Supramolecular Nanofiber Formation of Macrocyclic Dendrimer

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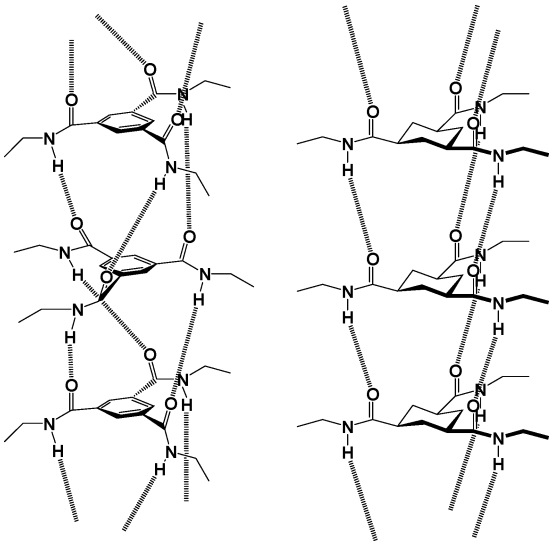
ABSTRACT: Novel macrocyclic dendrimers (Scheme 2), having two *cis*-1,3,5-cyclohexanetricarboxamide (**1**) or 1,3,5-benzenetricarboxamide units (**3**) in their core, were synthesized, and their self-assembly behaviors were evaluated in solution. Infrared spectroscopy of *cis*-1,3,5-cyclohexanetricarboxamide cored dendrimer (**1**) in $CHCl_3$ indicated that formation of strong hydrogen-bonding interactions is taking place among the core units. The ^{1}H NMR spectrum of **1** in $CDCl_3$ showed broadenings of all the peaks, which were sharpened by adding one drop of CF_3CO_2H. GPC analysis showed the formation of self-assembled particles having ultrahigh molecular weight, whose average diameter was evaluated as about 140 nm by DLS measurement. AFM observation of the cast on mica film showed that **1** forms a fibrous assembly of uniform thickness with a diameter of 6 nm. In sharp contrast to **1**, 1,3,5-benzenetricarboxamide units cored dendrimer (**3**) did not form a fibrous assembly under identical conditions because of the twisted arrangement of the core units.

Introduction

Secondary and tertiary structures of natural macromolecules such as polypeptides, polynucleotides, and polysaccharides are mostly controlled by noncovalent interactions. These interactions are very important in macromolecular chemistry where hydrogen bonding and other weak reversible interactions can make a major contribution to designing new polymeric architectures. In recent years, a number of concepts have been proposed that use noncovalent interactions for the construction of a supramolecular polymeric assembly.[1] To obtain a linear type supramolecular polymeric assembly,[2] it is desirable to have interactions sufficiently strong, directional, and sufficiently reversible to alternate covalent bonds. *cis*-1,3,5-Cyclohexanetricarboxamide[3] and 1,3,5-benzenetricarboxamide[4] units are potential scaffolds for the construction of supramolecular polymeric assembly systems. Both of them exhibit a discotic supramolecular assembly via intermolecular hydrogen bonding (Scheme 1). *cis*-1,3,5-Cyclohexanetricarboxamide has three unidirectional amide units in which the *cis*-1,3,5-cyclohexanetricarboxamide derivatives form a physical gel or viscoelastic fluid depending on the solvents.[3] 1,3,5-Benzenetricarboxamide derivatives also form unidirectional hydrogen bonds with a typical helical arrangement within the supramolecular assembly structure.[4]

On the other hand, dendrimers are nanometer-sized hyperbranched macromolecules with well-predictable three-dimensional shapes and potential building blocks for the construction of organized functional materials.[5,6] Since dendrimers have unique three-dimensional shapes, solution properties are predominantly dependent on the peripheral functionalities, and core structures are possibly insulated from the outer environment.[7] From this point of view, three-dimensional warping of the supramolecular assembly system using dendrimer frameworks has potentials for providing a very interesting aspect. In this paper, we demonstrate a novel fibrous supramolecular assembly[8] formation of a dendritic macrocycle with a significantly high molecular weight attributable to intermolecular hydrogen bonding in solution.

Scheme 1. Hydrogen-Bonding-Mediated Self-Assembly Structures of *cis*-1,3,5-Cyclohexanetricarboxamide (Right) and 1,3,5-Benzenetricarboxamide (Left)



Results and Discussion

Synthesis and Characteristic. A series of poly(benzyl ether) dendrimers (Scheme 2) having macrocyclic cores, which contain two *cis*-1,3,5-cyclohexanetricarboxamide or 1,3,5-benzenetricarboxamide units, were synthesized and characterized by ^{1}H NMR and MALDI−TOF−MS spectroscopy. Details of the synthetic methodology for the macrocyclic dendrimers are shown in Scheme 3. First, phthalimide was introduced to 3,5-di-*tert*-butyldiphenylsilyloxybenzyl alcohol (**4**) according to the Mitsunobu's coupling reaction.[9] Then, **5** thus obtained was reacted with Frechet's dendron bromide (**6**)[10] to get phthalimide cored dendron (**7**), which was changed to amine core dendrimer (**8**) using hydrazine. Tris-*p*-nitrophenyl-*cis*-1,3,5-cyclohexane tri-

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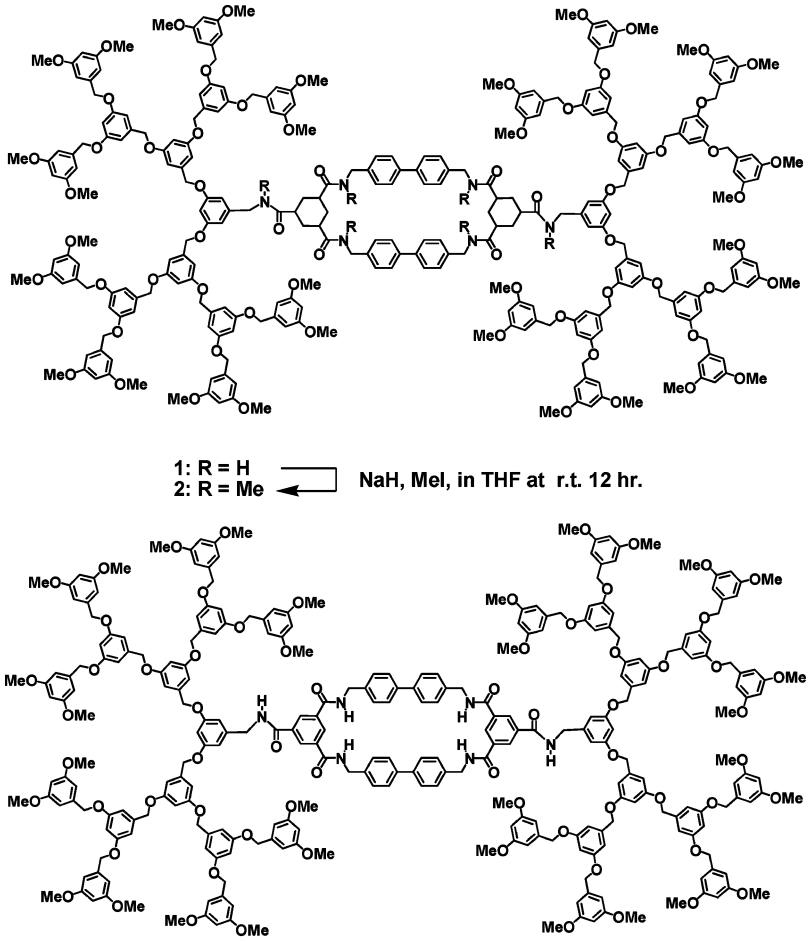
Scheme 2. Macrocyclic Dendrimers



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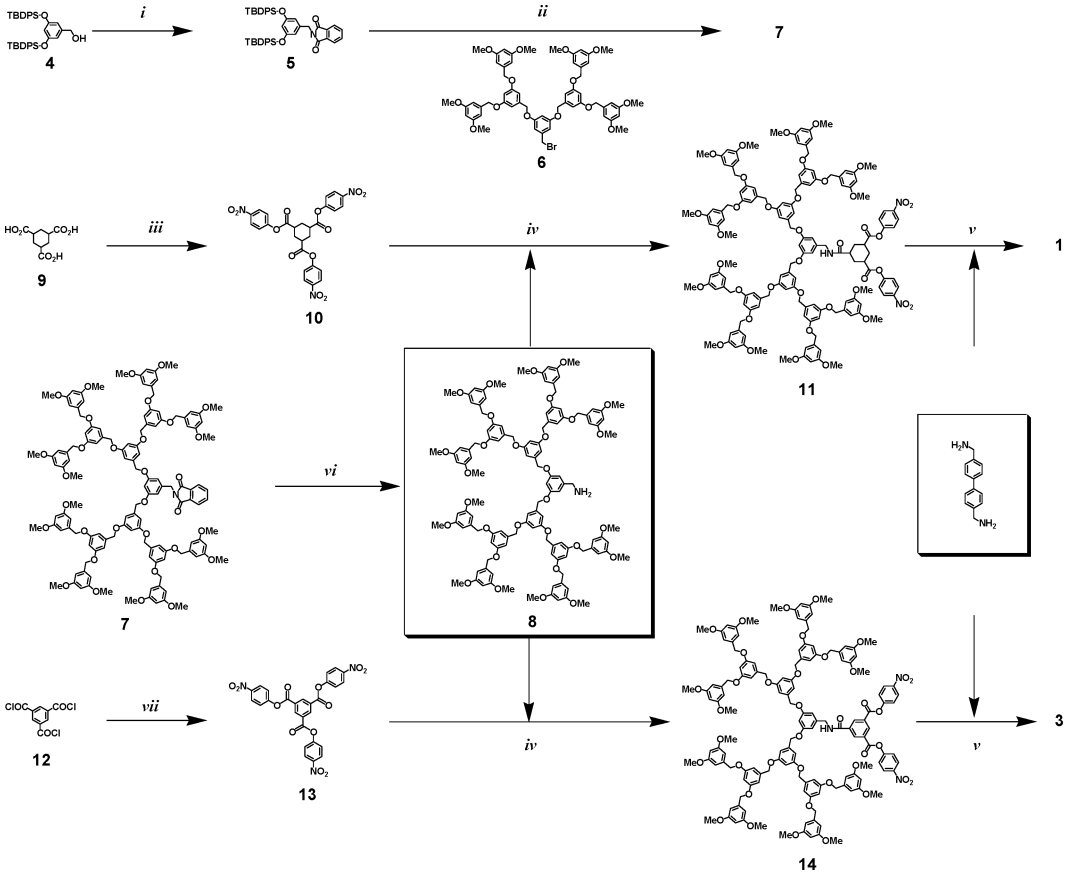
carboxylate (**10**) prepared by dicyclohexyl carbodiimide mediated condensation of *p*-nitrophenol and *cis*-1,3,5-cyclohexanetricarboxylic acid (**9**). Tris-*p*-nitrophenyl-benzene tricarboxylate (**13**) was prepared by condensation reaction of trimesoyl chloride (**10**) and *p*-nitrophenol. And then, **8** was reacted with **10** or **13** to get precursors for the macrocycle **11** or **14**, respectively. **11** or **14** thus obtained was reacted with 4,4′-biphenyldiaminomethyl to get the corresponding macrocyclic dendrimers **1** and **3**, respectively. **1** has two different isomeric structures because of the orientation of amide bonds of core cyclohexyl units. However, all the evaluation of **1** was performed as a mixture of the two isomers because the two isomers were not distinguishable or separable by the conventional analytic methods. The N-methylated derivative macrocyclic dendrimer (**2**) was prepared from **1** by alkali mediated coupling reaction with MeI. All the macrocyclic dendrimers were highly soluble to the halogenated solvents or polar aprotic solvents, such as $CHCl_3$, CH_2Cl_2, CH_2ClCH_2Cl, DMF, DMSO, etc.

Spectroscopic Studies of Macrocyclic Dendrimers. The infrared spectrum (IR) of $CHCl_3$ solution of **1** (5.0 mM) displayed relatively broad absorption bands at 3290 cm^{-1}, with sharp bands at 1640 and 1550 cm^{-1}, which are characteristics of stretching vibrations of N−H, amide I, and amide II, respectively.[11] These spectral characteristics indicate that the amide groups of **1** are hydrogen bonded to each other despite diluted concentration in solution. Very interestingly, however, the IR spectrum of $CHCl_3$ solution of **3** (5.0 mM) exhibited patterns quite different from that of **1**, where the N−H stretching vibration band was exhibited at 3390 cm^{-1} and stretching vibrations of amide I and II were exhibited at 1660 and 1518 cm^{-1}, respectively (Figure 1), indicating no hydrogen bonding.

On the other hand, the ^1H NMR spectrum of **1** in $CDCl_3$ (1 mM) displayed significantly broad bands of all the characteristic peaks (Figure 2a), whereas the ^1H NMR spectrum of **3** in $CHCl_3$ displayed simple sharp peaks. These observations again indicate possible formation of molecular assembly via hydrogen bonding, which leads to the broadening of ^1H NMR signals of **1** because of the restriction of conformational change in $CDCl_3$. It is interesting that all the peaks of **1** in $CDCl_3$ were changed to simple sharp peaks to be identified by the addition of a drop of CF_3CO_2H, a strong hydrogen-bonding acceptor (Figure 2b). These changes indicate that the CF_3CO_2H molecules dissociated the assembled dendrimers.

Dynamic Light Scattering (DLS) and Gel Permeation Chromatography (GPC). Figure 3 shows the histogram profile of DLS result of **1** (0.06 mM) in $CHCl_3$, which indicates the formation of quite a large particles. The average diameter of the particles was evaluated as 142 ± 48 nm. However, **3** has insufficient light scattering intensity in the DLS measurement to be detected as particles. Therefore, the average molecular weight of particles was examined by GPC. The result showed that **1** exhibited a peak at extremely high molecular weight region (Figure 4a), eluting at the time of the exclusion limit of a column (TSKgel GMHXL

Scheme 3. Synthesis of Macrocyclic Dendrimers[a]



[a] Reagents and reaction conditions: (*i*) DEAD, PPh_3, phthalimide, in THF at 0 °C for 1 h and 25 °C for 11 h; (*ii*) KF, 18-crown-6 ether, **6**, in acetone reflux 3 h; (*iii*) DCC, *p*-nitrophenol, in DMF at 0 °C for 1 h and 25 °C for 12 h; (*iv*) in DMF at 60 °C for 36 h; (*v*) in DMF at 60 °C for 72 h; (*vi*) $H_2NNH_2 \cdot H_2O$ in THF/EtOH (1/1) reflux 12 h; (*vii*) *p*-nitrophenol, 1,3,5-collidine, in DMF at 0 °C 1 h and 25 °C 12 h.

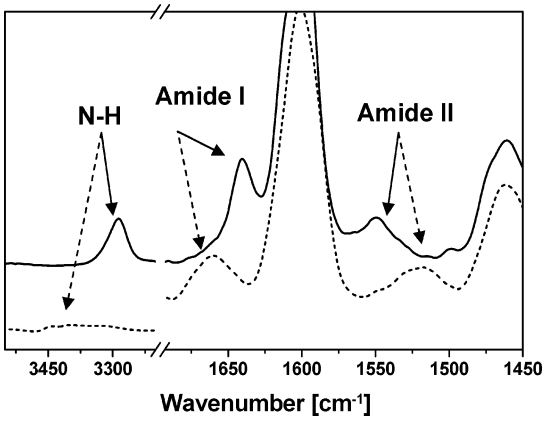


Figure 1. FT-IR spectra of **1** (solid) and **3** (dotted) in $CHCl_3$.

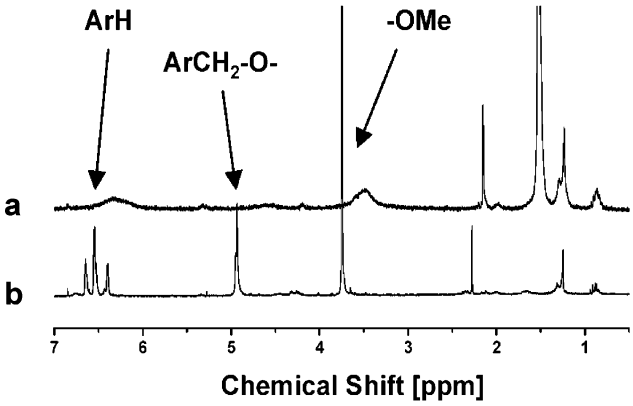


Figure 2. ^1H NMR spectra of **1** in $CHCl_3$ (a) and in TFA included $CHCl_3$ (b).

exclusion limit: $4 \times 10_8$, eluent: $CHCl_3$). Interestingly, when the solution containing a small amount of CF_3CO_2H was eluted, the retention time was significantly increased (Figure 4b). This observation agrees with the ^1H NMR result. As a non-hydrogen-bonding model compound, the N-methylated derivative (**2**) was newly synthesized and unambiguously characterized by ^1H NMR and MALDI−TOF−MS spectroscopy. The GPC profile of **2** exhibited a single sharp peak with the same retention time as the solution of **1** containing CF_3CO_2H, indicating that the addition of CF_3CO_2H dissociated the assembled macrocyclic dendrimers (Figure 4c). Considering the number of hydrogen-bonding sites, **3** also has a possibility to form a supramolecular assembly. However, IR and ^1H NMR spectra revealed that it was hard for **3** to form hydrogen bonds. GPC analysis of **3** also exhibited a single sharp peak with the same retention time as **2**, indicating that **3** does not associate under the GPC condition (Figure 4d).

Atomic Force Microscopic (AFM) Observation of Macrocyclic Dendrimer. To find the morphology of the dendrimer assembly, the $CHCl_3$ solution of macrocyclic dendrimers was spin-coated on a mica film and then subjected to AFM. Clearly **1** formed as entangled fibrous structures (Figure 5a). With sufficient dilution

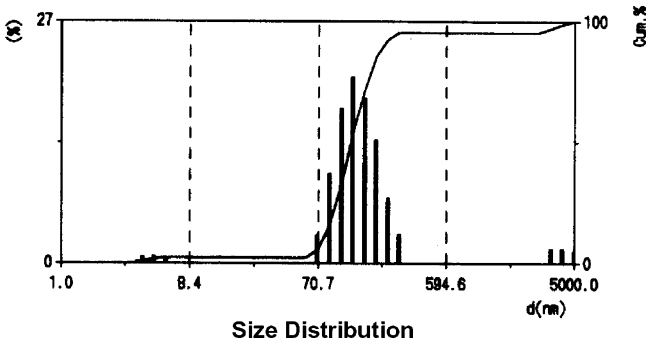


Figure 3. Histogram analysis of DLS measurement of **1** in $CHCl_3$ (0.06 mM).

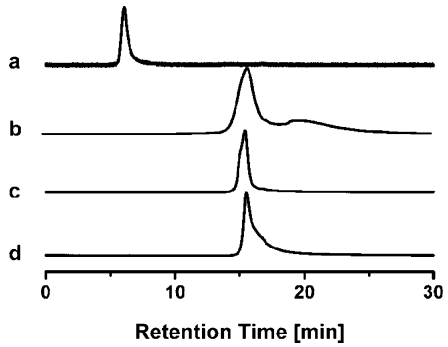


Figure 4. GPC profiles of **1** (a, b: including TFA), **2** (c), and **3** (d).

of the solution, we could get a single filament of the assembly (Figure 5b,c). This fibrous structure has a homogeneous thickness of 6 nm, which agrees with the computer-aided calculated diameter of the dendrimer, indicating a linear supramolecular assembly formation. In contrast to the result of **1**, the AFM results of **2** or **3** showed a clearly different feature. Under identical conditions, **2** or **3** exhibited only an agglomerated mass. Even though both core units of **1** or **3** have six amide bonds, with a potential to form a self-assembled supramolecular structure, only **1** formed the supramolecular polymeric assembly. It is assumed that 1,3,5-benzenetricarboxamide derivatives are twisted into a helical arrangement in the most stable hydrogen-bonding mode; thus, the two 1,3,5-benzenetricarboxamide units in the core of **3** cannot form hydrogen bonds simultaneously among the core units to form a linear type supramolecular polymeric assembly. In sharp contrast, the two *cis*-1,3,5-cyclohexanetricarboxamide units in the core of **1** can form the hydrogen bonds simultaneously to reinforce each other, so that **1** exhibits an ultrahigh molecular weight and a fibrous assembly formation even in solution.

Thermal Stability of Assembly. Variable-temperature ^1H NMR measurement was performed to check the thermal stability of hydrogen bond of self-assembled dendrimers (Figure 6). At room temperature, the ^1H NMR spectrum of **1** in *o*-dichlorobenzene-d_4 displayed broad bands of all the peaks, similar to that in $CDCl_3$. On raising the temperature, these broad bands remained up to 150 °C. At 150 °C, all the peaks sharpened enough to be identified. For comparison with the behavior in solution, the thermal behavior of the dried samples (**1** and **2**) was studied by differential scanning calorimetry (DSC). Each sample was prepared by evaporation from its $CHCl_3$ solution. Upon heating at a rate of 10 °C min^{-1} from 0 °C, both samples exhibited a single endothermic thermal transition, but the temperature was significantly different. **1** exhibited an endothermic transition at 144 °C ($\Delta H = -39.7$ kJ mol^{-1}), a much higher temperature than that of **2**, which appeared at 60 °C ($\Delta H = -26.6$ kJ mol^{-1}). The high transition temperature of **1** might be a result of the hydrogen-bonding interaction of amide units. Notably, the transition temperature of **1** was very close to the sharpening temperature of the ^1H NMR spectrum, revealing a very interesting aspect that the self-assembly of **1** remarkably stables even in solution.

Synthesis of Low Molecular Weight Model Compound. In our attempt to prepare macrocyclic compound without dendritic substitution, benzylamine, instead of **8**, was reacted with **10** to prepare a precursor for the macrocycle (Scheme 4). Benzylamine-substituted cyclohexane derivative (**15**) thus obtained was reacted with 4,4′-diphenyldiaminomethyl in the identical condition to that for **1**. Unlike the case of **1**, the reaction mixture formed an insoluble mass. By the MALDI−TOF−MS analysis of this mass, the existence of a dimeric macrocycle was definitely confirmed. However, purification of macrocyclic compound was impossible because of the disordered network formed by hydrogen bonding. This means that the dendritic substitution is important for the formation of a soluble assembly and might control the ordered interaction among the core amide groups. Therefore, the supramolecular assembly formation of large dendrimer possibly occurred by the three-dimensional warping of core groups by the dendritic wedges, which may prevent a disordered network formation and possibly stabilize hydrogen-bonding interactions because of the hydrophobic characteristics of the dendritic wedge in addition to possible van der Waals interaction.

Experimental Section

Preparation of Dendrimers: Chemicals. Chemicals were used as received from commercial sources (Aldrich, TCI). Solvents were freshly distilled according to literature methods.

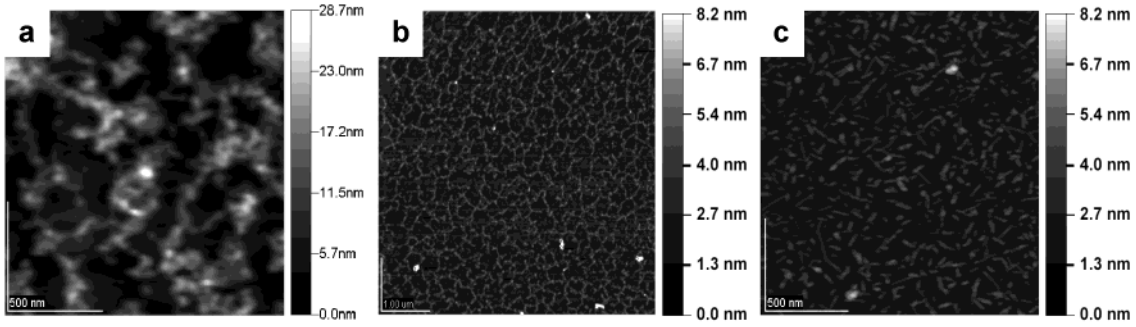


Figure 5. AFM image of fibrous assembly of **1**.

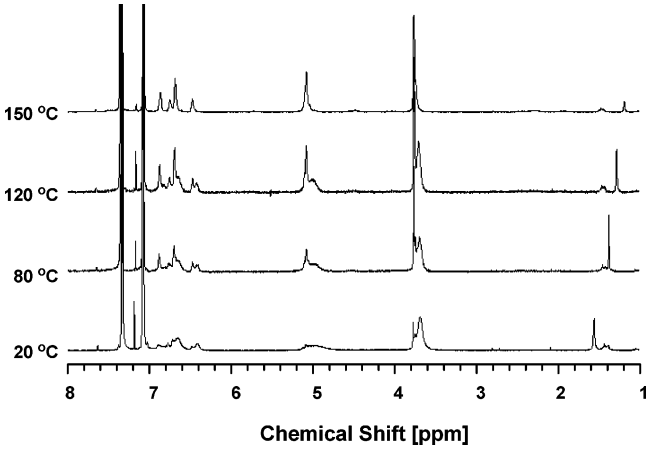


Figure 6. ^{1}H NMR spectra of **1** in *o*-dichlorobenzene at different temperatures.

5. To a tetrahydrofuran (THF) solution (60 mL) of a mixture of **4** (9.0 mmol), phthalimide (10.8 mmol), and triphenylphosphine (10.8 mmol) was added 40% toluene solution of diethylazodicarboxylic acid (DEAD; 10.8 mmol), and the resulting mixture was stirred under Ar at 0 °C for 1 h and 25 °C for 11 h. The reaction mixture was then evaporated to dryness, and the residue was chromatographed on silica gel with CH_2Cl_2 as eluent, where the second fraction was collected and evaporated to give **5** as transparent oil in 87% yield. MALDI−TOF−MS for $C_{48}H_{48}O_4Si_2$ *m/z*: calcd: 745 [M^+]; found: 745. ^{1}H NMR ($CDCl_3$): δ 0.94 (s, 18H; *tert*-Bu), 4.47 (s, 2H; $-CH_2-$), 6.04 (t, 1H; *p*-H in C_6H_3), 6.30 (d, 2H; *o*-H in C_6H_3), 6.03−7.48 (m, 20H; $-C_6H_5$), 7.69 and 7.76 (m, 4H, C_6H_4 in phthalimide).

7. A acetone solution (20 mL) of a mixture of **5** (0.8 mmol), **6** (1.6 mmol), and 18-crown-6 (0.2 mmol), containing KF (1.9 mmol), was refluxed under Ar for 3 h. The reaction mixture was poured into water (50 mL) and extracted three times with ethyl acetate (50 mL). The combined extracts were dried over anhydrous $MgSO_4$ and chromatographed on silica gel with CH_2Cl_2 as eluent, where the third fraction was collected and freeze-dried from benzene to give **7** as a white solid in 90% yield. MALDI−TOF−MS for $C_{129}H_{127}NO_{32}$ *m/z*: calcd: 2241 [M + K^+]; found: 2243. ^{1}H NMR ($CDCl_3$): δ 3.74 (s, 48H; −OMe), 4.73 (s, 2H; $-CH_2-$ N), 4.93 (s, 28H; $-CH_2-$), 6.35−6.65 (m, 45H; *o*, *p*-H in C_6H_3), 7.62 and 7.77 (m, 4H; C_6H_4 in phthalimide).

8. To a THF/EtOH (1:1) solution (20 mL) of **7** (0.72 mmol) was added hydrous hydrazine (10 mL), and the resulting mixture was refluxed for 12 h. Then, insoluble fractions were filtered off from the reaction mixture, and the filtrate was poured into water (100 mL) and extracted three times with ethyl acetate (50 mL). The combined extracts were dried over anhydrous $MgSO_4$ and evaporated to dryness and then freeze-dried from benzene to give **8** as a white solid in quantitative yield. MALDI−TOF−MS for $C_{121}H_{125}NO_{30}$ *m/z*: calcd: 2073 [M^+]; found: 2075. ^{1}H NMR ($CDCl_3$): δ 3.71 (s, 48H; −OMe), 4.78 (m, 28H, $-CH_2-$), 4.95 (s, 2H; $-CH_2-$N), 6.31−6.63 (m, 48H; *o*, *p*-H in C_6H_3).

10. To a DMF solution (10 mL) of **9** (4.6 mmol) and *p*-nitrophenol (16.1 mmol) was added dicyclohexylcarbodiimide (DCC; 16.1 mmol), and the reaction mixture was vigorously stirred at 0 °C for 1 h and 25 °C for 12 h. Insoluble fractions were filtered off from the reaction mixture, and the filtrate was evaporated to dryness. Then, the resulting mixture was washed with cold ethanol and recrystallized twice in hot ethanol to get **10** as a white crystalline solid in 32% yield. MALDI−TOF−MS for $C_{27}H_{21}N_3O_{12}$ *m/z*: calcd: 579 [M^+]; found: 579. ^{1}H NMR ($CDCl_3$): δ 1.90 (q, 3H; equatorial H of cyclohexyl), 2.69 (m, 3H; axial H of CH_2 in cyclohexyl), 2.91 (m, 3H; CH in cyclohexyl), 4.27 and 8.28 (m, 12H; H in nitrophenyl).

11. A DMF solution (10 mL) of a mixture of **10** (0.43 mmol) and **8** (0.14 mmol) was vigorously stirred under Ar at 60 °C for 36 h. The reaction mixture was poured into water and extracted with ethyl acetate. The combined extracts were washed three times with an aqueous solution of 1 M NaOH and evaporated to dryness. The resulting mixture was then subjected to recyclable preparative GPC, where the first fraction was collected and freeze-dried from benzene to give **11** as a white solid in 72% yield. MALDI−TOF-MS for $C_{142}H_{141}N_3O_{39}$ *m/z*: calcd: 2514 [M + H^+]; found: 2514. ^{1}H NMR ($CDCl_3$): δ 1.56−2.51 (m, 9H; cyclohexyl), 3.67 (s, 48H; −OMe), 4.23 (d, 2H; CH_2-N), 4.84 (s, 28H; $-CH_2-$), 5.86 (t, 1H; N−H), 6.28−6.56 (m, 45H; *o*, *p*-H in C_6H_3), 7.08 and 8.06 (m, 8H; C_6H_4 in *p*-nitrophenyl).

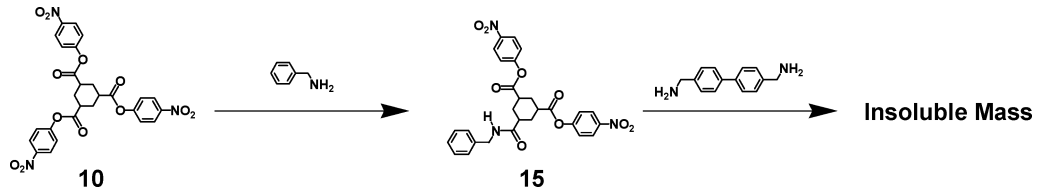
13. To a DMF solution (30 mL) of **12** (13.8 mmol) was added *p*-nitrophenol (48.3 mmol), and the reaction mixture was vigorously stirred at 0 °C for 1 h and 25 °C for 12 h. The reaction mixture evaporated to dryness and washed with cold ethanol and then recrystallized twice in hot ethanol to get **13** as a white crystalline solid in 12% yield. MALDI−TOF-MS for $C_{27}H_{15}N_3O_{12}$ *m/z*: calcd: 573 [M^+]; found: 573. ^{1}H NMR (DMSO-d_6): δ 7.71 and 8.38 (d, 12H; H in *p*-nitrophenyl), 8.91 (s, 3H; C_6H_3).

14. A DMF solution of a mixture of **13** (0.09 mmol) and **8** (0.75 mmol) was vigorously stirred under Ar at 60 °C for 36 h. The reaction mixture was treated in a manner similar to that for the preparation of **11** to give **14** as a white solid in 52% yield. MALDI−TOF-MS for $C_{142}H_{135}N_3O_{39}$ *m/z*: calcd: 2529 [M + Na^+]; found: 2531. ^{1}H NMR ($CDCl_3$): δ 3.73 (s, 48H; −OMe), 4.50 (d, 2H; CH_2-N), 4.89 (m, 30H; $-CH_2-$), 6.34−6.58 (m, 45H; *o*, *p*-H in C_6H_3 of dendritic wedge), 7.36 and 8.21 (d, 8H; C_6H_4 in *p*-nitrophenyl), 8.76 and 8.95 (m, 3H; C_6H_3 in core).

15. A DMF solution of a mixture of **10** (0.69 mmol) and benzylamine (0.35 mmol) was vigorously stirred under Ar at 60 °C for 3 h. The reaction mixture was treated in a manner similar to that for the preparation of **11** to give **15** as white solid in 75% yield. MALDI−TOF-MS for $C_{28}H_{25}N_3O_9$ *m/z*: calcd: 547 [M^+]; found: 547. ^{1}H NMR ($CDCl_3$): δ 1.84−2.76 (m, 9H; cyclohexyl), 4.45 (d, 2H; CH_2-N), 5.82 (t, 1H; N−H), 7.24−7.34 (m, 5H; C_6H_5), 7.26 and 8.06 (d, 8H; C_6H_4 in *p*-nitrophenyl).

1. A DMF solution of a mixture of **11** (0.2 mmol) and 4,4′-biphenyldiaminomethyl (0.2 mmol) was vigorously stirred under Ar at 60 °C for 72 h. The reaction mixture was poured into water and extracted with ethyl acetate. The combined extracts were washed three times with aqueous solution of 1 M NaOH and evaporated to dryness. The resulting mixture was then subjected to recyclable preparative GPC, where the first fraction, which is exceeded in the exclusion limit of the column, was collected and freeze-dried from benzene to give **11** as a white solid in 42% yield. MALDI−TOF−MS for $C_{288}H_{294}N_6O_{66}$ *m/z*: calcd: 4918 [M + Na^+]; found: 4919. ^{1}H NMR (TFA included $CDCl_3$): δ 1.65−2.37 (m, 18H, H in cyclohexyl) 3.75 (s, 90H, −OMe), 4.26 (m, 12H, CH_2-N), 4.94 (d, 60H; $-CH_2-$), 6.40−6.65 (m, 90H; *o*, *p*-H in C_6H_3), 7.16−7.40 (m, 8H; C_6H_4).

Scheme 4. Synthesis of Low Molecular Nondendritic Model



2. To a THF solution of a mixture of **1** (4 μmol) and NaH (12 μmol) was added MeI (12 μmol) and vigorously stirred under Ar at 25 °C for 12 h. Insoluble fractions were filtered off from the reaction mixture, and filtrate was evaporated to dryness. Then, the resulting mixture was subjected to recyclable preparative GPC, where the first fraction was collected and freeze-dried from benzene to give **2** as a white solid in quantitative yield. MALDI−TOF−MS for $C_{294}H_{306}N_6O_{66}$ *m*/*z*: calcd: 5002 [M + Na^+]; found: 5002. ^{1}H NMR ($CDCl_3$): δ 1.62−2.32 (m, 18H, H in cyclohexyl) 2.89 (s, 18H; N-Me), 3.74 (s, 90H, −OMe), 4.46−4.50 (m, 12H, CH_2−N), 4.93 (d, 60H; −CH_2−), 6.36−6.64 (m, 90H; *o*, *p*-H in C_6H_3), 7.36−7.46 (m, 8H; C_6H_4).

3. A DMF solution of a mixture of **14** (0.03 mmol) and 4,4′-biphenyldiaminomethyl (0.03 mmol) was vigorously stirred under Ar at 60 °C for 72 h. The reaction mixture was treated in a manner similar to that for the preparation of **11** to give **1** as a white solid in 55% yield. MALDI−TOF-MS for $C_{288}H_{282}N_6O_{66}$ *m*/*z*: calcd: 4906 [M + Na^+]; found: 4908. ^{1}H NMR ($CDCl_3$): 3.70 (s, 90H, −OMe), 4.42 (m, 12H, CH_2−N), 4.87 (d, 60H; −CH_2−), 6.32−6.59 (m, 90H; *o*, *p*-H in C_6H_3 of dendritic wedge), 7.17−7.30 (m, 8H; C_6H_4), 8.00 and 8.31 (m, 6H, C_6H_3 in core).

Measurement: Instruments. ^{1}H NMR spectra were measured in $CDCl_3$ or DMSO-d_6 at 21 °C on a JEOL GSX-270 spectrometer operating at 270 MHz, where the chemical shifts were determined with respect to $CHCl_3$ (δ 7.28 ppm) and CH_3SOCD_2H (δ 7.28 ppm). Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI−TOF−MS) was performed on a Bruker model Protein TOF mass spectrometer using 9-nitroanthracene (9NA) or indole acetic acid (IAA) as a matrix. FT-IR spectra were recorded on a JASCO model FT/IR 610. Dynamic light scattering (DLS) measurements were carried out using by an Otsuka model DLS-700 instrument at 25 °C.

GPC Measurements. Analytical GPC was carried out on a TOSOH model HLC-8020 equipped with TSKgel GMH_{XL} column as eluent of $CHCl_3$ at 25 °C. Recyclable preparative GPC was carried out on a JAI model LC-908 equipped with JAIGEL 2H and JAIGEL 3H column as eluent of $CHCl_3$ at 25 °C.

Atomic Force Microscopy (AFM). AFM was carried out on a JEOL model JSPM 4200. One drop of dilute solution of **1** (0.2 mM) in $CHCl_3$ was placed on a freshly cleaved mica surface and spin-cast for AFM observation.

Conclusion

In our demonstration of the self-assembly of dendritic macrocycle, spectroscopic studies revealed that the hydrogen bonding among core amide groups is the driving force for the supramolecular assembly. Ultrahigh molecular weight assembly formation of the macrocyclic dendrimer **1** was observed by GPC and DLS analysis, whereas **3** cannot form a high molecular weight supramolecular assembly, presumably because of the twist arrangement of hydrogen bonds between core 1,3,5-benzenetricarboxamide units. The linear stacking of macrocycle may provide a tubular structure.[12] **1** exhibited a fibrous supramolecular assembly structure by AFM. It is possible that the fibrous supramolecular assembly structure of dendritic macrocycle also have tubular internal space. A novel ultrahigh molecular weight supramolecular polymeric assembly which is composed of macrocyclic units was designed, and its solubility was controlled by introducing of a dendritic architecture.

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