit which formed a lamella structure in a dry gel state also self-assembled at the solid−liquid interface in 0.1% *n*-octanol solution to exhibit well-defined nanoribbons extending to several micrometers. In addition to hydrogen bonding of the dendritic branches and van der Waals interactions of the alkyl periphery, the architecture of the bridging moiety of the dimeric dendrons played a key role in the packing process of the self-assembly of dimeric dendron.

Introduction

Recent advances in self-assembly of dendrimers or dendrons provide a unique methodology to create supramolecular nanomaterials.[1−7] In particular, self-organization of dendron building blocks into ordered suprastructures has been demonstrated in several conditions. Percec has reported comprehensive results on the self-assembly of dendrons in a thermotropic fashion.[8−15] Self-organization behavior of some dendritic bolaamphiphiles in the aqueous phase was elucidated by Newkome.[16,17] In addition, unique characteristics of self-assembly of dendritic building blocks in organic media have been reported by several groups.[18−25] 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 the dry state depending on the structures of the dendron building blocks.[18,19] The key structural elements in the self-assembly of the amide dendron, for example, dendron **A** in Scheme 1, were amide branches for hydrogen bonding, carboxyl functionality at the focal

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* To whom correspondence should be addressed. E-mail: chk@inha.ac.kr.
[†] Inha University.
[‡] Hannam University.

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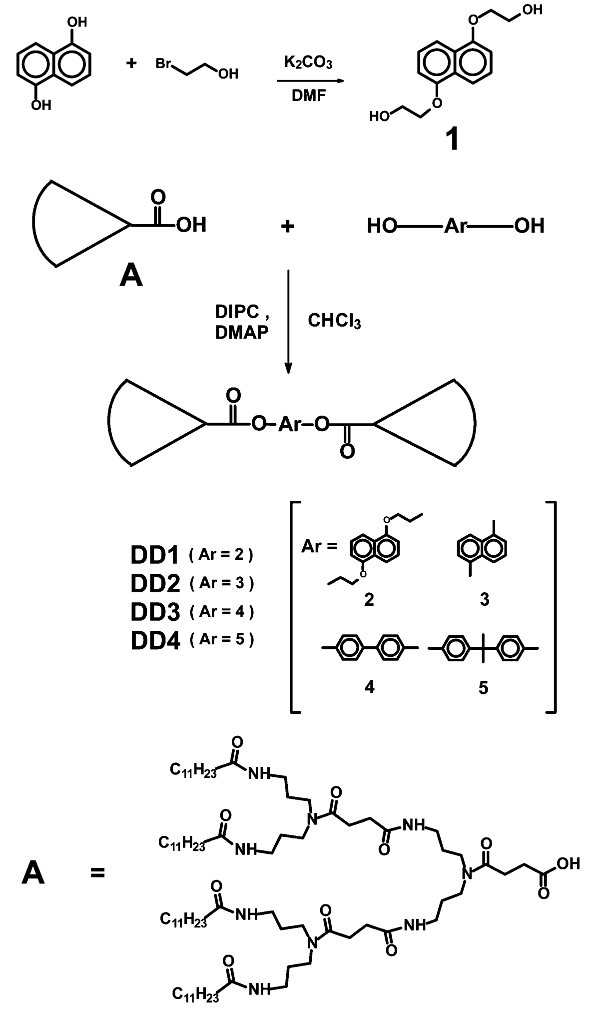
Scheme 1



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 nanosize cylinders or lamellar layers. Therefore, it is important to understand the self-assembly characteristics of dimeric dendrons with diverse bridge units. In this work, aromatic junctions such as biphenyl, naphthoxy, and isopropylidenediphenoxy groups are introduced as the bridge unit of the amide dendrons (Scheme 1). In addition, the self-assembly characteristics of theses dimeric dendrons were investigated not only in organic media but also at the solid−liquid interface.

Experimental Section

1. Materials and Instruments. 4-(Dimethylamino)pyridine (DMAP), 1,3-diisopropylcarbodiimide (DIPC), *N*,*N*-dimethylformamide, 7-methoxy-2-naphthol (98%) (all from Aldrich), 1,5-dihydoxynaphthalene, 4,4′-biphenol, 2,2-bis(4-hydroxyphenyl)propane, and 2-bromoethanol (all from TCI) were all used as received. Chloroform was used after distillation under calcium hydride. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity INOVA 400 spectrometer at 400 and 100 MHz, respectively, and were referenced to TMS. FT-IR spectra were obtained using a Perkin-Elmer System 2000 FT-IR spectrophotometer. Elemental analysis data were obtained using CE Instrument EA 1110. Mass data were obtained with a QUATTRO LC Triple Quadrupole Tandem Mass Spectrometer. MALDI spectra were obtained using a Voyager Biospectrometry time-of-flight mass spectrometer (PerSeptive Biosystem) operated at 25 kV accelerating voltage in reflector mode with positive ionization. Dithranol (solvent: $CHCl_3$) was used as the matrix. Transmission electron microscopy (TEM) was performed using a Philips CM 200, operated at an acceleration voltage of 80 kV. For the observation of the gel morphology, the gel was gently contacted on the surface of the 200 mesh copper grid coated with carbon. The sample on the grid was air-dried and shadowed with Au/Pd of 7−8 Å thickness at 20° tilted angles. Samples for the AFM study were prepared by dipping a silicon wafer into the 0.1 wt % (w/v) *n*-octanol solution of the dimeric dendron samples. AFM images were recorded under ambient conditions using a Park Scientific Instrument autoprobe CP with a cantilever of ultra lever 06D, operated with noncontact mode. X-ray diffraction was carried out at the 4C1 X-ray beamline of Pohang Accelerator Laboratory. The scattered data were collected using a two-dimensional CCD detector and the X-ray wavelength was 1.608 Å.

2. Synthesis. *Synthesis of **1***. A DMF solution (50 mL) of 1,5-dihydroxynaphthalene (3.00 g, 18.7 mmol) and potassium carbonate (7.75 g, 56.1 mmol) was added to a solution of 2-bromoethanol (5.15 g, 41.1 mmol) in DMF (5 mL). After the solution was stirred for 12 h at 80 °C, water (50 mL) was added into the product mixture. The product was extracted with ethyl acetate, which was then dried with anhydrous magnesium sulfate. The product was purified by column chromatography on silica gel (yield 3.04 g, 55%). mp 167 °C.

^{1}H NMR (DMSO-d_6): δ 3.83 (t, $J = 4.8$ Hz, 4H, $-O-CH_2-$), 4.13 (t, $J = 4.8$ Hz, 4H, $-CH_2-OCO-$), 6.96 (d, $J = 7.6$ Hz, 2H, ArH), 7.36 (t, $J = 8.0$ Hz, 2H, ArH), 7.79 (d, $J = 8.0$ Hz, 2H, ArH). ^{13}C NMR (DMSO-d_6): δ 59.73, 69.91, 105.76, 113.95, 125.25, 126.07, 154.08. IR (KBr) ν = 3341, 3099, 3066, 2938, 2911, 2867, 2207, 2125, 1930, 1594, 1509, 1462, 1416, 1366, 1266, 1080, 961, 902, 782, 628. Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.88; H, 6.53. MS calcd for $C_{14}H_{16}O_4$, 248.3. Found, 249.3 (m/z) $[m + H]^+$.

*Synthesis of **DD1***. A chloroform solution (25 mL) of dendron **A** (6.70 g, 4.83 mmol) was added to a solution of compound **1** (0.40 g, 1.61 mmol), DMAP (0.15 g, 1.23 mmol), and DIPC (1.22 g, 9.67 mmol) in chloroform (25 mL). After the solution was stirred for 6 h at 45 °C, the solvent was evaporated under reduced pressure. The product mixture was purified by recrystallization from THF (yield 2.04 g, 42%). mp 82 °C.

^{1}H NMR ($CDCl_3$): δ 0.84 (t, $J = 5.6$ Hz, 24H, CH_3-CH_2-), 1.21 (br s, 128H, $-CH_2-$), 1.60−1.83 (br, 32H, $-CH_2-CH_2-CO-$, $-NH-CH_2-CH_2-CH_2-N-$), 2.10−2.16 (m, 16H, $-CH_2-CO-$), 2.49−2.72 (br, 24H, $-CO-CH_2-CH_2-COO$), 3.11−3.32 (br, 48H, $-CO-NH-CH_2-$, $-CH_2-N-CO-$), 4.31 (t, $J = 4.0$ Hz, 4H, $Ar-O-CH_2-$), 4.55 (t, $J = 4.0$ Hz, 4H, $Ar-O-CH_2-CH_2-O-CO-$), 6.82 (d, $J = 8.0$ Hz, 2H, ArH), 7.33 (t, $J = 8.0$ Hz, 2H, ArH), 7.83 (d, $J = 8.0$ Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ 13.94, 22.49, 25.67, 25.71, 27.06, 27.43, 27.58, 27.84, 28.34, 28.46, 29.16, 29.25, 29.27, 29.38, 29.45, 29.48, 30.85, 31.72, 36.08, 36.31, 36.40, 36.56, 36.63, 42.68, 42.88, 45.13, 62.80, 66.16, 105.72, 114.66, 125.09, 126.51, 153.87, 171.31, 172.11, 172.28, 172.33, 172.66, 173.15, 173.51, 173.87. IR (KBr): ν = 3312, 2919, 2850, 1737, 1639, 1551, 1467, 1378, 1270, 1171, 1120, 1091, 963, 777, 721. MS (MALDI-TOF) calcd for $C_{170}H_{306}N_{18}O_{24}$, 2986.4. Found, 2986.0. Anal. Calcd for $C_{170}H_{306}N_{18}O_{24}$: C, 68.37; H, 10.33; N, 8.44. Found: C, 68.11; H, 10.49; N, 8.44.

*Synthesis of **DD2***. A chloroform solution (10 mL) of dendron **A** (1.00 g, 0.72 mmol) was added to a solution of 1,5-dihydoxynaphthalene (38.0 mg, 0.24 mmol), DMAP (22.0 mg, 0.18 mmol), and DIPC (23.3 mg, 1.42 mmol) in chloroform (10 mL). After the solution was stirred for 6 h at 45 °C, the solvent was evaporated under reduced pressure. The product was purified by recrystallization from THF (yield 0.50 g, 72%). mp 134 °C.

^{1}H NMR (CDCl$_3$): δ 0.84 (t, $J = 5.6$ Hz, 24H, $CH_3{-}CH_2{-}$), 1.21 (br s, 128H, $-CH_2-$), 1.60−1.83 (br, 32H, $-CH_2{-}CH_2{-}CO-$, $-NH{-}CH_2{-}CH_2{-}CH_2{-}N-$), 2.10−2.16 (m, 16H, $-CH_2{-}CO-$), 2.46−2.63 (br, 20H, $-CO{-}CH_2{-}CH_2{-}COO$, $-CO{-}CH_2{-}CH_2{-}COO{-}Ar$), 2.76 (t, $J = 4.0$ Hz, 4H, $-CO{-}CH_2{-}CH_2{-}COO{-}Ar$), 3.06−3.36 (br, 48H, $-CO{-}NH{-}CH_2-$, $-CH_2{-}N{-}CO-$), 7.22 (d, $J = 8.0$ Hz, 2H, ArH), 7.46 (t, $J = 8.0$ Hz, 2H, ArH), 7.83 (d, $J = 8.0$ Hz, 2H, ArH). ^{13}C NMR (CDCl$_3$): δ 13.99, 22.55, 25.75, 27.23, 27.47, 27.99, 28.37, 28.60, 29.22, 29.31, 29.34, 29.45, 29.51, 29.55, 30.19, 31.03, 31.78, 36.19, 36.45, 36.61, 42.75, 45.23, 118.72, 119.64, 126.07, 128.07, 146.67, 171.20, 172.12, 172.19, 172.33, 172.50, 172.79, 173.63, 173.94, 173.97. IR (KBr): $\nu = 3314$, 2918, 2850, 1760, 1640, 1553, 1466, 1364, 1251, 1120, 963, 790, 721. MS (MALDI-TOF) calcd for $C_{166}H_{298}N_{18}O_{22}$, 2898.3. Found, 2921.6 ($M + Na^+$). Anal. Calcd for $C_{166}H_{298}N_{18}O_{22}$: C, 68.79; H, 10.36; N, 8.70. Found: C, 68.67; H, 10.30; N, 8.33.

Synthesis of ***DD3***. A chloroform solution (10 mL) of dendron **A** (1.00 g, 0.72 mmol) was added to a solution of 4,4′-biphenol (44.7 mg, 0.24 mmol), DMAP (22.0 mg, 0.18 mmol), and DIPC (23.3 mg, 1.42 mmol) in chloroform (10 mL). After the solution was stirred for 6 h at 45 °C, the solvent was evaporated under reduced pressure. The product was purified by recrystallization from THF (yield 0.45 g, 64%). mp 141 °C.

^{1}H NMR (CDCl$_3$): δ 0.84 (t, $J = 5.6$ Hz, 24H, $CH_3{-}CH_2{-}$), 1.21 (br s, 128H, $-CH_2-$), 1.60−1.83 (br, 32H, $-CH_2{-}CH_2{-}CO-$, $-NH{-}CH_2{-}CH_2{-}CH_2{-}N-$), 2.10−2.16 (m, 16H, $-CH_2{-}CO-$), 2.46−2.63 (br, 20H, $-CO{-}CH_2{-}CH_2{-}COO$, $-CO{-}CH_2{-}CH_2{-}COO{-}Ar$), 2.92 (t, $J = 4.0$ Hz, 4H $-CO{-}CH_2{-}CH_2{-}COO{-}Ar$), 3.11−3.33 (br, 48H, $-CO{-}NH{-}CH_2-$, $-CH_2{-}N{-}CO-$), 7.12 (d, $J = 8.0$ Hz, 4H, ArH), 7.51 (d, $J = 8.0$ Hz, 4H, ArH). ^{13}C NMR (CDCl$_3$): δ 14.00, 22.56, 25.72, 27.18, 27.50, 27.75, 28.32, 29.22, 29.32, 29.44, 29.51, 29.54, 30.20, 30.98, 31.78, 36.10, 36.33, 36.49, 36.69, 42.66, 42.98, 45.13, 121.80, 127.91, 137.86, 150.11, 171.21, 172.06, 172.16, 172.34, 172.72, 173.50, 173.85. IR (KBr): $\nu = 3315$, 2919, 2850, 1758, 1636, 1557, 1467, 1364, 1252, 1199, 1167, 1120, 963, 721. MS (MALDI-TOF): calcd for $C_{168}H_{300}N_{18}O_{22}$, 2924.3. Found: 2925.3, 2947.5 ($M + Na^+$), 2964.2 ($M + K^+$). Anal. Calcd for $C_{168}H_{300}N_{18}O_{22}$: C, 69.00; H, 10.34; N, 8.67. Found: C, 68.98; H, 10.55; N, 8.97.

Synthesis of ***DD4***. A chloroform solution (10 mL) of dendron **A** (1.00 g, 0.72 mmol) was added to a solution of 2,2-bis(4-hydroxyphenyl)propane (54.8 mg, 0.24 mmol), DMAP (22.0 mg, 0.18 mmol), and DIPC (23.3 mg, 1.42 mmol) in chloroform (10 mL). After the solution was stirred for 6 h at 45 °C, the solvent was evaporated under reduced pressure. The product was purified by recrystallization from THF (yield 0.35 g, 49%). mp 128 °C.

^{1}H NMR (CDCl$_3$): δ 0.85 (t, $J = 5.6$ Hz, 24H, $CH_3{-}CH_2{-}$), 1.22 (br s, 128H, $-CH_2-$), 1.53−1.86 (br, 32H, $-CH_2{-}CH_2{-}CO-$, $-NH{-}CH_2{-}CH_2{-}CH_2{-}N-$), 2.10−2.16 (m, 16H, $-CH_2{-}CO-$), 2.50−2.74 (br, 20H, $-CO{-}CH_2{-}CH_2{-}COO$, $-CO{-}CH_2{-}CH_2{-}COO{-}Ar$), 2.88 (t, $J = 4.0$ Hz, 4H, $-CO{-}CH_2{-}CH_2{-}COO{-}Ar$), 3.09−3.38 (br, 48H, $-CO{-}NH{-}CH_2-$, $-CH_2{-}N{-}CO-$), 6.94 (d, $J = 8.0$ Hz, 4H, ArH), 7.17 (d, $J = 8.0$ Hz, 4H, ArH). ^{13}C NMR (CDCl$_3$): δ 14.02, 22.59, 25.74, 27.21, 27.59, 28.03, 28.37, 29.25, 29.35, 29.47, 29.54, 29.57, 31.08, 31.82, 36.11, 36.34, 36.52, 36.72, 42.35, 42.68, 45.16, 120.82, 127.66, 147.80, 148.50, 171.24, 172.09, 172.19, 172.37, 172.73, 173.49, 173.88. IR (KBr): $\nu = 3314$, 2918, 2850, 1753, 1637, 1552, 1467, 1364, 1252, 1206, 1172, 1145, 963, 721. MS (MALDI-TOF) calcd for $C_{171}H_{306}N_{18}O_{22}$, 2966.4. Found, 2989.5 ($M + Na^+$). Anal. Calcd for $C_{171}H_{306}N_{18}O_{22}$: C, 69.24; H, 10.40; N, 8.50. Found: C, 68.94; H, 10.30; N, 8.28.

Results and Discussion

Table 1. Gelation of Dimeric Dendrons in Organic Solvents[a]

	MC	THF	CHCl$_3$	*n*-octanol (T_c)	*n*-decanol (T_c)
DD1	G	G	S	G**(53−54)	G (54−55)
DD2	G	G	S	G* (52−53)	G (52−53)
DD3	G	G	S	G* (53−54)	G (52−53)
DD4	G	G	S	S	S

[a] G: gel. S: soluble. G*: 3 wt % (w/v). G**: 1 wt % (w/v). The concentration of gelation is 2 wt %. T_c: clearing temperature (°C).

The dimeric dendrons with amide branch units, alkyl periphery, and the aromatic bridging units such as naphthyl, biphenyl, or isopropylidenebiphenyl were synthesized as described in Scheme 1. The dendron dimers were prepared by the coupling of aromatic diols (**1**−**4**) with dendron **A**, which was synthesized via a convergent method as reported previously.[18] The diol compound **1** was prepared by the reaction of 1,5-dihyroxynaphthalene with 2-bromoethanol in DMF in the presence of potassium carbonate. Dendron **A** was reacted with diol compounds **1**, **2**, **3**, and **4** in the presence of DIPC and DMAP in chloroform to produce dimeric dendrons **DD1**, **DD2**, **DD3**, and **DD4**, respectively, as described in Scheme 1. The structural characterizations were carried out by using ^{1}H NMR, ^{13}C NMR, FT-IR, MALDI-TOF, and elemental analysis.

The self-organization characteristics of the dendrons in various organic media were investigated. As summarized in Table 1, dimeric dendrons **DD1**, **DD2**, and **DD3** formed immobile gels in methylene chloride, THF, *n*-octanol, and *n*-decanol. In particular, **DD1** formed gels in *n*-octanol even at 1.0 wt % solution, while the other dendrons, **DD2** and **DD3**, needed higher concentration to form a gel. The formation of self-assembled gels was thermoreversible in organic media. For example, the gels of **DD1** in *n*-octanol redissolved at 53−54 °C, **DD2** at 52−53 °C, and **DD3** at 53−54 °C, respectively. The clearing temperatures of the gels in *n*-decanol were similar to those of the gels in *n*-octanol, i.e., 54−55 °C for **DD1**, 52−53 °C for **DD2**, and 52−53 °C for **DD3**. After cooling to room temperature, all the solutions turned into immobile gels after several days. However, the dendron dimer with the isopropylidenebiphenyl central bridging unit, **DD4**, did not form gels in *n*-octanol and *n*-decanol. This can be attributed to the steric crowded kink structure of the central isopropylidenebiphenyl group which could hinder the packing process of the dendritic building blocks. In our previous studies on the self-assembly of dendrons containing amide branches with alkyl tails, it was shown that the hydrogen bonding of the amide branches and the van der Waals interactions of the alkyl periphery are the main driving force to allow the self-organization.[18,19] However, our results discussed above suggest that the structure of the central bridge of the dimeric dendron is another critical parameter to control the self-organization of the dimeric building blocks.

The structures of the dry gels were investigated by using transmission electron microscopy (TEM) and X-ray diffraction (XRD) techniques. The TEM images of dry gel of **DD1** from *n*-octanol in Figure 1 exhibited well-defined and continuous ribbons, while the other two gels of **DD2** and **DD3** from *n*-octanol revealed relatively short strands of fibrils. The X-ray diffractogram of **DD1** gel shown in Figure 2 revealed a lamellar structure with interlamellar spacing of 70 Å. Therefore, the TEM images of **DD1** gel in Figure 1 together with the XRD

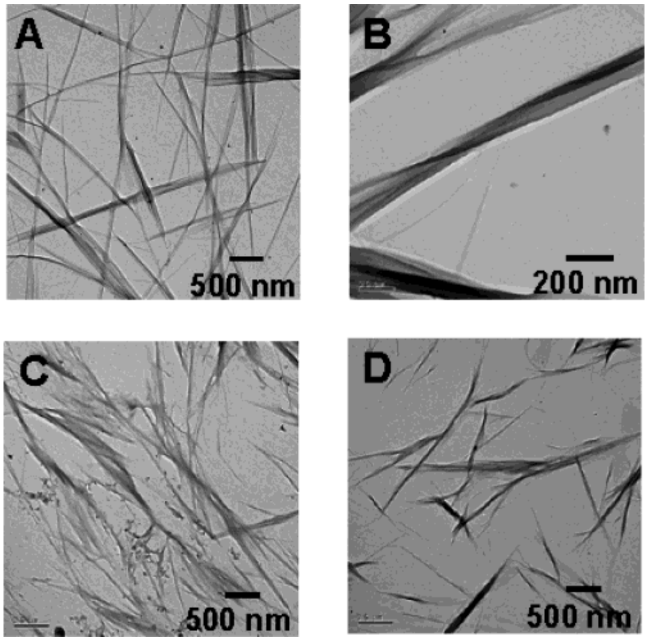


Figure 1. TEM images of gels of **DD1 (A** and **B)**, **DD2 (C)**, and **DD3 (D)**.

result suggest that **DD1** forms lamella nanoribbons. In Figure 1B, a twisted form of a lamella nanoribbon is observed. In contrast, **DD2** and **DD3** dimers exhibited the hexagonal columnar structure with the column diameter of 62.0 Å for **DD2** and 63 Å for **DD3**, respectively. Considering the dimensions of the fully stretched form of dimeric dendrons, **DD1** (84 Å), **DD2** (72 Å), and **DD3** (73 Å), the lamellar layer thickness or cylindrical column diameter is associated with the single dimeric dendron which is the primary building block in the packing process. 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.

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 **DD1** in *n*-octanol did not form any gel. However, dimeric dendron **DD1** 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 **DD1**. Figure 3A shows a TEM image of the self-assembled structure of **DD1**. It is notable that the width of each nanostack ranging from ∼10 nm to ∼40 nm is uniform throughout the entire length of the assembled structure. The AFM images in Figure 3B and 3C 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 3B and 3 nm in Figure 3C. Considering the

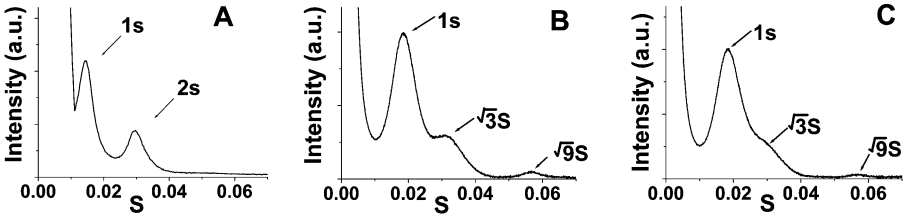
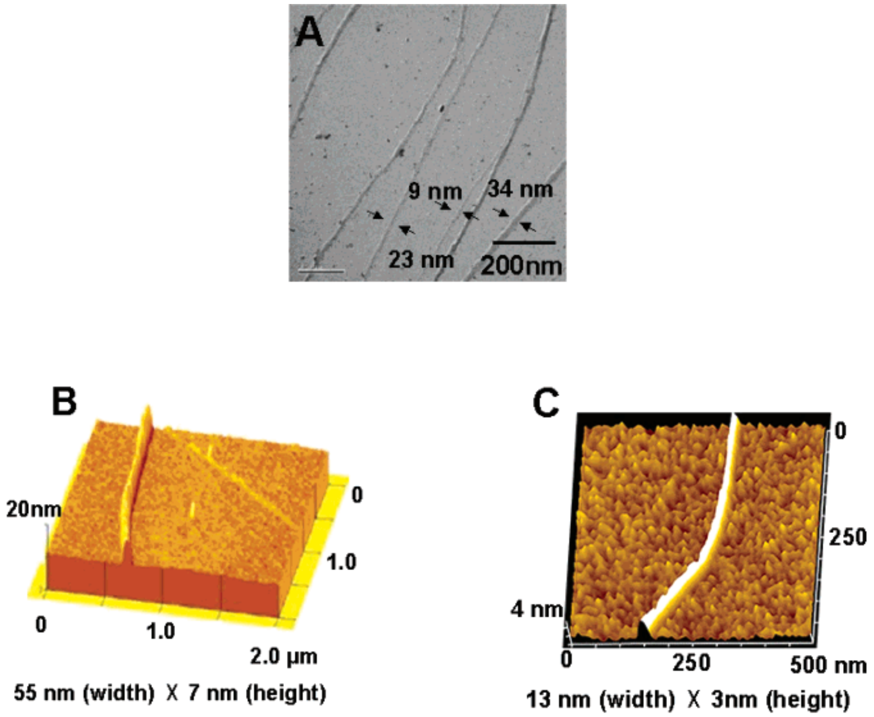


Figure 2. XRD data of **DD1 (A)**, **DD2 (B)**, and **DD3 (C)**. S (Å^{-1}) = ($n\lambda/2 \sin \theta$).



55 nm (width) X 7 nm (height)

13 nm (width) X 3nm (height)

Figure 3. TEM image of self-assembled **DD1** on a carbon-coated copper grid in 0.1 wt % *n*-octanol (A) and AFM images of **DD1** stacks on silicon wafer [(B) and (C)].

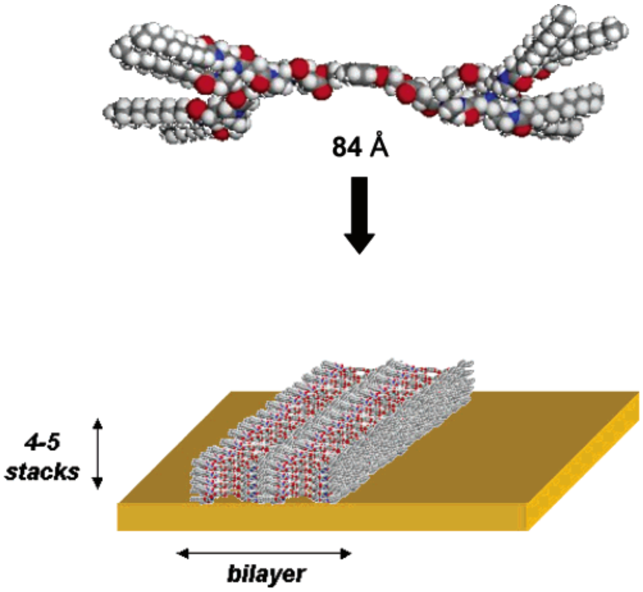


Figure 4. Molecular graphic presentation of **DD1** stacks on silicon wafer in Figure 3B.

dimension of **DD1** (84 Å) in the direction of long molecular axis, **DD1** 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 the in-plane direction, and the building blocks are assembled together to form a lamellar stack with a uniform width and a length of several micrometers. For example, the ~13 nm wide nanostack with 3 nm height in Figure 3C is formed by stacking of the two dimeric dendrons in the transverse direction and 4−5 building blocks in the vertical direction, which is schematically illustrated in Figure 4. The uniform line width of ~55 nm in the AFM image (Figure 3B) is equivalent to about 8 layers of dimer building block in the transverse direction, and the height of ~7 nm corresponds to 10−11 building blocks stacked in the vertical direction. The favored growth of the self-assembly in the direction along the side of the dimeric molecules resulted in the long nanoribbons of several micrometers.

On the contrary, other dimeric dendrons **DD2**, **DD3**, and **DD4** in a dilute solution (0.1 wt %) did not form assembled structures on the solid surfaces, possibly due to the different packing tendency of these dendritic building blocks. Dendrons **DD2** and **DD3** form columnar structures, as evidenced from the dry gel obtained from the 2 wt % *n*-octanol solution. The surface boundary condition in the self-assembly of the dimeric dendrons would be favorable for a lamellar arrangement of the building blocks, but not for a cylindrical organization. The kinked structure of the isopropylidenebiphenyl moiety in the core bridge of **DD4** would be unfavorable for the self-organization not only in the ordinary 2 wt % *n*-octanol solution but also at the solid−liquid interface.

Conclusions

Dimeric dendrons consisting of amide branches and alkyl periphery with the various aromatic core bridging units were synthesized. The supramolecular structures of the dry gel induced via self-assembly were highly dependent on the architecture of the aromatic bridging units at the core. The dimeric dendrons in *n*-octanol (2 wt %) formed lamellae or columnar arrays depending on the structural differences of the central bridging units of the dimers. In addition, extremely well-defined nanoribbons of **DD1** dimer with the 1,5-naphthoxy bridging unit were obtained on the solid surface when the solid surface was exposed to the very dilute *n*-octanol solution of **DD1** (0.1 wt %). On the contrary, the 0.1% solution of **DD1** did not self-assemble under the ordinary conditions. The noncovalent interactions such as hydrogen bonding between amide branch units and van der Waals interactions of alkyl periphery of the dendritic branches are important for the construction of organized structures. In addition, the dimeric architecture is a critical factor in determining the nature of the packing process in the self-assembly of the dendritic building blocks.

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