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Toward High-Generation Rotaxane Dendrimers That Incorporate a Ring Component on Every Branch: Noncovalent Synthesis of a Dendritic [10]Pseudorotaxane with 13 Molecular Components

Soo-Young Kim,[a] Young Ho Ko,[a] Jae Wook Lee,[a] Shigeru Sakamoto,[b] Kentaro Yamaguchi,[b] and Kimoon Kim*[a]

Abstract: By taking advantage of the fact that cucurbit[6]uril (CB[6]) forms exceptionally stable host–guest complexes with protonated amines, and that its homologue CB[8] can encapsulate a pair of electron-rich and electron-deficient guest molecules to form a stable 1:1:1 complex, we synthesized a novel dendritic [10]pseudorotaxane, or second-generation rotaxane dendrimer (from a topological point of view), in which 13 molecular components are held together by noncovalent interactions. A triply branched molecule containing an electron-deficient bipyridinium unit on each branch formed a branched [4]pseudorotaxane with 3 equivalents of CB[8]. Addition of 3 equivalents of 2,6-dihydroxynaphthalene produced a first-generation rotaxane dendrimer, which was characterized by NMR spectroscopy and CSI-MS. The reaction of the branched [4]pseudorotaxane with 3 equivalents of a triply branched molecule that has an electron-donor unit at one arm and CB[6]-containing units at the other two gave the dendritic [10]pseudorotaxane, the structure of which was confirmed by NMR spectroscopy, UV/Vis titration experiments, and CSI-MS.

Keywords: charge transfer · dendrimers · interlocked molecules · rotaxanes · supramolecular chemistry

Introduction

One of the fascinating developments in dendrimer chemistry[1] in recent years is the synthesis of rotaxane dendrimers,[2] dendritic molecules that contain rotaxane-like mechanical bonds to link their components. As dendrimers are composed of three distinct structural parts, the core, end groups, and branching units, rotaxane dendrimers are classified into three types depending on where the rotaxane-like moieties appear, that is, Type I, II, and III rotaxane dendrimers, which incorporate rotaxane-like features at the core, terminal, and branches, respectively.[1] Type III rotaxane dendrimers are further divided into two groups, Types III-A and III-B, depending on whether the ring components reside on the branches or at the branching points, respectively. The synthesis of Type I and II rotaxane dendrimers is relatively straightforward, whereas that of well-defined Type III rotaxane dendrimers (Figure 1), particularly those of second and higher generations, is not, which may explain why examples of the latter are still quite rare. To the best of our knowledge, only two examples of Type III-B rotaxane dendrimers have been reported,[3] both of which are first-generation (G1) dendrimers. Although, in principle, their synthetic strategies can be extended to second- (G2) and higher-generation dendrimers, the actual synthesis is extremely challenging because of the difficulty in controlling the reactions. The situation is not much different for Type III-A rotaxane dendrimers. Stoddart and co-workers reported a branched [4]rotaxane that can be considered as a G1

[a] Dr. S.-Y. Kim, Dr. Y. H. Ko, Dr. J. W. Lee,[+] Prof. Dr. K. Kim
National Creative Research Initiative Center for
Smart Supramolecules and
Department of Chemistry
Pohang University of Science and Technology
San 31 Hyojadong, Pohang 790-784 (Republic of Korea)
Fax: (+82) 54-279-8129
E-mail: kkim@postech.ac.kr

[b] Dr. S. Sakamoto, Prof. Dr. K. Yamaguchi
Laboratory of Analytical Chemistry and
Department of Pharmaceutical Technology
Faculty of Pharmaceutical Sciences at Kawaga Campus
Tokushima Bunri University
Shido, Sanuki-city, Kagawa 769-2193 (Japan)

[+] Current address:
Department of Chemistry, Dong-A University
840 Hadandong, Busan 604-714 (Republic of Korea)

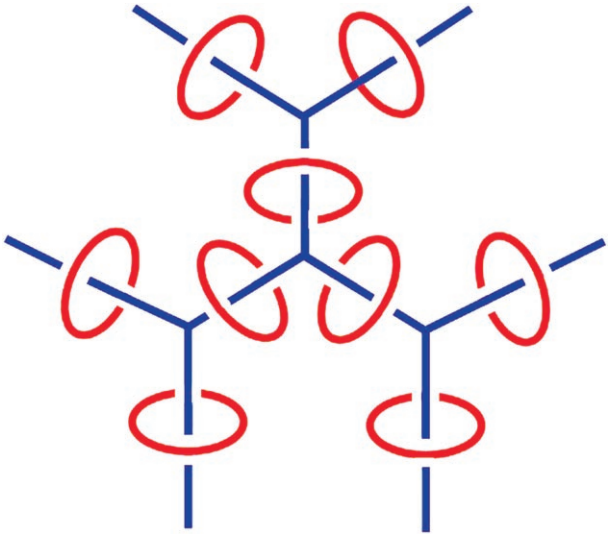

Figure 1. Type III-A (pseudo)rotaxane dendrimer in which a ring component is located on every branch.

Type III-A rotaxane dendrimer.[4] However, there is no report on well-defined second- or higher-generation Type III-A rotaxane dendrimers for the same reason as for Type III-B. The only example closely related to high-generation Type III-A dendrimers may be the hyperbranched polyrotaxanes assembled by the host–guest reaction between a triply branched receptor containing β-cyclodextrin (β-CD) and deoxycholate.[5] Investigation of the precipitate formed from the solution by scanning electron microscopy revealed several different types of fractal structures, which have been assigned as hyperbranched polyrotaxanes. Thus, the efficient synthesis of well-defined Type-III rotaxane dendrimers, especially those of second and higher generations, remains challenging.

Abstract in Korean:

쿠커비투[6]릴 (CB[6])이 암모늄이온과 안정한 1:1 복합체를 이루는 현상과 쿠커비투[8]릴 (CB[8])의 동공 내에서 전자주게와 전자받게 분자가 전하-이동 상호작용을 통해 안정한 1:1:1 복합체를 이루는 현상을 이용하여 덴드리머 형태의 [10]유사로택산 또는 2세대 로택산 덴드리머를 합성하였다. 먼저 1세대 로택산 덴드리머를 합성하기 위해서, 각 말단에 전자가 부족한 bipyridinium이 있는 삼발이 형태의 분자와 3당량의 CB[8]을 반응시켜 [4]유사로택산을 형성하고, 이 시료에 3 당량의 전자주게 2,6-dihydroxynaphthalene을 첨가하여 1세대 로택산 덴드리머를 합성하였다. 이러한 로택산 덴드리머의 합성은 핵자기공명 (NMR) 과 전자 이온 분무 질량(ESI mass) 분광법을 이용하여 확인하였다. 또한 한 쪽에는 전자받게가 달려있으며 나머지 두 쪽에는 CB[6]가 도입되어 있는 삼발이 형태의 리간드를 합성한 후, 이렇게 합성된 리간드3당량을 [4]유사로택산과 반응시킨 결과, CB[8]에 의해 안정화된 전하-이동 착물 형성을 통해 덴드리머형태의 [10]유사로택산 또는 (위상학적 관점에서 본) 2세대 로택산 덴드리머가 형성된다는 것을 NMR, UV 적정 실험 및 질량분광법을 이용하여 확인할 수 있었다.

Cucurbit[*n*]uril (CB[*n*], $n=5$–10), a family of macrocyclic compounds that comprise *n* glycoluril units, has a hydrophobic cavity accessible through two identical carbonyl-fringed portals.[6,7] They have been widely studied not only as synthetic receptors but also as building blocks for supramolecular assemblies.[6–10] In particular, CB[6] forms exceptionally stable host–guest complexes with protonated amines such as diaminobutane in aqueous solution (typically $K>10^5\,\mathrm{M}^{-1}$), which allowed us to synthesize a wide variety of supramolecular architectures such as polyrotaxanes and molecular necklaces.[6d] One of the larger members of this host family, CB[8],[7,8] which has a cavity comparable to that of γ-CD, shows unusual host–guest properties, including the formation of a stable 1:1 host–guest complex with electron-deficient molecules such as methyl viologen or *trans*-1,2-bis(1-methyl-4-pyridinio)ethylene iodide, as well as the encapsulation of a pair of electron-rich and electron-deficient guest molecules inside the cavity to form a stable 1:1:1 complex. The latter is driven by the remarkably enhanced charge-transfer (CT) interactions between the guests inside the hydrophobic cavity of CB[8].[8a] This discovery led us to build several novel supramolecular assemblies[11] such as redox-controllable vesicles,[8g] molecular loops,[8i] molecular necklaces,[8j] linear polyrotaxanes,[8l] and molecular machines[8m] by using the host-stabilized CT interactions. We therefore decided to build high-generation rotaxane dendrimers by combining the remarkable host–guest behavior of CB[6] and CB[8]. Herein we report the synthesis of a dendritic [10]pseudorotaxane, or a G2 Type III-A pseudorotaxane dendrimer (from a topological point of view), in which 13 molecular components are held together by noncovalent interactions.

Results and Discussion

As shown in Scheme 1, our strategy for the construction of a dendritic [10]pseudorotaxane by using noncovalent interactions involves 1) threading a CB[8] bead onto each of the three electron-deficient arms of a triply branched core molecule **1** to make a [4]pseudorotaxane, or G1 pseudorotaxane dendrimer **2**, 2) simultaneously synthesizing a triply branched wedge ligand **4** containing one electron-donor arm and two amine arms on each of which a CB[6] bead is threaded, and 3) linking the G1 pseudorotaxane dendrimer with three of the wedge ligands through CB[8]-stabilized CT interactions to form a dendritic [10]pseudorotaxane, or G2 pseudorotaxane dendrimer **6**.

With this idea in mind, we first designed a triply branched core molecule **1** containing an acceptor unit on each branch in such a way that each branch accepts a CB[8] bead to form a stable pseudorotaxane, which then binds an electron-donor molecule to form a host-stabilized CT complex, leading to the growth of the dendrimer. We decided to use the *trans*-1,2-bis(1-methyl-4-pyridinio)ethylene unit as an ac-

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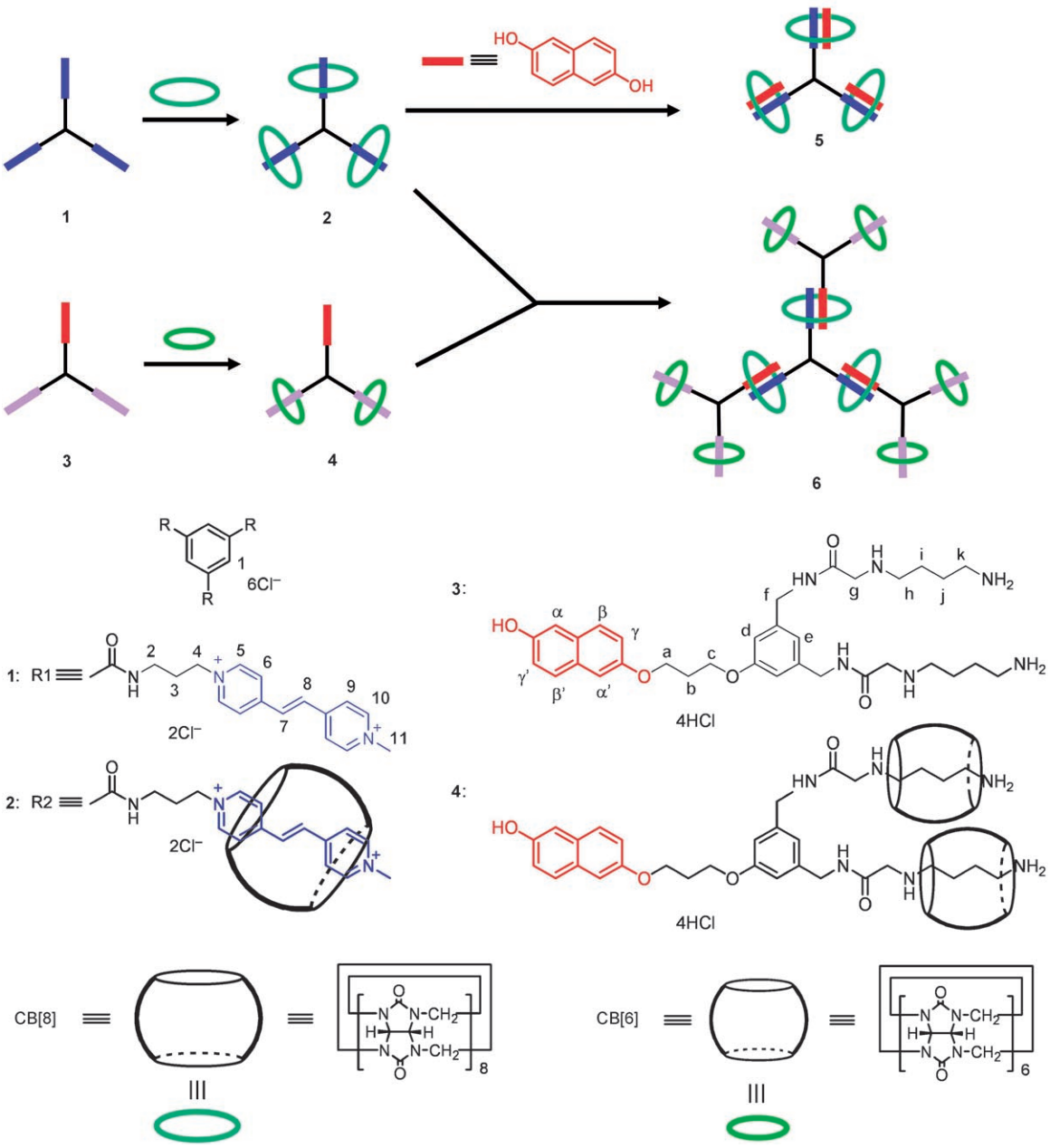
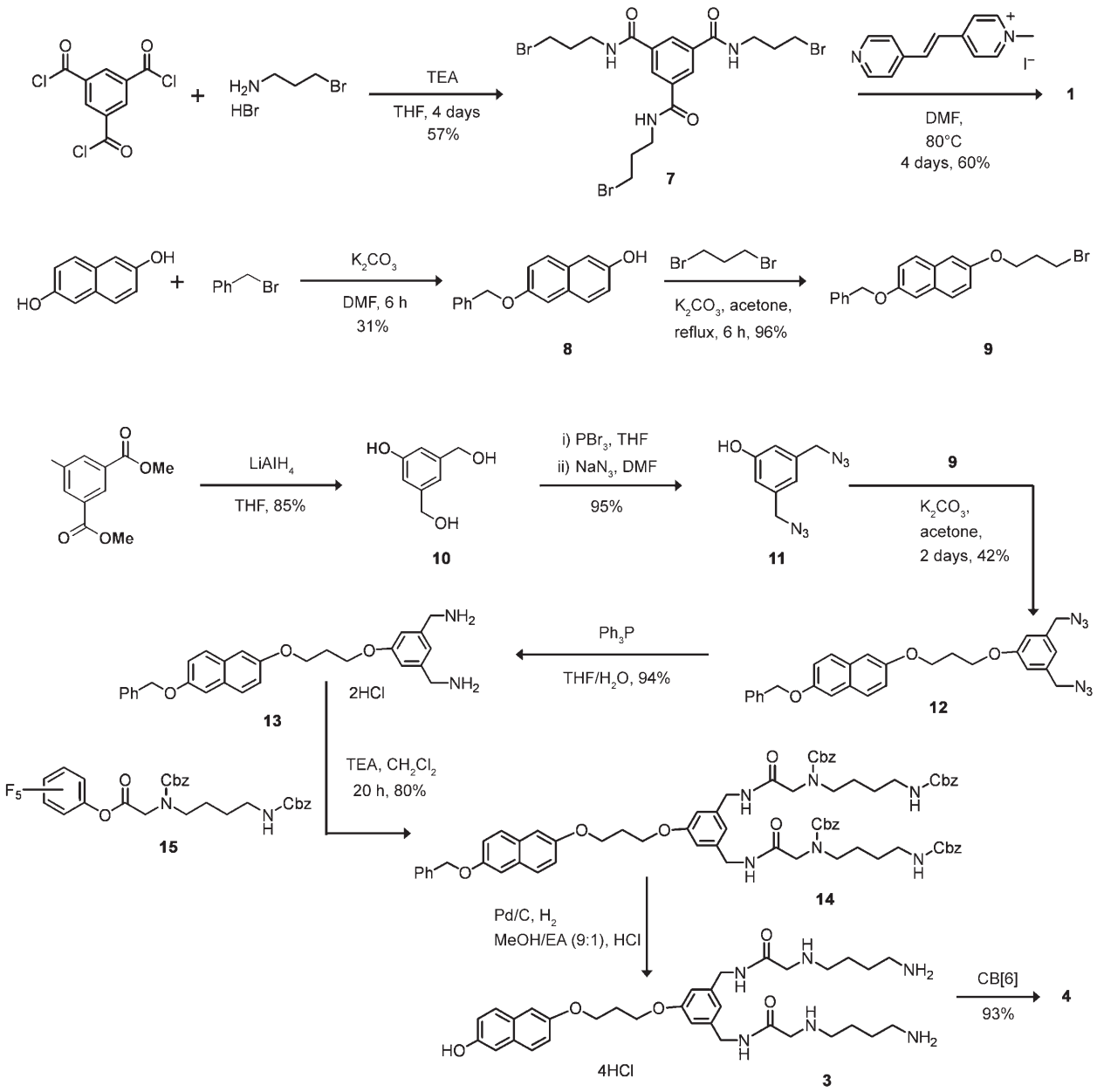


Scheme 1. Synthetic scheme for [10]pseudorotaxane **6** (G2 pseudorotaxane dendrimer).

ceptor unit for this purpose because our previous study showed that 1) *trans*-1,2-bis(1-methyl-4-pyridinio)ethylene forms a stable 1:1 complex with CB[8] and 2) the resulting 1:1 complex binds electron-rich guest molecules such as dihydroxynaphthalene (HN) ($K > 10^4\,\text{M}^{-1}$) to form a stable ternary complex.[8d,11] The synthetic scheme of **1**, **3**, and **4** is given in Scheme 2. Reaction of 1-(4-pyridyl)-2-[4-(*N*-methyl)pyridinio]ethylene iodide with **7** produced the core molecule **1**. Stirring of a mixture of **1** and 3 equivalents of CB[8] in water resulted in formation of stable [4]pseudorotaxane **2**, which may be considered as a G1 pseudorotaxane dendrimer. The overall +6 charge of **2** makes it soluble in water, although CB[8] itself is sparingly soluble. The formation of **2** was confirmed by NMR spectroscopy and mass spectrometry. In the NMR spectrum of **2**, all the signals corresponding to the bis(methylpyridinio)ethylene unit were shifted to higher field, whereas the core phenyl and alkyl signals were shifted downfield relative to those of **1** (Figure 2b and c), indicating that a CB[8] molecule is threaded on each acceptor arm in **2**. The broadening of the signals corresponding to the bis(methylpyridinio)ethylene moiety is due mainly to the shuttling motion of CB[8] along the electron-acceptor unit. The parent molecular-ion peak at $m/z = 818$ in the cold electrospray ionization (CSI) mass spectrum of **2** (see Supporting Information, Figure S1) confirmed the formation of a stable 1:3 host–guest complex between **1** and CB[8].

Before building a G2 rotaxane dendrimer with this approach, we tested whether the G1 pseudorotaxane dendri-



Scheme 2. Synthetic scheme for **1**, **3**, and **4**. Cbz = benzyloxycarbonyl, DMF = *N*,*N*-dimethylformamide, EA = ethyl acetate, TEA = triethylamine.

mer takes up three donor molecules to form a CB[8]-stabilized CT complex at each of the three terminals. Addition of 3 equivalents of HN to **2** in aqueous solution resulted in formation of **5** (Scheme 1), in which an HN molecule forms a stable CT complex with each bis(methylpyridinio)ethylene moiety inside the cavity of CB[8] as evidenced by UV/Vis and NMR spectroscopy. Upon addition of HN to **2**, the pale-yellow solution turned brown; the appearance of a new CT band at 546 nm in the UV/Vis spectrum confirms the formation of a CB[8]-stabilized CT complex. NMR spectroscopy provided more convincing evidence for the formation of **5**. The signals from the bis(methylpyridinio)ethylene protons and the HN protons in **5** were shifted to higher field relative to those in **2** and free HN, respectively (Figure 2c and d). In particular, the protons of the terminal pyridinium units, 9-H and 10-H, showed larger upfield shifts than those of the inner pyridinium unit, 6-H and 5-H, which indicates that the CB[8] bead is localized mainly on the outer pyridinium unit of the bis(methylpyridinio)ethylene moiety. The sharper signals for **5** relative to those for **2** are also congruent with the localization of CB[8]. The formation of **5** was also confirmed by CSI-MS (see Supporting Information, Figure S2).

Having established that **2** can accept electron-donor ligands to extend the dendritic structure, we synthesized the triply branched molecule **3** with one arm containing a hydroxynaphthalene unit, which serves as an electron donor, and each of the two remaining arms containing a diaminobutane unit, which is well-known to form a stable host–guest complex with CB[6] (Scheme 2). Reaction of HN with

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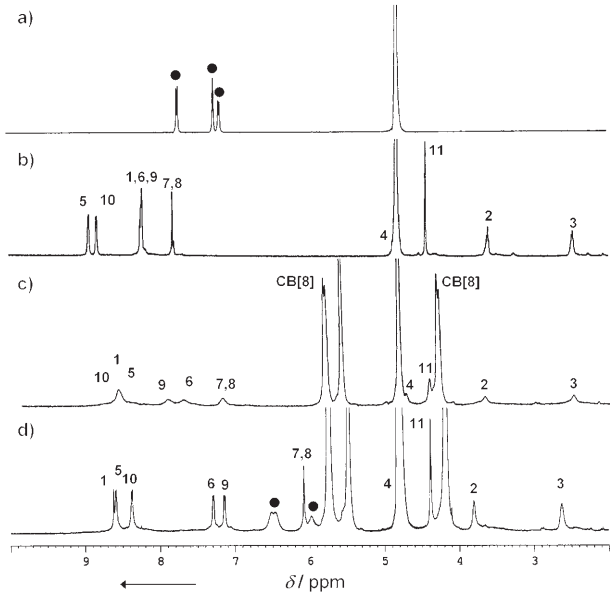

Figure 2. ^{1}H NMR spectra of a) HN, b) **1**, c) **2**, and d) **5** (G1 pseudorotaxane dendrimer) in D_2O. For atom labeling scheme, see Scheme 1.

benzyl bromide produced **8**, which was then treated with 1,3-dibromopropane to give **9**. Reduction of dimethyl 5-hydroxyisophthalate with $LiAlH_4$ yielded **10**, which was then brominated with PBr_3 and treated with sodium azide to afford **11**. The coupling reaction between **9** and **11** produced **12**, reduction of which with PPh_3 yielded **13**. Reaction of **13** with **15** produced **14**, which then underwent deprotection to yield **3**. Stirring of an aqueous solution of **3** and 2 equivalents of CB[6] yielded the wedge ligand **4**, in which a CB[6] bead is threaded on each of the diaminobutane units. Finally, mixing of **2** with 3 equivalents of **4** produced the dendritic [10]pseudorotaxane **6** (or G2 rotaxane dendrimer), which was characterized by UV/Vis spectroscopy and various NMR spectroscopic methods, including ^{1}H-^{1}H correlation spectroscopy (COSY), rotating-frame Overhauser effect spectroscopy (ROESY), and pulsed-field gradient (or diffusion) NMR techniques.[12] Upon addition of **4** to a solution of **2**, the solution turned brown, similar to the case of **5**; a new CT band appeared at around 526 nm in the UV/Vis spectrum. To establish the binding stoichiometry between **2** and **4**, a titration experiment was carried out with UV/Vis spectroscopy. The intensity of the band at 526 nm gradually increased with the addition of increasing amounts of **4** to **2** up to about 3 equivalents, finally reaching a plateau, which supports a 1:3 binding stoichiometry between **2** and **4** (Figure 3). A similar result was obtained by diffusion NMR spectroscopy. The diffusion coefficient of **2** decreased with an increasing amount of **4** until the latter reached about 3 equivalents; it then became constant (Figure 3).

Although the peaks in the aromatic region of the ^{1}H NMR spectrum of **6** (Figure 4) are broad and complicated, most of the signals were assigned by 2D NMR experiments including COSY and ROESY (see Supporting Information). As expected, the signals for the bis(methylpyridinio)ethylene protons of the core molecule and the naphthalene unit of the wedge ligand in **6** were shifted upfield relative to those of **2** and **4**, thus indicating the formation of a CT complex between the electron-acceptor unit of **2** and the electron-donor unit of **4** inside the CB[8] cavity. From the diffusion NMR data, the hydrodynamic volume of **6** was estimated to be 44600 Å^3, which is around 30 times larger than that of CB[8] (1500 Å^3). Taken together, the 2D and diffusion NMR data support the formation of a large [10]pseudorotaxane through CB[8]-stabilized intermolecular CT interactions.

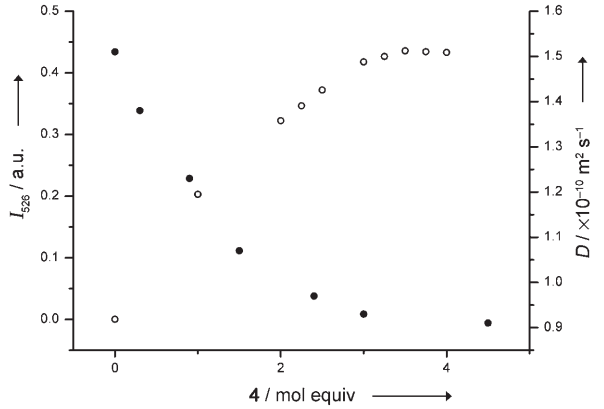

Figure 3. Changes in UV/Vis absorption at 546 nm (○) and diffusion coefficients (●) measured by diffusion NMR spectroscopy during the formation of [10]pseudorotaxane **6**.

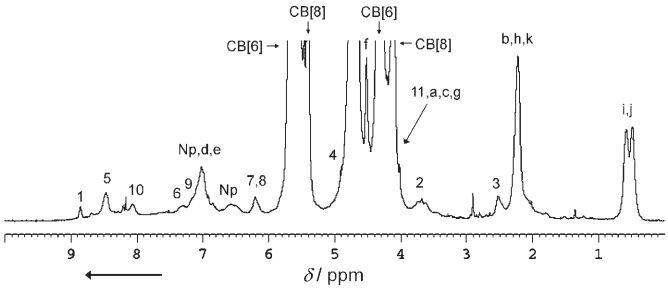

Figure 4. ^{1}H NMR spectrum of [10]pseudorotaxane **6** in D_2O. Np = protons of the hydroxynaphthalene unit.

Earlier attempts to detect the molecular-ion peaks of the dendritic [10]pseudorotaxane **6** by mass spectrometry failed, possibly due to its high molecular weight and charge; it has a molecular weight of 13351 Da, including nine molecular beads (6×CB[6], 3×CB[8]) and 18 counterions (Cl^-), which balance the +18 charge of the dendrimer framework. Similar difficulty in characterization of dendrimers with high molecular weights and charges by mass spectrometry has been reported.[13] Nevertheless, the formation of [10]pseudorotaxane **6** was recently confirmed by CSI-MS. Although weak, the peaks of the multiply charged ions of the parent complex as well as its fragments were observed (see Supporting Information).

Figure 5 shows the energy-minimized structures of G1 and G2 pseudorotaxane dendrimers **5** and **6**, respectively.[14] The distance from the center of the phenyl core to the periphery units is approximately 1.7 nm for **5** and 3 nm for **6**. These

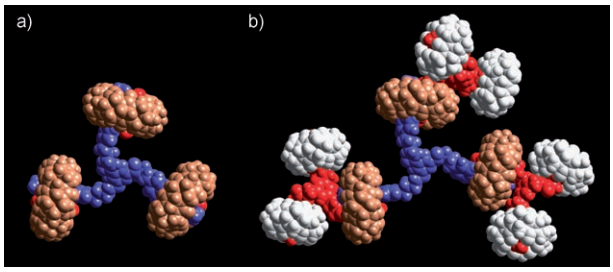

Figure 5. Energy-minimized structures of a) [4]pseudorotaxane **5** (G1 pseudorotaxane dendrimer) and b) [10]pseudorotaxane **6** (G2 pseudorotaxane dendrimer). Color code: core = blue, wedge = red, CB[8] = light brown, CB[6] = white.

numbers match reasonably well the hydrodynamic radii of **5** and **6** (1.4 and 2.2 nm, respectively) calculated from the diffusion coefficients (1.4×10^{-10} m^{2}s for **5**, 9.1×10^{-11} m^{2}s for **6**), which were measured by diffusion NMR spectroscopy with the Stokes–Einstein equation.[12] The somewhat smaller hydrodynamic radii relative to the calculated center-to-periphery distances indicate that the rotaxane dendrimers may adopt a folded conformation in solution.

Conclusions

We have synthesized a novel dendritic [10]pseudorotaxane, the first example of G2 Type III-A (pseudo)rotaxane dendrimers (from a topological point of view), in which 13 molecular components are held together by noncovalent interactions. A rational design based on the unique host–guest properties of CB[*n*] made the facile, noncovalent synthesis of such an elaborate supramolecular architecture with high complexity possible. As the host-stabilized CT interactions can be weakened or destroyed by reduction of electron-acceptor units or oxidation of electron-donor units, the dendritic [10]pseudorotaxane is expected to be disassembled upon addition of suitable redox stimuli. Finally, this work can be extended to the synthesis of higher-generation rotaxane dendrimers and other dendritic rotaxanes with specific functions, which may find application in areas such as light harvesting and drug delivery.

Experimental Section

General

All chemicals were of reagent grade and used without further purification. CB[8] was prepared according to the literature method.[7a] ^{1}H NMR measurements were carried out on a Bruker DRX500 NMR spectrometer operating at 500.23 MHz for ^{1}H. CSI mass spectra were obtained on a JEOL JMS-700T spectrometer. UV/Vis data were recorded on a Hewlett–Packard 8453 diode-array spectrophotometer.

Synthesis

7: 3-Bromopropylamine hydrobromide (1.56 g, 3.0 equiv) was added to a solution of 1,3,5-benzenetricarbonyl trichloride (620.0 mg, 2.34 mmol) and triethylamine (1.0 mL, 3.0 equiv) in THF, and the resulting mixture was stirred at room temperature for 4 days. After addition of water to the reaction mixture, the product was extracted with ethyl acetate. The organic layer was washed with brine and dried over magnesium sulfate. After removal of the solvent, purification by column chromatography on silica (ethyl acetate/hexanes = 4:1) yielded N^1,N^3,N^5-tris(3-bromopropyl)-benzene-1,3,5-tricarboxamide (**7**) (767.5 mg, 57 %). ^{1}H NMR (500 MHz, [D$_6$]dimethyl sulfoxide ([D$_6$]DMSO)): δ = 2.10 (quint, J = 6.6 Hz, 6H), 3.40 (t, J = 6.6 Hz, 6H), 3.59 (t, J = 6.6 Hz, 6H), 8.38 (s, 3H), 8.76 ppm (t, J = 5.3 Hz, 6H); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 32.2, 32.4, 37.9, 128.5, 134.5, 165.5 ppm; HRMS (FAB): *m/z* calcd for $C_{18}H_{25}N_3O_3Br_3$: 567.9446 $[M]^+$; found: 567.9444.

1-(4-Pyridyl)-2-[4-(*N*-methyl)pyridinio]ethylene iodide:[8l] Methyl iodide (285.0 mL, 0.8 equiv) was added to a solution of 4,4′-(1,2-ethenediyl)bispyridine (1.0 g, 5.5 mmol) at 5 °C, and the mixture was stirred at room temperature for 2 days. After filtration, the residue was washed with THF to give the resulting orange product (1.24 g, 84 %). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 4.29 (s, 3H), 7.67 (d, J = 6.0 Hz, 2H), 7.77 (d, J = 16.5 Hz, 1H), 7.97 (d, J = 16.4 Hz, 1H), 8.28 (d, J = 6.7 Hz, 2H), 8.70 (d, J = 6.0 Hz, 2H), 8.94 ppm (d, J = 6.7 Hz, 2H); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 48.1, 122.6, 125.2, 128.6, 133.5, 143.0, 146.4, 151.4, 152.3 ppm.

1: Compound **7** (100.0 mg, 17.5 μmol) and 1-(4-pyridyl)-2-[4-(*N*-methyl)-pyridinio]ethylene iodide (284.0 mg, 5.0 equiv) were dissolved in DMF (7.0 mL), and the mixture was stirred at 80 °C for 4 days. The reaction mixture was cooled to room temperature before acetonitrile was added to give an orange solid (200.0 mg, 70 %). This solid was dissolved in distilled water, and aqueous NH_4PF_6 was added until no further precipitation was observed. The precipitate was collected by filtration, washed with H_2O and redissolved in acetonitrile. (nBu)$_4$NCl was added to the solution to yield a precipitate, which was collected and washed with acetonitrile to give **1** (124.6 mg, 86 %). ^{1}H NMR (500 MHz, D_2O): δ = 2.48 (br, 6H), 3.58 (br, 6H), 4.41 (s, 9H), 4.80 (br, 6H), 7.78 (s, 6H), 8.19–8.22 (m, 15H), 8.81 (d, J = 6.5 Hz, 6H), 8.92 ppm (d, J = 6.3 Hz, 6H); ^{13}C NMR (125 MHz, D_2O): δ = 30.0, 37.4, 48.1, 59.9, 125.9, 126.2, 129.3, 133.7, 134.2, 134.7, 145.0, 145.7, 151.1, 151.8, 168.2 ppm; MS (ESI): *m/z* calcd for $C_{57}H_{60}N_9O_3$: 306.16 $[M-3Cl-3HCl]^{3+}$; found: 306.13.

8: Benzyl bromide (817.0 μL, 1.1 equiv) was added to a suspension of 2,6-dihydroxynaphthalene (1.0 g, 6.24 mmol) and potassium carbonate (1.7 g, 2.0 equiv) in DMF at 5 °C, and the mixture was stirred for 6 h at room temperature. Water was added to the reaction mixture, and the product was extracted with ethyl acetate. The organic layer was washed with brine and dried over magnesium sulfate. After removal of the solvent, purification by column chromatography on silica (ethyl acetate/hexanes = 1:2) yielded 6-benzyloxynaphthalen-2-ol (**8**) (488 mg, 31 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.14 (s, 2H), 7.08 (d, J = 13.1 Hz, 1H), 7.17 (s, 1H), 7.18–7.19 (m, 2H), 7.32–7.34 (m, 1H), 7.37–7.40 (m, 2H), 7.45–7.47 (m, 2H), 7.58–7.62 ppm (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 70.1, 107.5, 109.7, 113.6, 118.0, 119.7, 127.6, 127.6, 127.8, 128.0, 128.5, 128.6, 129.7, 140.0, 137.0, 155.3 ppm; HRMS (FAB): *m/z* calcd for $C_{17}H_{15}O_2$: 251.1072 $[M+H]^+$; found: 251.1062.

9: 1,3-Dibromopropane (1.21 mL, 20.0 equiv) was added to a suspension of **8** (150 mg, 0.6 mmol) and potassium carbonate (250 mg, 3.0 equiv) in acetone, and the mixture was heated at reflux for 2 days. Water was added to the reaction mixture before the product was extracted with ethyl acetate. The organic layer was dried over magnesium sulfate and evacuated to give 2-benzyloxy-6-(3-bromopropoxy)naphthalene (**9**) (214 mg, 96 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.26 (quint, J = 5.90 Hz, 2H), 4.17–4.19 (m, 4H), 4.24 (s, 4H), 5.09 (s, 2H), 6.77–6.78 (m, 3H), 7.06–7.07 (m, 2H), 7.12–7.14 (m, 2H), 7.32–7.35 (m, 1H), 7.41–7.42 (m, 2H), 7.60–7.64 ppm (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 30.3, 32.6, 65.6, 70.3, 107.4, 107.8, 119.3, 119.6, 127.8, 128.2, 128.4, 128.5, 128.8, 130.0, 130.1, 137.3, 155.5, 155.6 ppm; HRMS (EI): *m/z* calcd for $C_{20}H_{19}O_2Br$: 370.0568 $[M]^+$; found: 370.0569.

10:[15] Lithium aluminum hydride (0.7 g, 4.0 equiv) was added to a solution of dimethyl-5-hydroxyisophthalate (1.0 g, 4.76 mmol) in THF at 5 °C, and the mixture was stirred for 6 h at room temperature. The reaction was quenched with MeOH, and the mixture was neutralized with HCl. The resulting mixture was dried over magnesium sulfate and filtered. The filtrate was evaporated to dryness in vacuo to give 3,5-bis(hydroxymeth-

yl)phenol (**10**) (623 mg, 85%). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 4.49 (s, 4H), 4.89 (br, 1H), 6.69 (s, 2H), 6.75 (s, 1H), 7.82 ppm (s, 2H).

11: Phosphorous tribromide (1.07 mL, 4.0 equiv) was added to a solution of **10** (440 mg, 2.85 mmol) in THF at 5°C, and the mixture was stirred for 6 h at room temperature. The reaction was quenched with water, and the product was extracted with ethyl acetate and dried over magnesium sulfate. The product was used in the next step without further purification. The product and sodium azide (1.85 g, 10.0 equiv) were dissolved in DMF and heated at 70°C overnight. Water was added to the reaction mixture, and the product was extracted with ethyl acetate. The organic layer was washed with brine and dried over magnesium sulfate. After removal of the solvent, purification by column chromatography on silica (ethyl acetate/hexanes = 1:4) yielded 3,5-bis(azidomethyl)phenol (**11**) (550 mg, 95%). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 4.30 (s, 3H), 4.89 (s, 1H), 6.75 (s, 2H), 6.82 ppm (s, 1H); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 54.3, 114.8, 120.0, 137.9, 156.2 ppm; HRMS (EI): *m/z* calcd for $C_8H_8N_6O_5$: 204.0760 $[M]^+$; found: 204.0760.

12: Compound **9** (383.8 mg, 0.74 equiv) was added to a solution of **11** (284.2 mg, 1.39 mmol) and potassium carbonate (527.0 mg, 3.0 equiv) in acetone, and the mixture was heated at reflux for 2 days. Water was added to the reaction mixture, and the product was extracted with ethyl acetate. The organic layer was washed with brine and dried over magnesium sulfate. After removal of the solvent, purification by column chromatography on silica (ethyl acetate/hexanes = 1:8) yielded 2-benzyloxy-6-[3-(3,5-bis(azidomethyl)phenoxy)propoxy]naphthalene (**12**) (214 mg, 42%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 2.36 (quint, J = 6.1 Hz, 2H), 3.63 (t, J = 6.5 Hz, 2H), 4.18 (t, J = 5.8 Hz, 2H), 5.14 (s, 2H), 7.09–7.10 (m, 2H), 7.17–7.20 (m, 2H), 7.28–7.29 (m, 1H), 7.32–7.35 (m, 2H), 7.41–7.42 (m, 2H), 7.55–7.58 ppm (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 29.7, 54.9, 64.7, 65.2, 70.5, 107.5, 107.9, 114.4, 119.5, 119.8, 120.4, 128.0, 128.4, 128.6, 128.7, 129.0, 137.5, 138.0, 155.7, 160.1 ppm; HRMS (EI): *m/z* calcd for $C_{28}H_{26}N_6O_3$: 494.2066 $[M]^+$; found: 494.2062.

13: Triphenylphosphine (445.0 mg, 4.0 equiv) was added to a solution of **12** (210.0 mg, 0.43 mmol) in THF, and the resulting solution was stirred at room temperature for 12 h. After removal of the solvent by evaporation, the residue was redissolved in ethyl acetate. Addition of HCl (133.0 μL, 3.0 equiv) to the solution produced a white precipitate, which was collected and washed with ethyl acetate to yield 3-aminomethyl-5-[3-(6-benzyloxynaphthalen-2-yloxy)propoxy]benzylamine dihydrochloride (**13**) (205.4 mg, 94%). ^{1}H NMR (500 MHz, D$_2$O): δ = 2.28–2.30 (m, 2H), 4.05 (s, 4H), 4.26–4.33 (m, 4H), 5.14 (s, 2H), 6.95 (s, 1H), 7.01 (s, 2H), 7.23–7.25 (m, 2H), 7.39–7.50 (m, 7H), 7.28–7.29 (m, 1H), 7.63–7.65 ppm (m, 2H); ^{13}C NMR (125 MHz, D$_2$O): δ = 28.8, 43.0, 65.3, 65.6, 70.4, 108.2, 108.4, 116.1, 119.3, 121.8, 128.2, 128.7, 128.8, 129.0, 129.8, 130.0, 135.4, 136.9, 154.8, 155.2, 159.4 ppm; MS (FAB; free amine): *m/z* calcd for $C_{28}H_{30}N_2O_3$: 442.23 $[M+H]^+$; found: 443.02; elemental analysis: calcd (%) for $C_{28}H_{32}N_2O_3Cl_2$: C 65.24, H 6.26, N 5.43; found: C 65.33, H 6.34, N 5.00.

14: Compound **15** (422.0 mg, 2.5 equiv) was added to a solution of **13** (150.0 mg, 0.29 mmol) and triethylamine (164.0 μL, 4.0 equiv) in dichloromethane, and the resulting solution was stirred at room temperature for 20 h. Removal of the solvent by evaporation followed by column chromatography (ethyl acetate/hexanes = 4:1) yielded {4-[benzyloxycarbonyl({3-({2-[benzyloxycarbonyl(4-benzyloxycarbonylaminobutyl)amino]acetyl-amino}methyl)-5-[3-(6-benzyloxynaphthalen-2-yloxy)propoxy]benzylcarbamoyl}methyl)amino]butyl}carbamic acid benzyl ester (**14**) (287.0 mg, 80%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.20 (br, 4H), 1.32 (br, 4H), 2.19 (quint, J = 5.5 Hz, 2H), 3.00 (br, 4H), 3.25 (br, 4H), 3.82 (br, 4H), 4.01–4.04 (m, 2H), 4.25 (br, 4H), 4.90 (s, 4H), 4.99 (s, 4H), 5.09 (s, 2H), 6.62 (br, 4H), 7.09–7.12 (m, 2H), 7.19–7.23 (m, 2H), 7.26–7.28 (m, 8H), 7.31–7.33 (m, 8H), 7.32–7.35 (m, 2H), 7.40–7.42 (m, 2H), 7.52–7.54 ppm (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 25.3, 26.9, 29.3, 40.4, 43.1, 48.0, 64.3, 64.5, 66.6, 67.7, 70.1, 107.0, 107.5, 119.1, 119.3, 127.5, 127.8, 127.9, 127.9, 128.0, 128.1, 128.2, 128.5, 128.6, 129.7, 129.8, 136.2, 136.6, 127.0, 155.3, 155.3, 156.4 ppm; HRMS (FAB): *m/z* calcd for $C_{72}H_{79}N_6O_{13}$: 1235.5705 $[M+H]^+$; found: 1235.5706.

2: Compound **1** (2.0 mg, 1.76 μmol) and CB[8]·H_2SO_4·16H_2O (8.9 mg, 3.2 equiv) were dissolved in D$_2$O (1.5 mL). After the undissolved CB[8] was removed by filtration, the filtrate was slowly evaporated under reduced pressure to yield **2** (8.3 mg, 92%). ^{1}H NMR (500 MHz, D$_2$O) δ = 2.44 (br, 6H), 3.64 (br, 6H), 4.27 (d, J = 14.3 Hz, 48H), 4.41 (s, 9H), 4.80 (br, 6H), 5.56 (s, 48H), 5.77 (d, J = 14.3 Hz, 48H), 7.15 (br, 6H), 7.72 (br, 6H), 7.93 (br, 6H), 8.54–8.68 ppm (m, 15H); MS (CSI): *m/z* calcd for $C_{201}H_{207}N_{105}O_{51}$: 817.78 $[M-6Cl]^{6+}$; found: 818.04.

4: Palladium activated on carbon (10%) was added to a solution of **14** (90.0 mg, 71.8 μmol) in methanol/ethyl acetate (1:4), and the mixture was stirred at room temperature under hydrogen atmosphere for 12 h. After removal of the catalyst by filtration, the solution was acidified with HCl to produce **3**. As **3** is very hygroscopic, it was used for the next step without isolation. A slight excess of CB[6] was added to the solution of **3**, and the resulting mixture was stirred for 10 min. After the undissolved CB[6] was filtered off, the solvent was removed by evaporation under reduced pressure to produce **4**, which was recrystallized from ethanol (190.2 mg, 93%). ^{1}H NMR (500 MHz, D$_2$O): δ = 0.52 (br, 4H), 0.60 (br, 4H), 2.27 (br, 10H), 4.18 (s, 4H), 4.26–4.33 (m, 28H), 4.37 (s, 4H), 5.55 (s, 24H), 5.67 (d, J = 15.6 Hz, 12H), 5.73 (d, J = 15.6 Hz, 12H), 7.04 (s, 2H), 7.06 (s, 1H), 7.21–7.23 (m, 2H), 7.30 (d, J = 13.6 Hz, 2H), 7.73–7.77 ppm (m, 2H); MS (CSI): *m/z* calcd for $C_{105}H_{124}N_{54}O_{29}$: 1302.5 $[M-2Cl]^{2+}$, 868.3 $[M-3Cl]^{3+}$, 651.2 $[M-4Cl]^{4+}$; found: 1302.1, 868.3, 651.6; elemental analysis: calcd (%) for $C_{105}H_{124}N_{54}O_{39}Cl_4$·14$H_2O$: C 42.03, H 5.11, N 25.21; found: C 41.89, H 4.93, N 25.32.

5: 2,6-Dihydroxynaphthalene (1.2 mg, 3.0 equiv) was added to an aqueous solution of **2** (2.0 mL, 1.17 mM), and the resulting solution was stirred for 10 min, during which the solution turned brown. After the volume of the solution was decreased to about 0.5 mL under reduced pressure, methanol was added to the solution to precipitate the product **5**, which was filtered, washed with ethanol, and dried (9.0 mg, 69%). ^{1}H NMR (500 MHz, D$_2$O): δ = 2.62 (br, 6H), 3.80 (br, 6H), 4.18 (d, J = 14.5 Hz, 48H), 4.38 (s, 9H), 4.80 (br, 6H), 5.48 (s, 48H), 5.74 (d, J = 14.5 Hz, 48H), 5.98 (br, 6H), 6.08 (s, 6H), 6.49 (br d, J = 19.0 Hz, 12H), 7.14 (d, J = 5.9 Hz, 6H), 7.29 (d, J = 6.0 Hz, 6H), 8.38 (d, J = 6.1 Hz, 6H), 8.59 (d, J = 6.2 Hz, 6H), 8.62 ppm (s, 3H); MS (CSI): *m/z* calcd for $C_{231}H_{231}N_{105}O_{57}$: 897.81 $[M-6Cl]^{6+}$; found: 898.00.

6: Compound **4** (6.30 mg, 3.0 equiv) was added to an aqueous solution of **2** (600 μL, 1.17 mM), and the mixture was stirred for 10 min. Compound **6** was isolated by the same procedure as for **5** (8.0 mg, 84%). The product ($C_{516}H_{579}N_{267}O_{138}Cl_{18}$) was slightly contaminated with organic impurities, (nBu)$_4$NCl (from the synthesis of **1**), and methanol as judged by ^{1}H NMR spectroscopy. In the ^{1}H NMR spectrum of **1**, the peaks from the n-butyl protons of (nBu)$_4$NCl were found at 0.8, 1.3, 1.6, and 3.2 ppm. A signal from the methyl protons of methanol was also observed at 2.9 ppm. A satisfactory elemental analysis of **6** was obtained by addition of 2 mol of (nBu)$_4$NCl and 3 mol of methanol. ^{1}H NMR (500 MHz, D$_2$O): δ = 0.48 (br, 12H), 0.58 (br, 12H), 2.22 (br, 36H), 3.69 (br, 6H), 4.12 (br, 81H), 4.31 (br, 72H), 4.52 (s, 9H), 5.41 (s, 48H), 5.65 (br, 192H), 6.20 (br, 6H), 6.52 (br, 12H), 7.01 (br, 21H), 7.29 (br, 6H), 8.05 (br, 6H), 8.46 (br, 6H), 8.85 ppm (s, 3H); MS (CSI): *m/z* calcd for $C_{516}H_{579}N_{267}O_{138}$: 706.76 $[M-18Cl]^{18+}$, 750.39 $[M-17Cl]^{17+}$, 855.10 $[M-15Cl]^{15+}$, 992.03 $[M-13Cl]^{13+}$; found: 706.20, 750.00, 855.64, 992.00; elemental analysis: calcd (%) for $C_{551}H_{913}N_{269}O_{266}Cl_{20}$: C 40.67, H 5.66, N 23.16; found: C 40.69, H 5.26, N 22.81.

UV/Vis Titration Experiment

A solution of **4** in water (0.10 mL, 6.67 mM) was gradually added to a solution of **2** in water (0.28 mL, 0.59 mM) with stirring while the UV/Vis spectrum was recorded. The observed intensity at 526 nm was corrected to compensate for dilution.

2D NMR Experiments

COSY and ROESY experiments were performed to assign the proton resonances of **6** on a Bruker DRX500 NMR spectrometer operating at the proton Larmor frequency of 500.23 MHz at 298 and 323 K. ROESY spectra were recorded by using the time-proportional-phase-increment method with a mixing time of 0.3 s and a recycle delay of 2 s.

Diffusion NMR Experiments

Measurements of diffusion coefficient were carried out by using a 5-mm Bruker QNP probe with an actively shielded *z*-gradient coil. Diffusion coefficients were extracted from a series of ^{1}H NMR spectra acquired with the bipolar pulse longitudinal encode–decode (BPPLED) pulse sequence as a function of gradient amplitude. In each experiment, the gradient duration was 2.0 or 2.5 ms, and the amplitudes of the gradient pulses ranged from 1 to 40 G cm^{-1}. The diffusion time was 30–50 ms.

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