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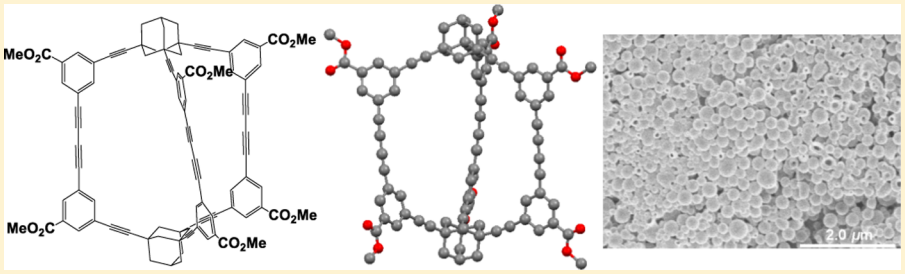
Hollow Sphere Formation from a Three-Dimensional Structure Composed of an Adamantane-Based Cage

Masahide Tominaga,*[,†] Kazuaki Ohara,[†] Kentaro Yamaguchi,[†] and Isao Azumaya*[,‡]

[†]Faculty of Pharmaceutical Sciences at Kagawa Campus, Tokushima Bunri University, 1314-1 Shido, Sanuki Kagawa 769-2193, Japan

[‡]Faculty of Pharmaceutical Sciences, Toho University, 2-2-1 Miyama, Funabashi, Chiba 274-8510, Japan

Supporting Information



ABSTRACT: An adamantane-based cage with a three-dimensional (3D) framework was synthesized by the copper-mediated acetylene coupling reaction, in which two 1,3,5-triethynyladamantane units were linked by phenyldiacetylenic bridges possessing ester groups. X-ray crystallography revealed that the cage has an internal space and accommodates a solvent molecule, which afforded molecular networks through CH/O interactions between cage molecules. Furthermore, the cage containing six ester groups spontaneously self-assembled into hollow spherical aggregates with an average diameter of 230 nm in a mixed solvent.

Hollow three-dimensional (3D) structures have attracted significant interest because of their potential in guest inclusion, the stabilization of reactive intermediates, and specific chemical transformations.[1−4] A number of 3D structures including cages, capsules, tubes, and others have been produced using directional noncovalent interactions such as hydrogen bonds and metal coordination in addition to the construction of covalently bound 3D molecules.[5−7] A wide variety of molecular cages have been used as receptors for guest molecules and also as building blocks for the self-assembled nanostructures of higher hierarchy in the fields of supramolecular chemistry and materials science.[8−10] In particular, vesicles as unique and basic spherical objects have received attention because of their practical applications as light-harvesting systems and in drug delivery.[11−13] To construct these vesicular aggregates, numerous synthetic amphiphiles have been designed as surfactants with polar head groups and hydrophobic tails. Recently, large π-conjugated aromatic molecules have been transformed into innovative amphiphilic molecules, which turn into vesicles with desirable and tunable sizes, stabilities, and functions because of their π-stacking ability in aqueous and polar organic solutions. In addition to the use of amphiphilic polymers[14] and disk- or rodlike molecules,[15] vesicular structures derived from amphiphilic macrocyclic molecules such as calixarenes, cyclodextrins, cucurbiturils, and cyclophanes have been reported.[16] In contrast, the preparation of synthetic molecular cages with 3D frameworks for direct self-assembly into spherical architectures has been limited. The reverse-vesicle organization of hydrogen-bonded arylamide-derived hexaammonium capsules in apolar solvents has been described by Li and co-workers.[17] Recently, we demonstrated the synthesis and crystal structure of a series of adamantane-based molecules with multiple branching and macrocyclic frameworks, which provided network structures with cavities and one-dimensional channels.[18] Trisubstituted adamantanes are especially versatile building blocks for the construction of novel 3D frameworks because their bulky skeletons allow them to form internal spaces. Therefore, we designed an adamantane-based cage (**1**) in which two 1,3,5-triethynyladamantane units were linked by three phenyldiacetylenic bridges bearing ester groups. In this paper, we report the construction and structural analysis of a nanosized synthetic cage. Furthermore, a molecular cage with ester groups at its periphery spontaneously assembled into uniform hollow spherical aggregates with a multilayer membrane, vesicle-like aggregates, in a mixed solvent.

An adamantane-based cage with a cavity was designed and synthesized according to Scheme 1. We selected triethynyladamantane as a trisubstituted adamantane derivative because it has proven to be a versatile scaffold.[19] Triethynyladamantane can be prepared in two steps from adamantane according to the routes of Malik and co-workers.[20] We chose 3-iodo-5-[(trimethylsilanyl)ethynyl]benzoic acid methyl ester as the bridge moiety and prepared it by the method established by Moore et al. and Keana et al.[21] A Sonogashira coupling reaction between triethynyladamantane and 3-iodo-5-[(trimethylsilanyl)ethynyl]benzoic acid methyl ester afforded

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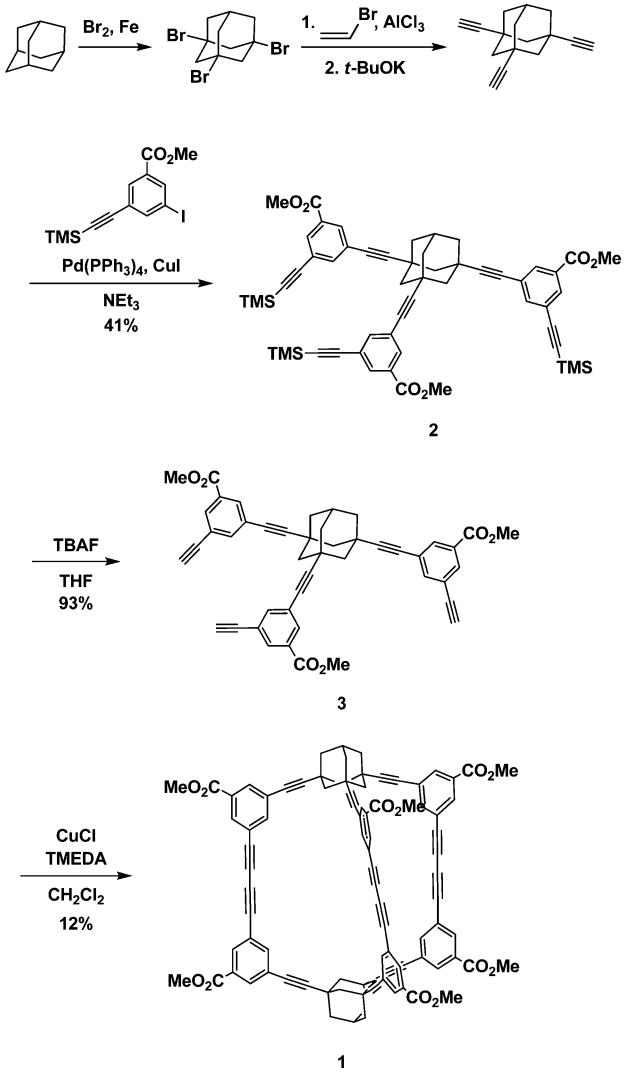
Scheme 1. Synthesis of the Adamantane-Based Cage 1



2 in 41% yield. Desilylation (93%) followed by Hay acetylene coupling provided cage **1** in 12% yield. Adamantane-based cage **1** was characterized by ^{1}H and ^{13}C NMR spectroscopy, and only one signal for the methine proton and one signal for the carbon of the adamantane parts were found, respectively, indicating that the product was synthetic cage **1**. The mass spectroscopy data of cage **1** are in agreement with the structures presented.

The structure of cage **1** was unambiguously determined by single-crystal X-ray analysis (Figure 1). Single crystals of cage **1** were obtained by the vapor diffusion of hexane into a chloroform/mesitylene solution of **1**. X-ray crystallographic analysis revealed that the compound crystallized in the *P*-1 space group with one molecule of **1**, one molecule of hexane, and four molecules of mesitylene in the asymmetric unit. The crystal structure of **1** exhibited a cagelike shape with an internal space where the distance between the two bridgehead protons in the two adamantane moieties was 19.8 Å. The distances between the methyl carbons in the ester groups were 15.85−19.93 Å. The acetylene parts deviate slightly from linearity with C≡C−C angles of 177.0−179.7°. Each cage molecule was packed into a 3D network architecture through CH/O interactions between ester oxygen atoms and phenyl ring protons, methyl protons of ester groups, or methylene protons

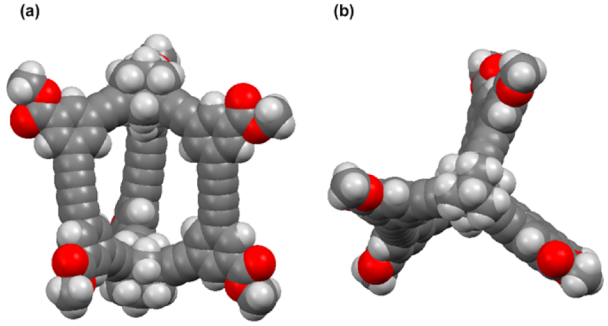


Figure 1. (a) Side view and (b) top view of the crystal structure of cage **1** as a space-filling model. Hexane and mesitylene molecules are omitted for clarity.

of adamantane in a neighboring cage molecule and in the crystalline lattice (Figure 2). Two different types of channels

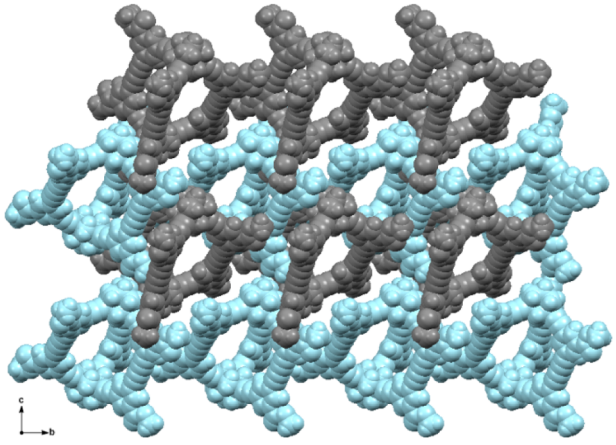


Figure 2. Packing diagram of crystal **1**. View of the network structure viewed along the *a* axis. Hexane and mesitylene molecules are omitted for clarity.

were thus formed along the *a* axis, and these were composed of the cavities of the cages and the void spaces between the cages. The hexane and mesitylene molecules were accommodated within the internal spaces.

Molecular cage **1** dissolved in tetrahydrofuran, chloroform, and benzene, whereas it was only slightly soluble in methanol and hexane. The aggregation behavior of the molecular cage was examined in a polar mixed solvent of methanol and tetrahydrofuran (1:2, v/v) using dynamic light scattering (DLS), field-emission scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM). Cage **1** was dissolved in tetrahydrofuran (6.7×10^{-4} M) at 40 °C and allowed to stand for 5 days at 25 °C. DLS measurements revealed a low scattering intensity, indicating that no large aggregates were formed in solution. In the mixed solvent, cage **1** showed aggregation behavior with a narrow size distribution, and the diameter of the spherical assemblies was estimated to be 230 nm (Figure S1, Supporting Information). The generation of cage-based spheres was also confirmed by the FE-SEM experiment, and spherical shapes with a uniform diameter in the range of 150−300 nm were obtained (Figure 3a). The SEM image indicated that the resultant aggregates are robust and stable because they retain their spherical shape without collapsing despite being dried on a solid surface. Most of the vesicles built using various amphiphiles have been found

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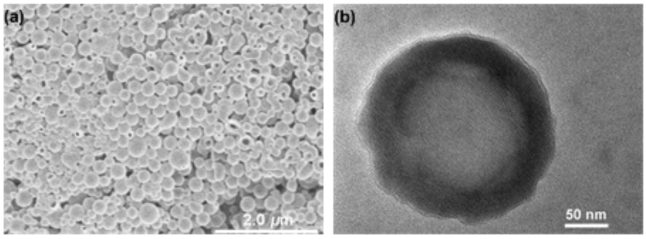

Figure 3. Hollow spherical assemblies prepared in a mixed solvent with adamantane-based cage **1** (6.7×10^{-4} M): (a) SEM and (b) TEM micrographs.

to be flat on the surface under similar conditions.[22] Furthermore, several spherical aggregates had holes in their periphery, revealing a hollow center. The TEM measurements also provided evidence for the generation of hollow spheres. The TEM images indicated a clear contrast between the peripheries and the centers of the spherical structures. The wall thickness of the hollow spheres was estimated to be 25−30 nm, which again indicates multilayer structures (Figure 3b). Additionally, burst spherical structures were partly present (Figure S2, Supporting Information). These findings are consistent with the results obtained from the DLS and SEM experiments. The cage-based spheres were relatively stable in solution under these conditions without precipitation occurring, and they were of similar shape and size after 2 weeks. In a more polar mixed solvent of methanol and tetrahydrofuran (1:1, v/v), larger spherical assemblies were observed by SEM (Figure S3, Supporting Information). However, after 2 weeks under these conditions, precipitated solids were present among the spherical assemblies in solution. Conversely, spherical aggregates were not present when using adamantane-based cage **1** in a mixed solvent of methanol and tetrahydrofuran (1:4, v/v). These results indicate that the polarity in a mixed solvent considerably influences the stability and size of the spherical assemblies.

The crystal structure of cage **1** showed that molecule **1** is ca. 2.0 nm wide. We thus assume that the hollow spheres end up with multilayer morphology by the two- and three-dimensional packing of cage frameworks. The six polar carboxylic ester groups are likely exposed to the polar organic solvents by being bound to the outside of the spherical assemblies, whereas the cage frameworks that consist of aromatic and aliphatic units are packed into layered structures, which minimizes the interaction with polar solvents. In contrast to more common amphiphiles with large polar head groups and hydrophobic tails, the adamantane-based cage **1** possesses a large nonpolar scaffold and polar groups on its periphery.

In summary, we produced nanosized synthetic cages based on adamantane by the macrocyclization of a trisubstituted adamantane bearing acetylenic aromatic ring units through copper-mediated oxidative coupling. X-ray diffraction experiments of the cage revealed that the cage molecule has an internal space and that it formed molecular networks containing two types of channels. This was possible because of weak noncovalent interactions in the crystalline lattices with the solvent molecules that were accommodated within the internal spaces. The adamantane-based cage afforded well-defined hollow spheres with a multilayer membrane in the organic solvents. The spherical aggregates derived from the discrete 3D framework possess the potential properties of liposomes and 3D hosts, and the findings in this study may allow for the exploitation of host−guest systems and specific delivery. Furthermore, the cages possess ester groups, which allow for the incorporation of additional functional molecules at the periphery of the cages. The linking of a variety of functional groups to the six ester groups resulted in six functional groups being incorporated into the spherical assemblies. The design and self-assembly of cage molecules functionalized with biofunctional groups such as sugars and peptides is the subject of our current studies.

EXPERIMENTAL SECTION

General Information. All solvents and reagents were obtained from commercial suppliers and were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded with a 400 MHz NMR instrument in $CDCl_3$ at 298 K using tetramethylsilane as an internal standard. Mass spectra were obtained by FAB-MS or high-resolution ESI-MS experiments. X-ray crystal structure data were collected using a Quantum Q315 CCD area detector at the beamline of BL38B1 of SPring-8. The structure was refined with the SHELX-97 programs. Dynamic light-scattering experiments were performed on an instrument equipped with a 4 mW He−Ne laser (633 nm wavelength) at a fixed detector angle of 90°. SEM and TEM samples were prepared by depositing the solution of **1** on Al foil and a carbon-coated copper grid and dried in vacuo. SEM samples were then coated with Pt/Pd in an ion coater for 40 s. SEM images were obtained at an accelerating voltage of 1.5 kV on a FE-SEM. TEM measurements were performed using a transmission electron microscope at an accelerating voltage of 120 kV.

1,3,5-Triethynyladamantane. This compound was synthesized as described in the literature:[20] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 2.14 (s, 3H), 2.11 (t, J = 3.2 Hz, 1H), 1.95 (s, 6H), 1.78 (d, J = 3.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 90.0, 68.2, 46.2, 40.4, 29.8, 27.8.

3-Iodo-5-[(trimethylsilanyl)ethynyl]benzoic Acid Methyl Ester. This compound was prepared as described in the literature:[21] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.30 (t, J = 1.6 Hz, 1H), 8.07 (t, J = 1.2 Hz, 1H), 7.97 (t, J = 1.6 Hz, 1H), 3.92 (s, 3H), 0.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 164.9, 144.3, 138.2, 132.2, 131.7, 125.4, 102.0, 97.1, 93.1, 52.5, −0.3.

1,3,5-Tris-[(3-(methoxycarbonyl)-5-[(trimethylsilanyl)-ethynyl]phenyl)ethynyl]adamantane (2). A mixture of 1,3,5-triethynyladamantane (0.47 g, 2.28 mmol), 3-iodo-5-[(trimethylsilanyl)ethynyl]benzoic acid methyl ester (3.43 g, 9.57 mmol), $Pd(PPh_3)_4$ (0.26 g, 0.23 mmol), and CuI (43.8 mg, 0.23 mmol) in triethylamine (30 mL) was refluxed for 3 days under an argon atmosphere. After being cooled to room temperature, the reaction mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was dissolved in $CHCl_3$, and then the dark brown solution was washed with H_2O and brine and dried over Na_2SO_4. Evaporation of the solvent followed by silica gel column chromatography (eluent: $CHCl_3$/hexane = 1:4) and gel permeation chromatography (eluent: $CHCl_3$) afforded the title compound as a solid (0.84 g, 0.93 mmol) in 41% yield: mp 99−100 °C; FT-IR (ATR, cm^{-1}) 2947, 2850, 2161, 1725, 1507, 1324, 1236, 1112, 1003, 775. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.02 (t, J = 1.6 Hz, 3H), 7.98 (t, J = 1.6 Hz, 3H), 7.67 (t, J = 1.6 Hz, 3H), 3.92 (s, 9H), 2.24 (br s, 1H), 2.11 (s, 6H), 1.90 (d, J = 2.0 Hz, 6H), 0.25 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 165.8, 138.8, 132.4, 132.0, 130.5, 124.2, 123.8, 103.1, 96.9, 95.9, 79.2, 52.3, 46.3, 40.5, 30.7, 28.0, −0.2; MS (FAB, m/z) calcd for $C_{55}H_{59}O_6Si_3$ ($M + H^+$) 899.45, found 898.9. Anal. Calcd for $C_{55}H_{58}O_6Si_3$: C, 73.46; H, 6.50. Found: C, 73.19; H, 6.53.

1,3,5-Tris[(3-(methoxycarbonyl)-5-[(ethynylphenyl)-ethynyl]]adamantane (3). A mixture of **2** (0.89 g, 1.0 mmol) and tetrabutylammonium fluoride (1.89 g, 6.0 mmol) in dried THF (30 mL) was stirred for 12 h at room temperature under an argon atmosphere. The reaction was quenched with 1 M HCl at 0 °C, and the mixture was extracted with chloroform. The extracts were washed with water and brine and dried over Na_2SO_4. Evaporation of the

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solvent followed by silica gel column chromatography (eluent: $CHCl_3$) afforded the title compound as a solid (0.65 g, 0.93 mmol) in 93% yield: mp 88−90 °C; FT-IR (ATR, cm^{-1}) 3293, 2936, 2910, 2857, 2164, 1724, 1590, 1440, 1320, 1235, 1223, 1112, 771; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.05 (t, J = 1.2 Hz, 3H), 8.02 (t, J = 1.2 Hz, 3H), 7.68 (t, J = 1.2 Hz, 3H), 3.92 (s, 9H), 3.12 (s, 3H), 2.26 (br s, 1H), 2.13 (s, 6H), 1.92 (d, J = 2.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 165.7, 138.9, 132.9, 132.2, 130.6, 124.4, 122.8, 97.1, 81.9, 79.1, 78.5, 52.4, 46.2, 40.4, 30.7, 28.0; HRMS (ESI, m/z) calcd for $C_{46}H_{34}O_6Na$ ($M + Na^+$) 705.2248, found 705.2224.

Adamantane-Based Cage (1). A mixture of **3** (137 mg, 0.20 mol), copper(I) chloride (198 mg, 2.00 mmol), and *N,N,N′,N′*-(tetramethylethylene)diamine (TMEDA) (233 mg, 2.00 mmol) in CH_2Cl_2 (80 mL, 2.5 mM) was stirred for 12 h at room temperature. The reaction mixture was washed with water and brine, and dried over Na_2SO_4. Evaporation of the solvent followed by silica gel column chromatography (eluent: $CHCl_3$) and gel permeation chromatography (eluent: $CHCl_3$) afforded the title compound (16.3 mg, 0.012 mmol) as a solid in 12% yield: mp >300 °C dec; FT-IR (ATR, cm^{-1}) 2968, 2870, 2160, 1740, 1506, 1490, 1318, 1260, 1112, 1001, 793; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.05 (t, J = 1.6 Hz, 6H), 8.03 (t, J = 1.6 Hz, 6H), 7.79 (t, J = 1.6 Hz, 6H), 3.93 (s, 18H), 2.30 (br s, 2H), 2.23 (d, J = 12.8 Hz, 6H), 2.14 (d, J = 12.4 Hz, 6H), 1.94 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 165.5, 140.6, 132.6, 131.8, 130.9, 124.6, 122.3, 97.4, 80.3, 79.0, 74.8, 52.5, 46.8, 39.7, 30.8, 27.9; HRMS (ESI, m/z) calcd for $C_{92}H_{63}O_{12}$ ($M + H^+$) 1359.4314, found 1359.4316. Crystallographic data for **1**: $C_{67}H_{61.26}O_6$, M_r = 962.42, triclinic, P-1, a = 13.782(3) Å, b = 19.442(4) Å, c = 21.953(4) Å, α = 88.24(3)°, β = 76.49(3)°, γ = 86.79(3)°, V = 5710(2) Å^3, Z = 4, D_c = 1.120 Mg m^{-3}, $2\theta_{max}$ = 52.98°, T = 300 K, 12911 reflections measured and 8045 unique (R_{int} = 0.0544). μ = 0.070 mm^{-1}, T_{max} = 0.9958, and T_{min} = 0.9916. The final R_1 and w$R_2(F^2)$ was 0.0914 and 0.2486 ($I > 2\sigma(I)$), 0.1404 and 0.2955 (all data). CCDC 973447.

■ ASSOCIATED CONTENT

Supporting Information

^1H and ^{13}C NMR spectra for compounds **1**−**3**, X-ray crystallographic file (CIF), DLS data, and SEM and TEM images for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: tominagam@kph.bunri-u.ac.jp.

*E-mail: isao.azumaya@phar.toho-u.ac.jp.

Notes

The authors declare no competing financial interest.

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