Preparation of Supramolecular Polymers from a Cyclodextrin Dimer and Ditopic Guest Molecules: Control of Structure by Linker Flexibility

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ABSTRACT: Cyclodextrin based supramolecular polymers have been prepared using a β-cyclodextrin dimer and ditopic guest dimers having adamantyl groups. The ditopic guest dimers with various flexibility and adamantyl moieties were prepared to investigate the conformation of supramolecular polymers. The ditopic adamantane guest dimer **C0** has a stiff spacer having a 4,4′-bipyridinium group between adamantyl groups. The ditopic adamantane guest dimers, **C2** and **C3**, have flexible methylene spacers. The ROESY spectra of the β-cyclodextrin dimer with the ditopic adamantane guest dimers showed NOE between the protons of adamantyl substituents and the inner protons of cyclodextrin. The ditopic adamantane guest dimers, **C2** and **C3** formed cyclic supramolecular oligomers in aqueous solutions. The cyclic structure was observed by atomic force microscopy (AFM). On the contrary, the ditopic adamantane guest dimer **C0** formed the high molecular weight supramolecular polymers.

Introduction

Supramolecular polymers are ubiquitous in nature, especially in biological systems. The field of supramolecular chemistry is now extending to supramolecular polymer chemistry.[1−3] There have been some papers on the construction of supramolecular polymers using hydrogen bonding,[4−9] coordination by metals,[10,11] crown ether-ammonium systems,[12,13] and calix[*n*]arenes.[9,14,15] However, in biological systems, more complicated and sophisticated systems of supramolecular polymers, such as viruses, phages, microtubules, and microfilaments, play important roles in realizing unique structures and functions.[16] We have been trying to design and construct larger and more complicated and/or higher order supramolecular polymers using host−guest systems. Previously, we reported preparation and structures of cyclodextrins (CDs) having a hydrocinnamoyl group (6-HyCiO-CD) or a cinnamoyl group (6-CiO-CD) as a guest.[17] Although HyCiO-β-CD was found to form intramolecular complexes, 6-CiO-α-CD gave intermolecular complexes to give supramolecular oligomers of the degree of polymerization up to three. When the supramolecular complexes were stabilized by attaching bulky stoppers, cyclic tri[2]rotaxanes, daisy chain necklaces, were obtained.[18] These supramolecular polymers were constructed by the incorporation of a host part into a guest part in a single molecule. To obtain larger complexes, formation of small cyclic complexes should be avoided. Although, there are many papers on the cooperative binding of guests by CD dimers,[19] there are few on the formation of intermolecular complexes of CD dimers with guest dimers.[20−23] The synthesis of supramolecular complexes using the β-CD random polymer and the adamantane dimer has been reported. However, it is difficult to define the structure of the supramolecular complex because the β-CD polymer has random structures.[20,21] Therefore, we have decided to use a CD dimer and guest dimers with various flexibilities. More recently, while we were preparing for this manuscript, Liu et al. reported intermolecular complexes of β-CD dimers with fullerene.[24] However, fullerene has a very low association constant for β-CD because the size of fullerene was too large to include in a β-CD cavity. Kuroda et al. reported the supramolecular assemblies of a cyclodextrin dimer and a water-soluble porphyrin to form a small cyclic assembly.[25] Now we found that a CD dimer formed supramolecular polymers with ditopic guest molecules. The products have been characterized by ROESY, turbo ion spray mass spectroscopy, vapor pressure osmometry, and atomic force microscopy.

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Experimental Section

General Procedures. All manipulations were carried out by the use of standard Schlenk techniques under an argon atmosphere. DMF was dried and deoxygenated by distilling from BaO under the reduced pressure. β-CD, *p*-toluenesulfonyl chloride, sodium hydroxide, sodium azide, 28% ammonium solution, triphenylphosphine, *N,N*′-dicyclohexylcarbodiimide (DCC), and 1-hydroxybenzotriazole (HOBT) were obtained from Nacalai Tesque Inc. 1-Adamantyl bromomethyl ketone, 4,4′-trimethylene-dipyridine, and 1-(1-adamantyl)pyridinium bromide were obtained from Aldrich Chem. Co. 1,2-Bis(4-pyridyl)ethane was obtained from Acros Organics. 1,1′-Carbonylbis-1*H*-imidazole (CDI) and 4,4′-dipyridyl were obtained from Tokyo Kasei Inc. 6-*p*-Toluenesulfonyl-β-CD[26−28] and 6-amino-β-CD[29] were prepared according to the literature.

Measurements. The ^{1}H NMR spectra were recorded at 270 and 400 MHz, and ^{13}C NMR spectra were recorded at 67.5 and 100 MHz with a JEOL-EX270 and a JEOL-GSX 400 spectrometers. Chemical shifts were referenced to the solvent values (δ 2.50 ppm for DMSO-d_6 and δ 4.70 ppm for HOD). The 2D NMR (NOESY, ROESY) experiments were conducted at 600 MHz with a VARIAN UNITY plus NMR spectrometer and 500 MHz with a JEOL LA-500 NMR spectrometer in D_2O at 30.0 °C. The positive-ion matrix assisted laser desorption ionization time-of-flight (MALDI−TOF) mass spectra measurements was performed on a Shimadzu/KRATOS AXIMA-CFR spectrometer with DHBA as a matrix. Turbo ion spray mass spectrometry was performed with Q-STAR supported by Applied Biosystems Japan.

Determination of Association Constants. The determination of the association constants of the complex between

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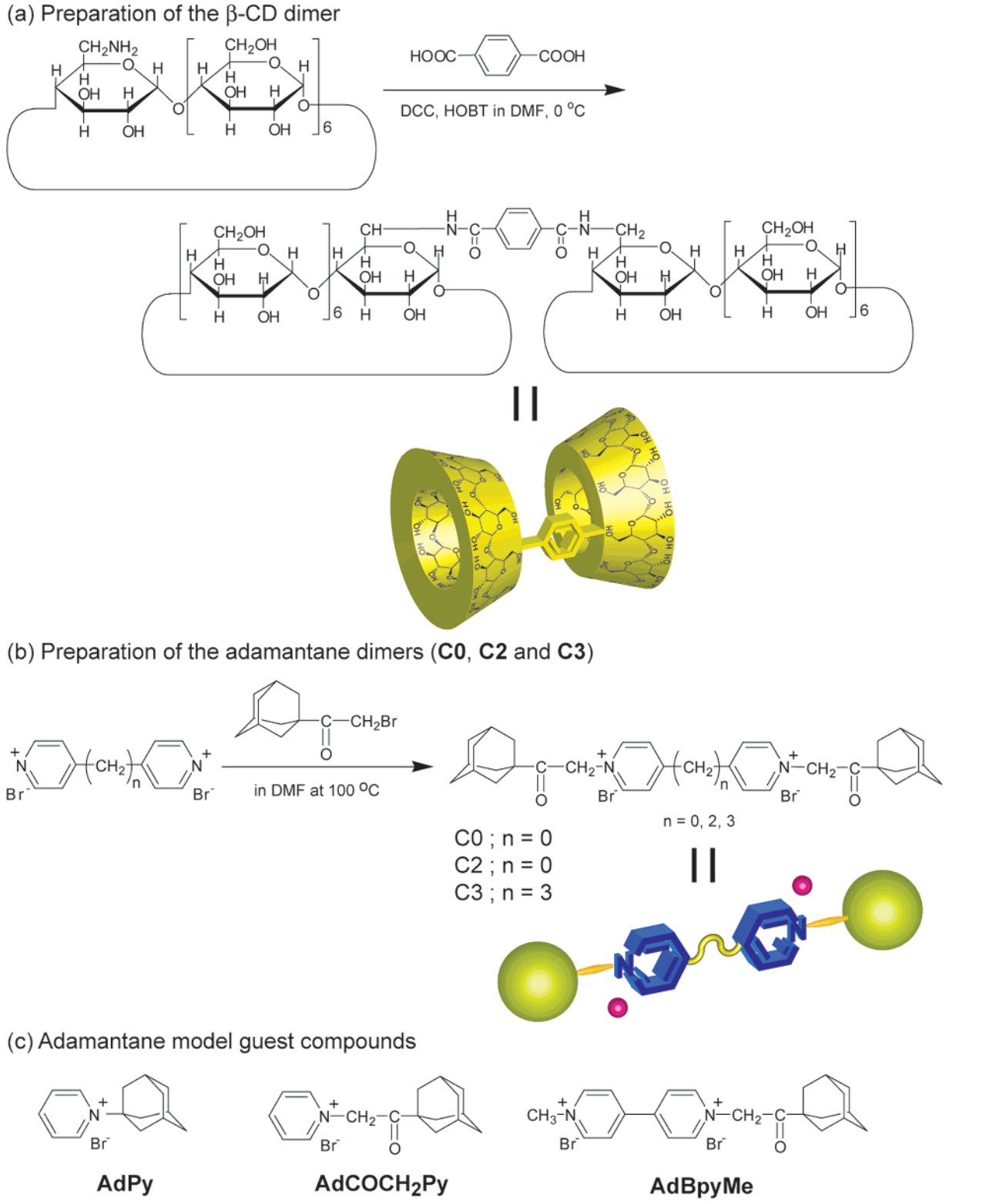
Scheme 1. Syntheses and Structures of *β*-CD Dimer, Adamantane Guest Dimers, and Model Guest Compounds



β-CD and adamantane model guest compounds were carried out by measuring the difference between the chemical shifts of the model guest compounds alone and the same guest with increasing the concentration of *β*-CD. For the systems of a 1:1 inclusion complex between guest and host, equilibrium constants (K_C) were estimated by a modification of the Benesi–Hildebrand equation,[22] using eq 1:

$$\frac{1}{\Delta Hz} = \frac{1}{K_C}\frac{1}{[R]_0\Delta\delta}\frac{1}{[\beta\text{-CD}]} + \frac{1}{[R]_0\Delta\delta} \qquad (1)$$

The association constants can be calculated from the slope of the straight line obtained by plotting 1/ΔHz vs 1/[*β*-CD]. (Figures S2 − S4 in the Supporting Information)

Determination of Molecular Weight by VPO. Vapor pressure osmometry measurements used a KNAUER No. A0280 vapor osmometer at 40 °C in water. Two paired thermistors, comprising a part of a Wheatstone bridge circuit for differential measurement, are located in a cell saturated with solvent. The cell temperature, adjustable over a wide range, is electronically thermostated to a temperature constancy of 1/1000 °C. We used an aqueous solution of NaCl and

an aqueous solution of α-CD as the instruments standard. The calibration was carried out by using solutions of NaCl in various concentrations. These results were plotted as divisions/C vs concentration to give the *y*-intercept for the calibration P_{cal} with dimensions

$$P_{cal} = \frac{\text{scale divisions}}{\text{mol/kg}}$$

and for the measurement of the unknown substance $P_{measured}$ with the dimensions

$$P_{measured} = \frac{\text{scale divisions}}{\text{g/kg}}$$

To obtain the molecular weight, these values are used in the following equation:

$$\bar{M}_n \frac{P_{cal}}{P_{measured}}$$

Preparation of Terephthalic Acid Bridged *β*-CD Dimer (Figure S1). To a solution of 6-NH_2-*β*-CD (2.96 g, 2.61 mmol) in 50 mL of DMF was added telephthalic acid (114 mg, 0.69 mmol). After the solution was cooled below 0 °C, *N,N′*-dicyclohexylcarbodiimide (367 mg, 1.78 mmol) and 1-hydroxybenzotriazole (223 mg, 1.65 mmol) were added. The resulting mixture was stirred at room temperature for 7 days. After the insoluble materials were removed by filtration, the filtrate was poured into acetone (1.5 L), and the precipitate was collected and washed with acetone and then dried under vacuum to give 3.36 g of the crude product. The crude product (3.36 g) was purified by column chromatography on DIAION HP-20 (eluted with water/methanol = 100/0 to 50/50). The 60/40 (water/methanol) eluent was concentrated and recrystallized from water/ethanol to give 1.08 g of the desired product. Yield: 65%. ^{1}H NMR (DMSO-d_6, 270 MHz): *δ* 8.24 (bs, 2H, −CO−NH−), 7.88 (s, 4H, phenyl), 5.82−5.65 (m, 28H, O(2)H and O(3)H of *β*-CD), 4.96−4.84 (m, 14H, C(1)H of *β*-CD), 4.44−4.30 (m, 18H, O(6)H and C(6′)H of *β*-CD), 3.85−3.16 (m, overlaps with HOD); ^{13}C NMR (DMSO-d_6, 67.8 MHz): *δ* 165.9 (C of −CONH−), 136.4, 127.0 (C of phenyl), 101.9 (C(1) of *β*-CD), 83.7 (C(4′) of *β*-CD), 81.5 (C(4) of *β*-CD), 73.0 (C(3) of *β*-CD), 72.4 (C(2) of *β*-CD), 72.0 (C(5) of *β*-CD), 59.9 (C(6) of *β*-CD), 56.0 (C(6′) of *β*-CD). Anal. Calcd for $C_{92}H_{144}N_2O_{70}\cdot 9.4H_2O$: C, 43.04; H, 6.39; N, 1.09. Found: C, 43.05; H, 6.43; N, 1.30.

Preparation of C0 Guest Dimer. 1-Adamantylbromomethyl ketone (1.0 g, 3.9 mmol) and 4,4′-dipyridyl (270 mg, 1.7 mmol) were allowed to react in DMF (10 mL) at 100 °C for 3 h. After being cooled to room temperature, the yellow precipitate was collected by centrifugation and washed with diethyl ether to yield 1.1 g of crude product. The crude product was purified by recrystallization from methanol to yield 810 mg of desired product as a yellow solid. Yield: 77%. ^{1}H NMR (DMSO-d_6, 270 MHz): *δ* 9.19 (d, 4H, α aromatic H), 8.86 (d, 4H, *β* aromatic H), 6.12 (s, 4H, −COCH2-), 2.07 (s, 6H, adamantane), 1.95 (s, 12H, adamantane), 1.74 (s, 12H, adamantane). Anal. Calcd for $C_{34}H_{42}N_2O_2Br_2\cdot 0.55H_2O$: C, 60.02; H, 6.38; N, 4.12. Found: C, 60.01; H, 6.35; N, 4.15.

Preparation of C2 Guest Dimer. 1-Adamantylbromomethyl ketone (2.1 g, 8.2 mmol) and 1,2-bis(4-pyridyl)ethane (500 mg, 2.7 mmol) were allowed to react in DMF (25 mL) at 100 °C for 2 h. After being cooled to room temperature, the yellow precipitate was collected by centrifugation and washed with acetone and diethyl ether to yield 1.8 g of crude product. The crude product was purified by recrystallization from methanol to yield 300 mg of desired product as a pale yellow solid. Yield: 20%. ^{1}H NMR (DMSO-d_6, 270 MHz): *δ* 8.79 (d, 4H, α aromatic H), 8.15 (d, 4H, *β* aromatic H), 5.95 (s, 4H, $-COCH_2-$), 3.40 (s, 4H, $-CH_2-CH_2-$), 2.05 (s, 6H, adamantane), 1.90 (s, 12H, adamantane), 1.72 (s, 12H, adamantane). Anal. Calcd for $C_{36}H_{46}N_2O_2Br_2\cdot 0.25H_2O$: C, 61.50; H, 6.67; N, 3.98. Found: C, 61.49; H, 6.51; N, 3.99.

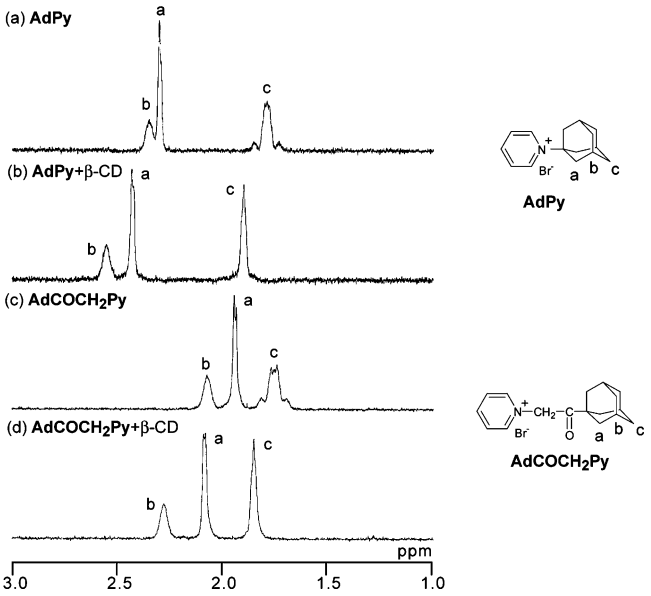


Figure 1. 270 MHz ^{1}H NMR spectra of **AdPy** in 1 mM (a), **AdPy** with *β*-CD in 1 mM (b), **AdCOCH$_2$**Py in 1 mM (c), and **AdCOCH$_2$**Py with *β*-CD in 1 mM (d) in D_2O at 30 °C.

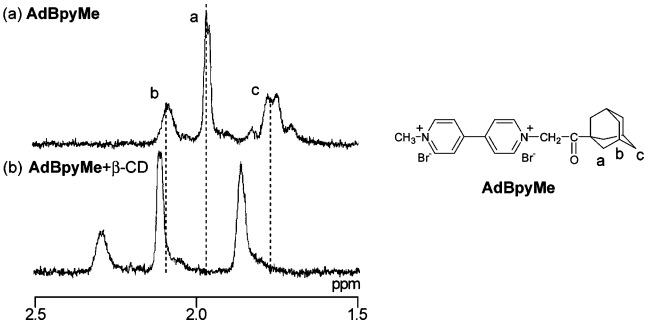


Figure 2. 270 MHz ^{1}H NMR spectra of **AdBpyMe** in 1 mM (a) and **AdBpyMe** with *β*-CD in 1 mM (b) in D_2O at 30 °C.

Preparation of C3 Guest Dimer. 1-Adamantylbromomethyl ketone (2.2 g, 8.4 mmol) and 4,4′-trimethylene dipyridyl (550 mg, 2.8 mmol) were allowed to react in DMF (10 mL) at 100 °C for 3 h. After being cooled to room temperature, the brown precipitate was collected by centrifugation and washed with acetone and diethyl ether to yield 1.7 g of crude product. The crude product was purified by recrystallization from methanol to yield 850 mg of desired product as a brown solid. Yield: 43%. ^{1}H NMR (DMSO-d_6, 270 MHz): *δ* 8.74 (d, 4H, α aromatic H), 8.10 (d, 4H, *β* aromatic H), 5.92 (s, 4H, $-CH_2CO-$), 3.02 (t, 4H, $-CH_2CH_2CH_2-$), 2.16 (t, 2H, $-CH_2CH_2CH_2-$), 2.06 (s, 6H, adamantane), 1.92 (s, 12H, adamantane), 1.74 (s, 12H, adamantane). Anal. Calcd for $C_{37}H_{42}N_2O_2Br_2\cdot 2.2H_2O$: C, 59.08; H, 7.02; N, 3.72. Found: C, 59.11; H, 6.95; N, 3.72.

Preparation of Adamantane Carbomethylpyridinium Bromide (AdCOCH$_2$Py). 1-Adamantylbromomethyl ketone (530 mg, 2.0 mmol) and pyridine (10 mL, 120 mmol) were allowed to react at 100 °C for 3 h. After the evaporation of pyridine, the residue was washed with diethyl ether to yield 670 mg of the crude product. The crude product was purified by recrystallization from methanol to yield 360 mg of desired product as a white solid. Yield: 69%. ^{1}H NMR (DMSO-d_6, 270 MHz): *δ* 8.86 (d, 2H, α aromatic H), 8.67 (t, 1H, *γ* aromatic H), 8.21 (t, 2H, *β* aromatic H), 6.00 (s, 2H, $-COCH_2-$), 2.14 (s, 3H, adamantane), 1.92 (s, 6H, adamantane), 1.77 (s, 6H, adamantane). Anal. Calcd for $C_{17}H_{22}NOBr\cdot 0.35H_2O$: C, 59.60; H, 6.68; N, 4.09. Found: C, 59.61; H, 6.64; N, 4.12.

Preparation of *N*-Methyl-*N′*-adamantane Carbomethyl-4,4′-bipyridinium Dibromide (AdBpyMe). Methyl iodide (6.2 g, 0.44 mmol) and 4,4′-dipyridyl (5.0 g, 0.32 mmol) were

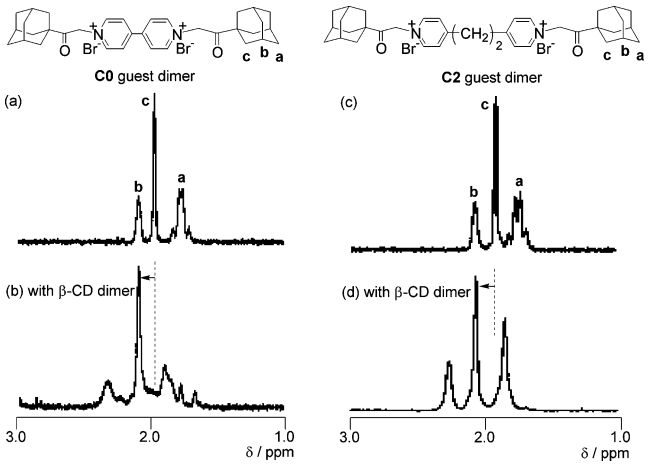


Figure 3. ^{1}H NMR specta of the guest dimer **C0** in 1 mM (a), the guest dimer **C0** with the β-CD dimer in 1 mM (b), the guest dimer **C2** in 1 mM (c), and the guest dimer **C2** with the β-CD dimer in 1 mM (d) in D_2O at 30 °C.

allowed to react in acetone (60 mL) at room temperature for a night. The yellow precipitate was collected by filtration and washed with acetone to yield 9.3 g of 1-methyl-4-(4′-pyridyl)-pyridinium. This product (1.0 g, 3.3 mmol) and 1-adamantylbromomethyl ketone (1.3 g, 5.1 mmol) were allowed to react in DMF (20 mL) at 100 °C for 18 h. After being cooled to room temperature, the red precipitate was collected by centrifugation and washed with acetone to yield 1.0 g of 1-adamantyl-(1-methyl-4-(1′-methyl-4′-pyridinium)pyridinium) ketone; **AdBpyMe** (yield: 54%). This product was dissolved in water and $NaClO_4$ was added to this solution. The white precipitate was collected by centrifugation and washed with water. Again, the precipitate was dissolved in CH_3CN and Et_4NCl was added to this solution. The white precipitate was collected by centrifugation, washed with CH_3CN and then dried under vacuum. ^{1}H NMR (DMSO-d_6, 270 MHz): δ 9.33 (d, 2H, α aromatic H), 9.25 (d, 2H, α aromatic H), 8.87 (d, 2H, β aromatic H), 8.80 (d, 2H, β aromatic H), 6.19 (s, 2H, $-COCH_2-$), 4.46 (s, 3H, $-CH_3$), 2.07 (s, 3H, adamantane), 1.95 (s, 6H, adamantane), 1.74 (s, 6H, adamantane). Anal. Calcd for $C_{23}H_{22}N_2OCl_2 \cdot 2.5H_2O$: C, 59.48; H, 7.16. Found: C, 59.54; H, 6.94.

Results and Discussions.

Syntheses of a Ditopic Host Dimer and Guest Dimers. β-CD dimer has been prepared by the reaction of 6-amino-β-CD with phathalic acid using DCC in DMF (Scheme 1a). β-CD dimer has a phthaloyl group as a rigid spacer to give intermolecular complexes with ditopic guest dimers. The ditopic guest dimers, **C0**, **C2**, and **C3**, were prepared by the reaction of bipyridine derivatives with 1-adamantylbromomethyl ketone (Scheme 1b). To investigate the effect of spacer groups in the ditopic guest molecules, three kinds of guest dimers have different spacer groups between adamantane end groups. The adamantane guest dimer **C0** has stiff spacer, because a 4,4′-bipyridinium group is used as a spacer. In contrast, the adamantane guest dimers, **C2** and **C3,** are more flexible than the adamantane guest dimer **C0** because of the existence of methylene groups in the spacer groups. An adamantyl moiety as a guest part was chosen because adamantane derivatives are known to be included in a β-CD cavity strongly, which were reported to bind to a β-CD cavity with an association constant of 10^4 M^{-1}. Model guest compounds, adamantane pyridinium (**AdPy**), adamantane carbomethylpyridinium bromide (**AdCOCH$_2$Py**) and *N*-methyl-*N*′-adamantane carbomethyl-4,4′-bipyridinium dibromide (**AdBpyMe**) were also prepared by the same procedure as the ditopic guest dimers (Scheme 1c).

Association Constants of Model Guest Compounds. Figures 1 and 2 show the ^{1}H NMR spectra of the mixture of β-CD and adamantane model guest compounds, **AdPy**, **AdCOCH$_2$Py**, and **AdBpyMe**. The signals of methylene and methine protons of the adamantyl group on model compounds were shifted toward downfield with an increase in the concentration of β-CD.

The association constants K_a of the complex between β-CD and adamantane model guest compounds were determined using the Benesi−Hildebrand plots based on the chemical shifts of methine proton of adamantane with various concentrations of β-CD (Figure S2 and S3 in Supporting Information). The Benesi−Hildebrand plots of the mixture of these model guest compounds and β-CD gave a linear relation between the reciprocal of the concentration of β-CD and these model guest compounds of the shift, giving the association constants of average 1.9×10^3 M^{-1} (**AdPy**), average 8.3×10^3 M^{-1} (**AdCOCH$_2$Py**) and average 1.3×10^4 M^{-1} (**AdBpyMe**).

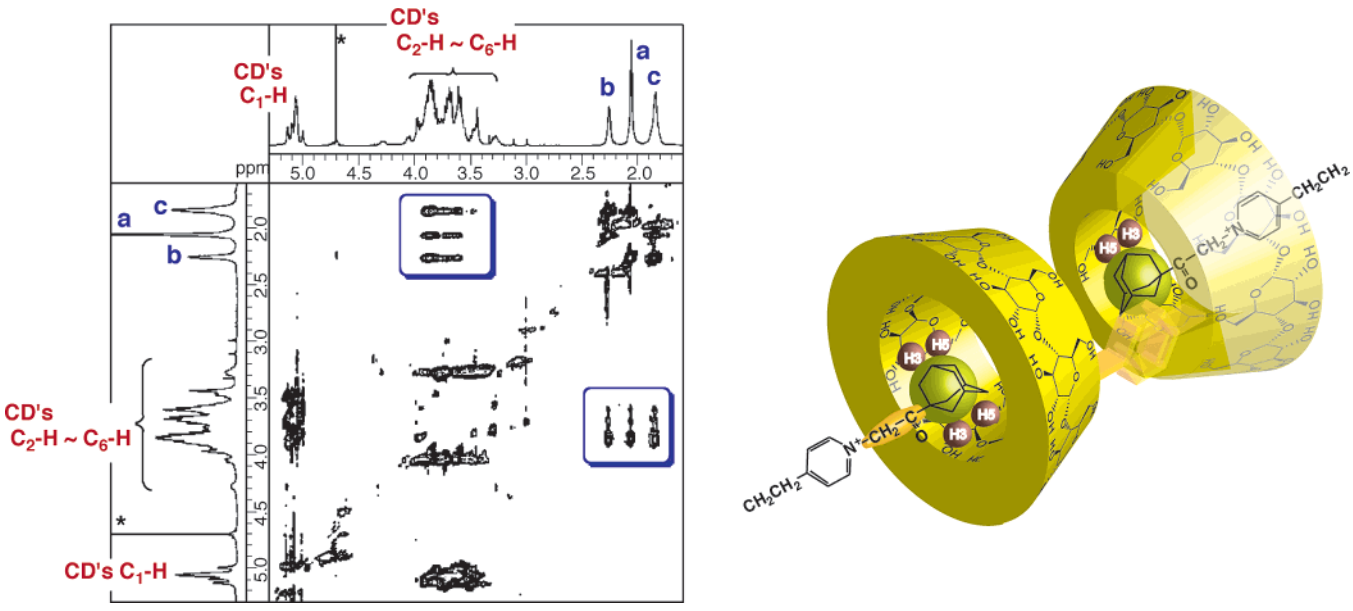


Figure 4. 500 MHz ROESY spectrum of a 1:1 mixture of the β-CD dimer and the guest dimer **C2** of 5 mM in D_2O at 30 °C.

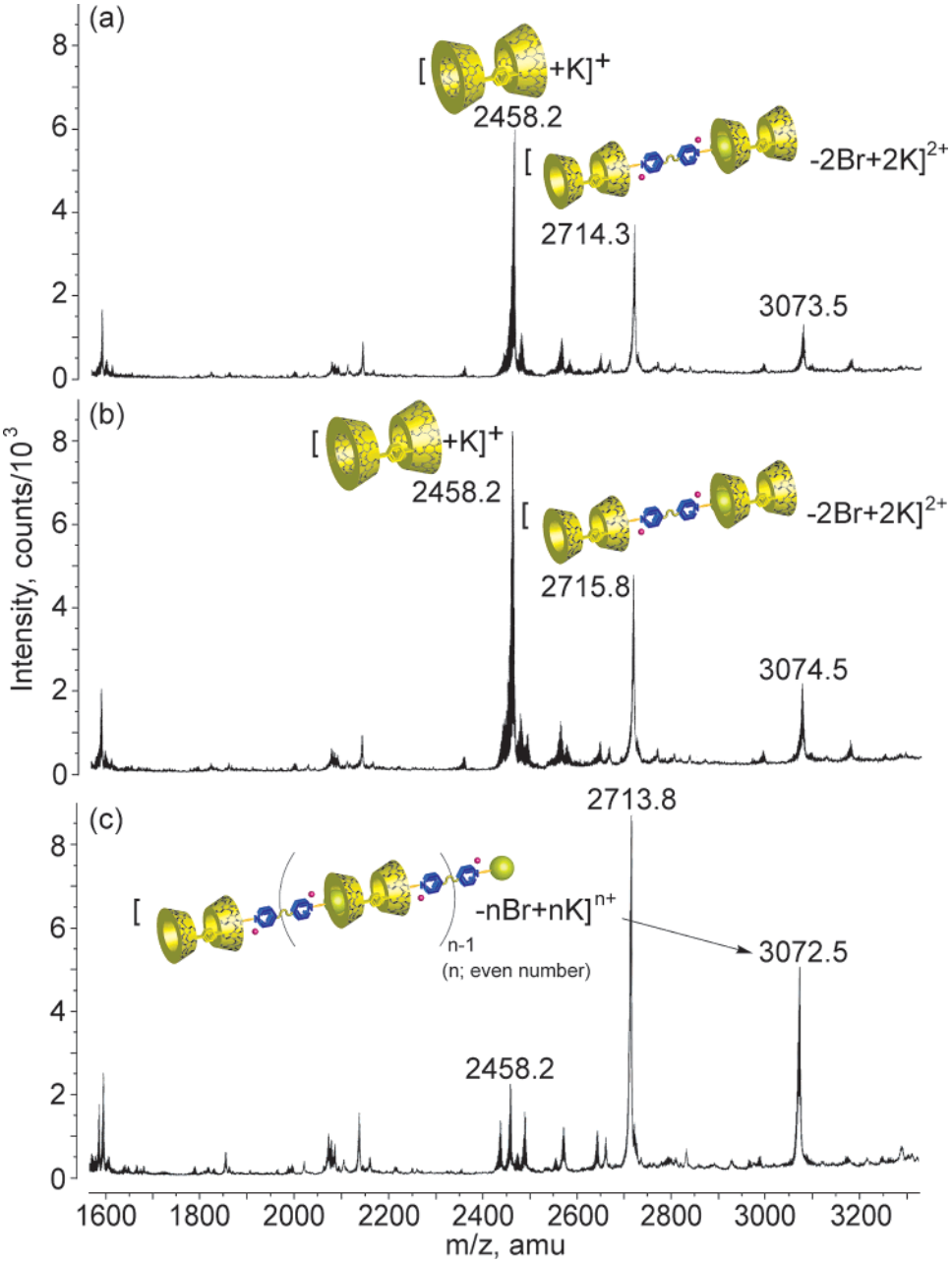


Figure 5. Turbo ion spray mass spectra of a 1:1 mixture of the β-CD dimer and the guest dimer **C3** of 1 (a), 3 (b), and 5 mM (c) in H_2O.

The association constant between adamantyl carboxylate and β-CD was reported to be 3.98×10^4 M^{-1}.[30] Association constants of these adamantane model guest compounds were smaller than that of adamantyl carboxylate, suggesting that the decrease of association constants was induced by the electrostatic repulsion of β-CD away from pyridinium cation. Therefore, the association constant of the complex between β-CD and **AdBpyMe** was larger than that of **AdPy**. We tried to determine the association constant of the complex between the adamantane guest dimer and β-CD. However, since the peak shifts of protons of the adamantyl group were saturated rapidly with two equivalent molar of β-CD, it is difficult to determine the association constants of these complexes of guest dimers. The association constants of the complex between the adamantane guest dimer and β-CD might be estimated to be larger than that of **AdBpyMe**.

NMR Measurements of the Mixture of β-CD Dimer and Adamantane Guest Dimers. Figure 3 shows the ^{1}H NMR spectra of the mixture of the β-CD dimer and the adamantane guest dimer (**C0** or **C2**) in D_2O. The peaks of methylene and methine protons of adamantane (a, b, c) shifted downfield. However, comparing the guest dimer **C0** system with the guest dimer **C2** or **C3** systems, the guest dimer **C0** system showed dispersed peaks of methylene and methine protons of adamantane, while the peaks of methylene and methine protons of adamantane in the guest dimers **C2** or **C3** appeared as three single peaks, indicating that the guest dimer **C0** system was expected to contain free adamantyl moieties which are not included in a β-CD cavity.

The ROESY spectrum of the mixture of the β-CD dimer (5 mM) and the guest dimer **C0** (5 mM) showed that the peaks of methylene and methine protons of adamantane (a, b, c) were correlating well with proton

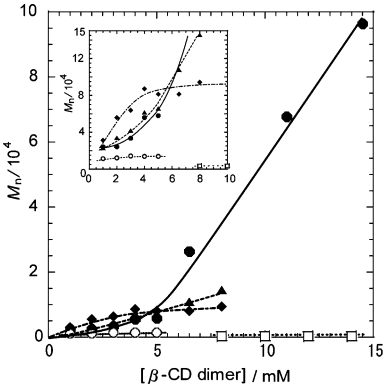


Figure 6. Concentration dependence of number-average molecular weights (M_n) for 1:1 mixtures of the β-CD dimer and the adamantane guest dimers, for **AdCOCH$_2$Py**, and for the mixture of β-CD and **AdCOCH$_2$Py** at 40 °C by VPO measurement. β-CD dimer−**C0** guest dimer (filled circle), β-CD dimer−**C2** guest dimer (filled rhombus), β-CD dimer−**C3** guest dimer (filled triangle), **AdCOCH$_2$Py** (open circle), and β-CD−**AdCOCH$_2$Py** (open square).

peaks of β-CD (C3-*H* and C5-*H*), indicating that an adamantane part is included in a cavity of β-CD (Figure S4). The guest dimer (**C2**) also showed cross-peaks between adamantane and β-CD in the ROESY spectra (Figure 4).

Turbo Ion Spray Mass Spectra Measurements. Figure 5 shows the turbo ion spray mass spectrometry of the mixture of the β-CD dimer and the adamantane guest dimer (**C3**) with various concentrations (1, 3, and 5 mM). The species of supramolecular cyclodextrin complexes between the β-CD dimer and the adamantane guest dimer (**C3**) was found to increase with increasing the concentration. The signals in the turbo ion spray mass spectra in 1 and 3 mM can mainly be assigned as potassium cation adducts of the β-CD dimer (m/z = 2458.2) and the di-potassium cation adducts of two β-CD dimer with the guest dimer **C3** with a deficiency of two bromide counteranion (m/z = 2714.3−2715.8). However, the spectrum in 5 mM shows that the signal of m/z = 3072.5 was larger than that of other low concentrations, which was assigned as the complexes between the even number-potassium cation adducts of two β-CD dimers and two guest dimers **C3** with a deficiency of even number bromide counteranions. These results indicate that the cyclodextrin supramolecular polymers were formed in aqueous solutions and that the molecular weight of supramolecular polymer depends on the concentration.

Vaper Pressure Osmometry Measurement. NMR methods were used to determine stoichiometries and association constants in host−guest chemistry. However, it is difficult to estimate the size of supramolecular polymers by NMR measurements because the formation and dissociation of intermolecular complexes are too fast to detect the end of supramolecular polymer on the NMR time scale. In contrast, VPO (vapor pressure osmometry) is more sensitive to the number of species.[31] Recently, the technique of VPO has been used to estimate association constants of supramolecular complexes.[32] When we investigated the molecular weight for **AdCOCH$_2$Py** and for the mixture of β-CD and **AdCOCH$_2$Py** by VPO, the molecular weights of

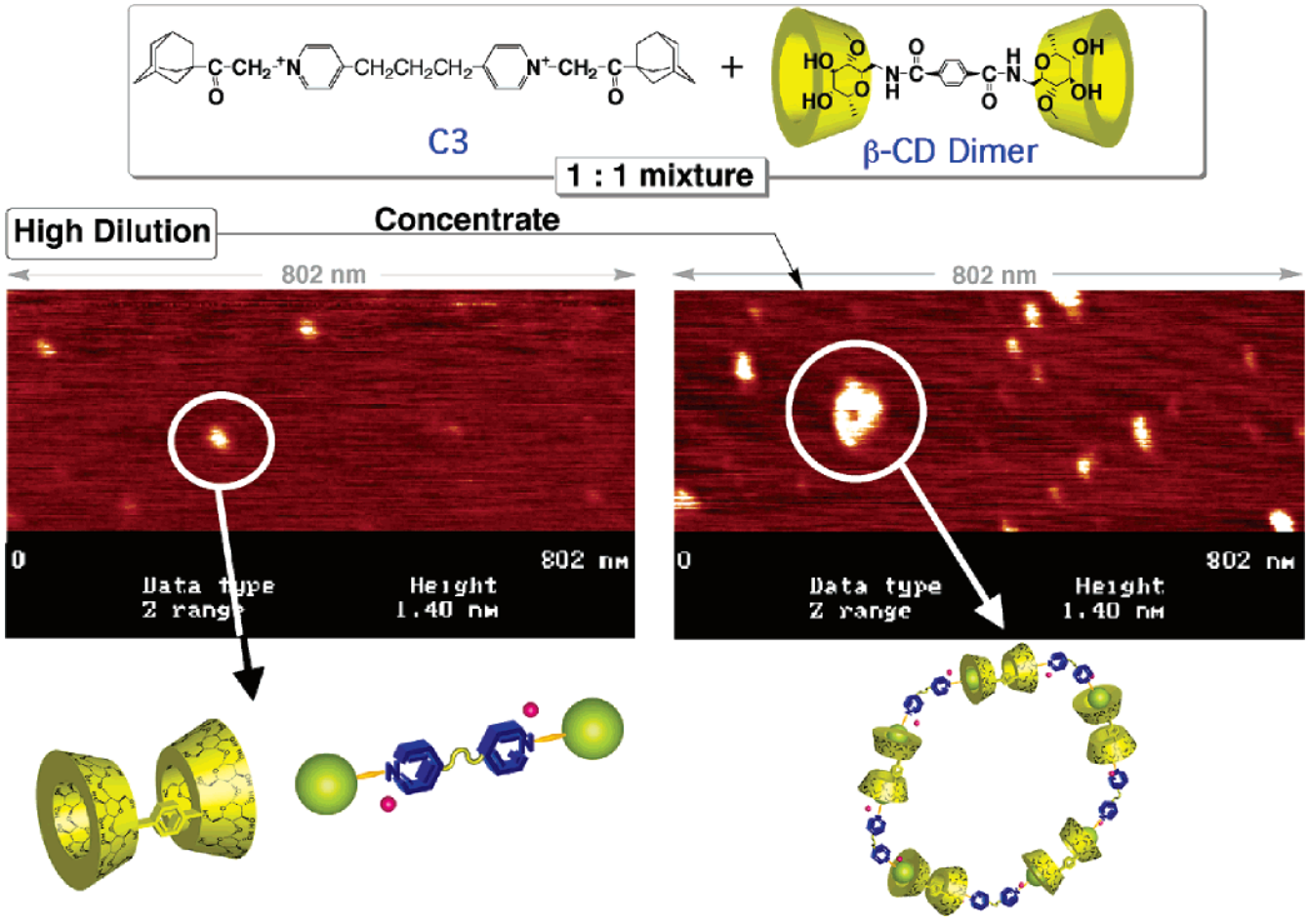


Figure 7. AFM images of 1:1 mixtures of the β-CD dimer and the guest dimer **C3**.

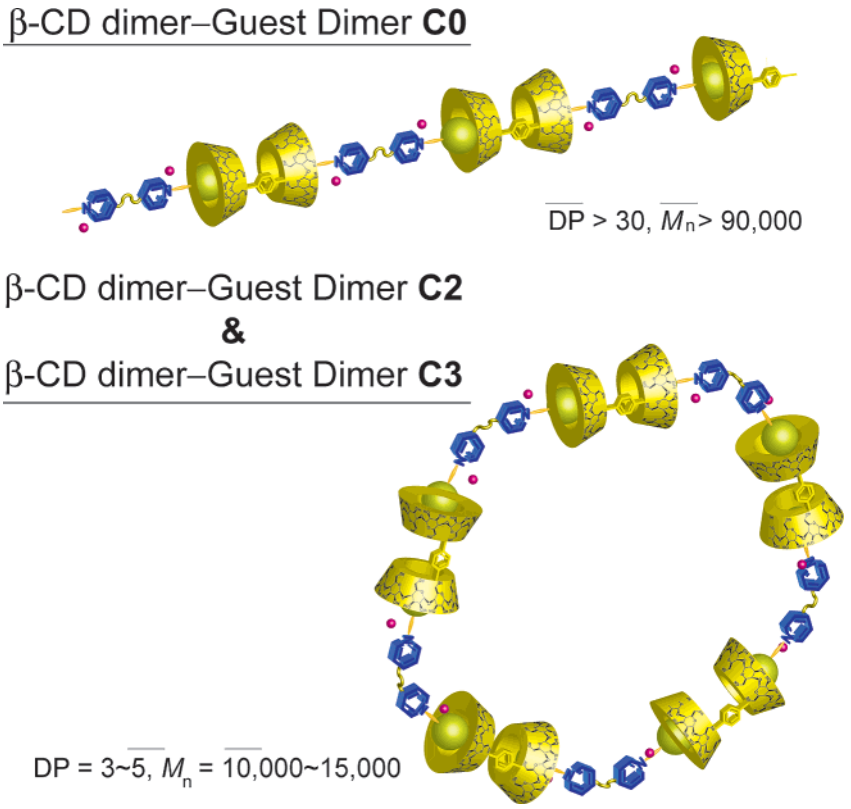


Figure 8. Proposed structures of supramolecular polymers constructed by the β-CD dimer and the guest dimer **C0** and cyclic supramolecular oligomers constructed by the β-CD dimer and the guest dimers, **C2** or **C3.**

AdCOCH$_2$Py and of the mixture of β-CD and **AdCOCH$_2$Py** were independent of the concentrations (Figure 6), suggesting that these guest model compounds cannot form supramolecular polymers. The M_n for the guest dimer **C0** and the β-CD dimer at 3 mM is about 3.0×10^3, indicating the formation of a 1:1 complex. However, the M_n for the guest dimer **C0** and the β-CD dimer over 14 mM is more than 9.0×10^4. The observed M_n was found to increase with increasing 1:1 mixtures of the concentration, which shows the dependence on the concentration and the formation of supramolecular polymers with high molecular weights. When the guest dimer **C2** was used as a guest dimer, M_n saturated at almost 9.4×10^3 even in concentrated solutions over 8 mM. The M_n for the β-CD dimer and the guest dimer **C3** reached about 1.5×10^4 to form supramolecular pentamer at 8 mM. It is difficult to desolve the **C2** guest dimer and the guest dimer **C3** in water over 8 mM because of low solubility. The ^{1}H NMR spectra of β-CD dimer−**C2** guest dimer and β-CD dimer−**C3** guest dimer showed that all the adamantane moieties are included and no free (nonincluded) adamantane groups could be detected (Figure 3), suggesting that the guest dimer **C2** and the guest dimer **C3** formed cyclic oligomers with the β-CD dimers because of their flexibility.

Atomic Force Microscopy Measurement. We used AFM (atomic force microscopy). When the sample was made from a mixture of the β-CD dimer and a guest dimer in dilute solution, only a small object, only the β-CD dimer, could be detected. However, cyclic objects could be clearly observed in an AFM image measured on the samples in a 1:1 mixture of the β-CD dimer and guest dimers (**C2** and **C3**) from higher concentrations, indicating that **C3** (or **C2**) formed cyclic polymers (Figure 7). These results indicate that the guest dimer **C0** formed linear supramolecular polymers of high molecular weight with the β-CD dimer because of its stiffness (Figure 8).

Conclusion

We have prepared a β-cyclodextrin dimer and ditopic adamantane guest dimers having various spacers. β-Cyclodextrin has been shown to bind the adamantane model compound, *N*-methyl-*N*′-adamantane carbomethyl-4,4′-bipyridinium dibromide, with the association constant of 1.3×10^4 M^{-1}. A 1:1 mixture of the β-cyclodextrin dimer and the adamantane dimers showed ROE correlations between the protons of adamantyl groups and the inner protons of β-cyclodextrin, indicating the formation of the inclusion complex between the β-cyclodextrin dimer and adamantane dimers. The mixture of the β-cyclodextrin dimer and adamantane guest dimers was investigated in water by turbo ion spray mass spectrometry. The mixture of the β-cyclodextrin dimer and the adamantane guest dimer (**C0**) formed supramolecular polymers of high molecular weight ($M_n > 9.0 \times 10^4$) measured by vapor pressure osmometry. The samples in a mixture of the β-cyclodextrin dimer and the adamantane guest dimer (**C3**) from higher concentrations formed a supramolecular cyclic oligomer which was observed by atomic microscopy. The β-cyclodextrin dimer forms supramolecular polymers with a stiff guest molecule, **C0**, to give high molecular weight supramolecular polymers, and the β-cyclodextrin dimer gives cyclic supramolecular oligomers with flexible ditopic guest dimers, **C2** and **C3**. Thus, the structures of supramolecular polymers could be controlled by the combination of the host dimer and guest dimers. Now we are studying the dynamic aspects and properties of the supramolecular polymers.

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Supporting Information Available: Figures showing selected NMR data (1D NMR and ROESY spectrum) and VPO. This material is available free of charge via the Internet at http://pubs.acs.org.

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