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Construction and Charge-Transfer Complexation of Adamantane-Based Macrocycles and a Cage with Aromatic Ring Moieties

Masahide Tominaga,* Hyuma Masu, and Isao Azumaya*

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

tominagam@kph.bunri-u.ac.jp; azumayai@kph.bunri-u.ac.jp

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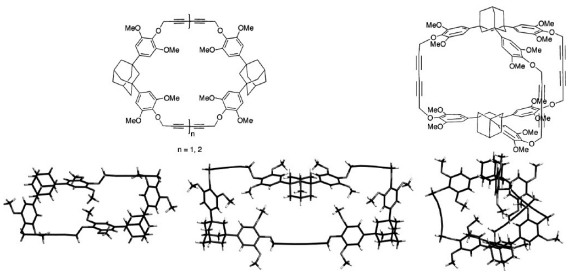

Adamantane-based macrocycles and a cage with aromatic ring moieties have been developed and structurally revealed by X-ray crystallographic analysis. The dimerized (**1**) and trimerized (**2**) macrocycles of binary molecules based on adamantane with acetylenic aromatic ring moieties were designed and effectively synthesized. Similarly, a cryptand-like macrobicyclic cage (**3**) was constructed from a trisubstituted adamantane derivative. Single-crystal X-ray analysis revealed that both cyclic compounds have nearly a rectangular shape with or without a solvent molecule in the cavity. The macrobicyclic cage has an inner space and accommodates a chloroform molecule via C−H$\cdots\pi$ interactions. Macrocycles and cage encapsulate 1,3,5-trinitrobenzene (**4**) as an electron-poor guest in a one-to-one complex via charge-transfer interactions in a parallel fashion, and showed the formation of molecular networks such as columns, tubes, 2D layers, and 3D networks composed of two different types through noncovalent interactions in the solid state.

Introduction

In the last two decades, two- and three-dimensional host molecules have been investigated as attractive platforms for functional materials in the fields of organic and materials chemistry.[1] Inspired by the remarkable functionality of macrocyclic structures, significant attention has been directed to the creation of macrocycles for their potential applications in areas such as molecular recognition, transmembrane transport, ion-channel formation, and gas adsorption.[1,2] A number of synthetic routes have been developed to produce various macrocyclic compounds from simple organic molecules and cycles with diameters of up to several nanometers such as calixarenes,[3] calixpyrroles,[4] and so on[5] have been

*To whom correspondence should be addressed. M.T.: phone 81-87-894-5111 ex. 6305, fax 81-87-894-0181. I.A.: phone 81-87-894-5111 ex. 6308, fax 81-87-894-0181.

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obtained. The construction of host−guest complexes formed between macrocycles and guest molecules can offer a good foundation for understanding guest-induced structural motifs and molecular recognition, leading to the development of unique chemical and physical properties.[6] The macrocyclic host molecules allow complexation with a wide variety of ions, atoms, and small molecules through noncovalent interactions such as hydrogen bonding, hydrophobic interactions, aromatic stacking, and van der Waals interactions.[7] In particular, macrocycles consisting of electron-rich aromatic rings are able to form complexes with electron-deficient guest molecules via charge-transfer interactions.[8] Such macrocycles have been used in the design of host−guest inclusion compounds[9] and diverse supramolecular architectures such as catenanes,[10] rotaxanes,[11] folded aedamers,[12] and macrocycle-tweezer complexes.[13] However, the components of such systems have generally involved substructures[10−14] such as *N*-benzylbipyridinium units, pyromellitic diimide parts, and alkoxynaphthalene moieties, and macrocycles consisting of alternative units are essential in the design of solid state structures and functions based on host−guest chemistries. Adamantane and its derivatives[15] are a class of structurally unique compounds because they are mechanically rigid and conformationally well-defined. Adamantane derivatives as rigid, tetrahedrally symmetrical compounds with two- or three-dimensional scaffolds have been found in numerous applications in medicinal chemistry and material sciences. However, the design and synthesis of adamantane-based hosts and their applications in host−guest chemistry remain largely unexplored. Recently, we have demonstrated that the complexation of disubstituted adamantane consisting of 2,6-dimethoxyphenol as an electron-rich unit with 1,3,5-trinitrobenzene[16] as an electron-poor guest assembles in the solid state to form a molecular network through donor−acceptor interactions.[17] We have therefore applied this moiety as a structural fragment to construct macrocyclic and cage frameworks, in which two or three units of binary molecules based on adamantane, and two units of trisubstituted adamantane are covalently linked by a 1,6-dioxahexa-2,4-diyne spacer with relatively rigid and directional characteristics. Acetylenic units are used as bridges to provide rigidity to the cyclic framework and the number of acetylenic units in the bridge and its connectivity to the arene units define the size and shape of the cavity in the macrocycle and cage.[18] In this paper, we report the construction and structural analysis of two types of macrocycles and a cryptand-like macrobicyclic cage, which encapsulate electron-poor guest molecule in a one-to-one complex via charge-transfer interactions. Further, macrocycles and cage including guest molecule showed the generation of unique molecular networks in the crystal lattice.

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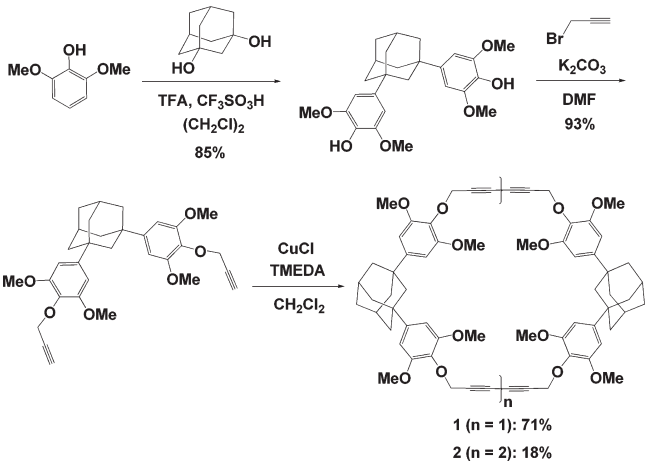
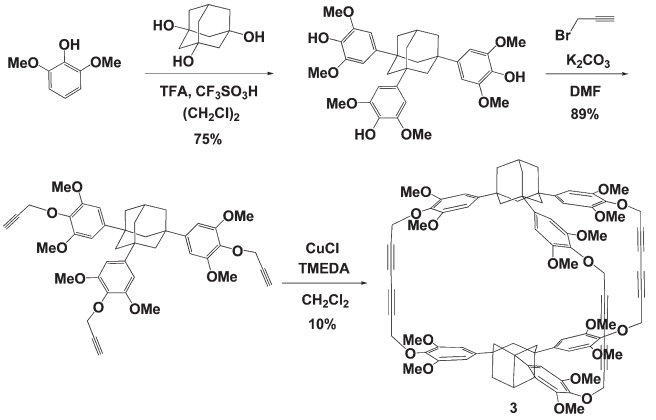
SCHEME 1. The Synthesis of Macrocycles 1 and 2



SCHEME 2. The Synthesis of a Cryptand-like Macrobicyclic Cage 3



Results and Discussion

The copper-mediated oxidative acetylene dimerization has been utilized as ring closure reactions to prepare the macrocycle and cage compounds with well-defined structures because of the directional property of the diacetylenic bridge unit. To construct a macrocyclic framework with a large cavity, macrocycles were designed and effectively synthesized in three steps from commercially available starting materials (Scheme 1). The reaction of 2,6-dimethoxyphenol with 1,3-adamantanediol gave a binary molecule based on adamantane (85%), which was subsequently treated with propargyl bromide to afford disubstituted adamantane with a yield of 93%. The Hay acetylene coupling provided dimerized macrocycle **1** (71%) and trimerized macrocycle **2** (18%) in high-dilution conditions. The molecular cage **3** was also readily synthesized from 1,3,5-adamantanetriol in three steps according to Scheme 2. The macrocycles **1**, **2**, and **3** were characterized by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and FAB mass spectroscopy. The results of the characterization are in full agreement with the structures presented. The macrocyclic structures of **1**−**3** are identified from the ^{1}H and ^{13}C NMR spectra, which showed only one signal for the methine proton and carbon of the adamantane moieties, respectively. The singlet for the aromatic protons indicates that each aromatic ring rotates freely at room temperature in the macrocyclic framework.

Single crystals of macrocycles **1** and **2** were obtained from vapor diffusion of hexane into a chloroform solution of **1**. The crystal **1** crystallized in the triclinic system, space group $P\bar{1}$, and included one molecule of **1** and two molecules of chloroform in the unit cell. X-ray crystallographic analysis showed that the macrocyclic structure of **1** was a rectangular shape, where the distance between the centroids of opposing rings is 15.85 and 8.04 Å, respectively (Figure 1a). Two chloroform molecules were accommodated in the cavity of macrocycle **1**, where intermolecular C−H···O interactions (the C···O distance is 3.20 Å) were observed between the methine proton of the chloroform molecule and the oxygen atom of the methoxy groups. The crystal **2** crystallized in the orthorhombic system, space group *Pnma*, and included only molecule of **2**. In the crystals of **2**, macrocyclic structure of **2** is a rectangular shape, where the distances between the centroids of opposing rings are 12.29, 22.42, and 12.29 Å, respectively (Figure 1b). The cyclic framework has a C_s symmetry in the solid state and is ascribed to the packing effect. Specifically, macrocycle **2** is relatively flexible in comparison to **1** such that the cavity was filled with a portion of the macrocycle. Single crystals of compound **3** were obtained from vapor diffusion of cyclohexane into a chloroform solution of **3**. X-ray crystallographic analysis showed that the crystal belonged to the space group $P2_1/c$, which contains one molecule of both **3** and cyclohexane, and two molecules of chloroform in the unit cell (Figure 1c,d). The crystal structure reveals that the distance between the two bridgehead carbons in the two adamantane moieties of **3** is 12.90 Å, and the two sets of distances between the methylene carbons in the linker units are 13.54, 12.98, and 12.50 Å and 13.46, 13.17, and 12.25 Å, respectively. The cage **3** in the solid state is twisted by the rotation of the triphenyladamantane moieties to minimize the more energetically favorable structure and is due to the flexibility of the 1,6-dioxahexa-2,4-diyne bridges relative to each other. Therefore, the cage framework contains a set of enantiomeric helical conformers with left- and right-handed helical twists in the crystal lattice. The angle of the twist between the two adamantane parts at both ends of the molecule is 52.6°. One chloroform molecule was included in the cavity of cage **3**, where intermolecular C−H···π interactions (the distance measured from the center of the ring to the carbon atom of the chloroform molecule is 3.89 Å) were observed between the methine proton of the chloroform molecule and the aromatic ring part.

The adamantane-based macrocycles and cage containing aromatic ring moieties as electron donors have a rigid framework and are expected to potentially entrap the electron-deficient guests. 1,3,5-Trinitrobenzene (**4**) was chosen as a substrate, which represents an agent for crystalline π−π donor−acceptor complexes. In fact, the adamantane-based macrocycles and cage encapsulate electron-poor guest molecule in a one-to-one complex via charge-transfer interactions in the solid state. Single crystals of complex **1**·**4** were obtained as pale yellow blocks by vapor diffusion of hexane into a chloroform solution containing **1** and **4** as an electron donor in 1:4 molar ratio. The crystal of complex **1**·**4** was significantly different in color from that of the component solids. The crystal of complex **1**·**4** crystallized in the monoclinic system, space group $P2_1/c$, and included one molecule

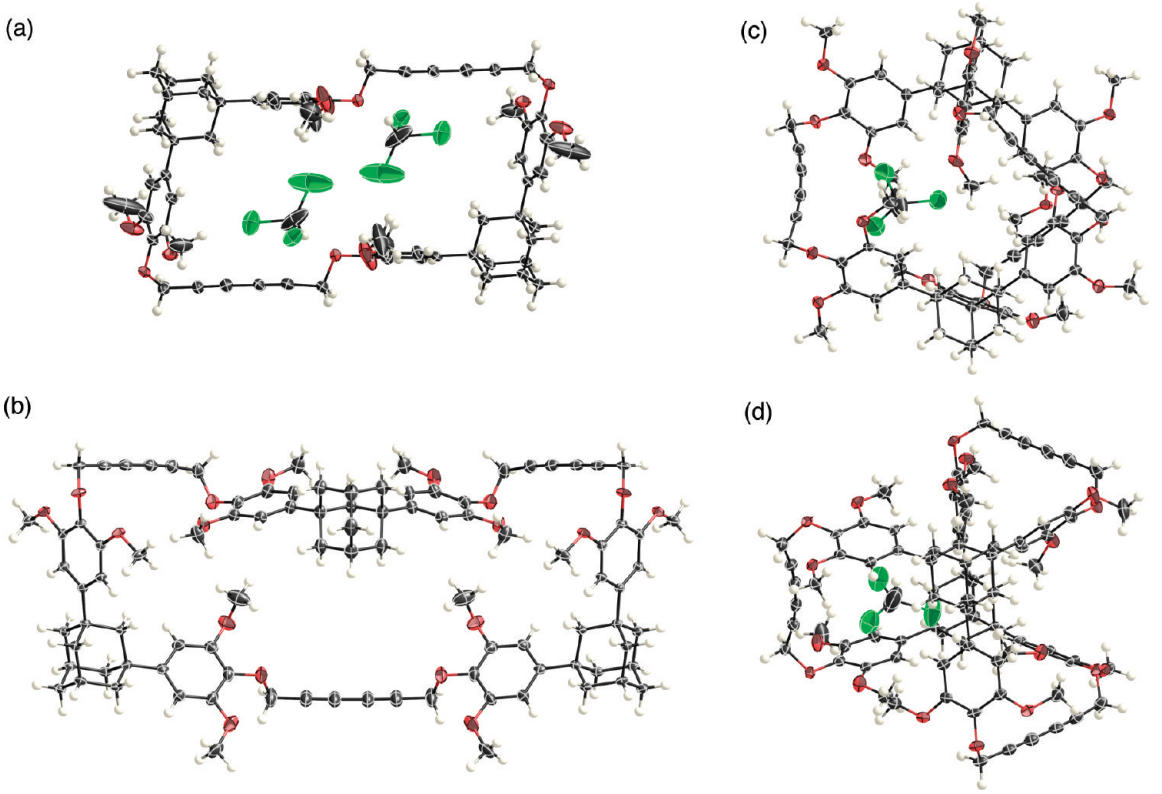


FIGURE 1. Crystal structures of **1** (a), **2** (b), side view of **3** (c), and top view of **3** (d) in the thermal ellipsoid model.

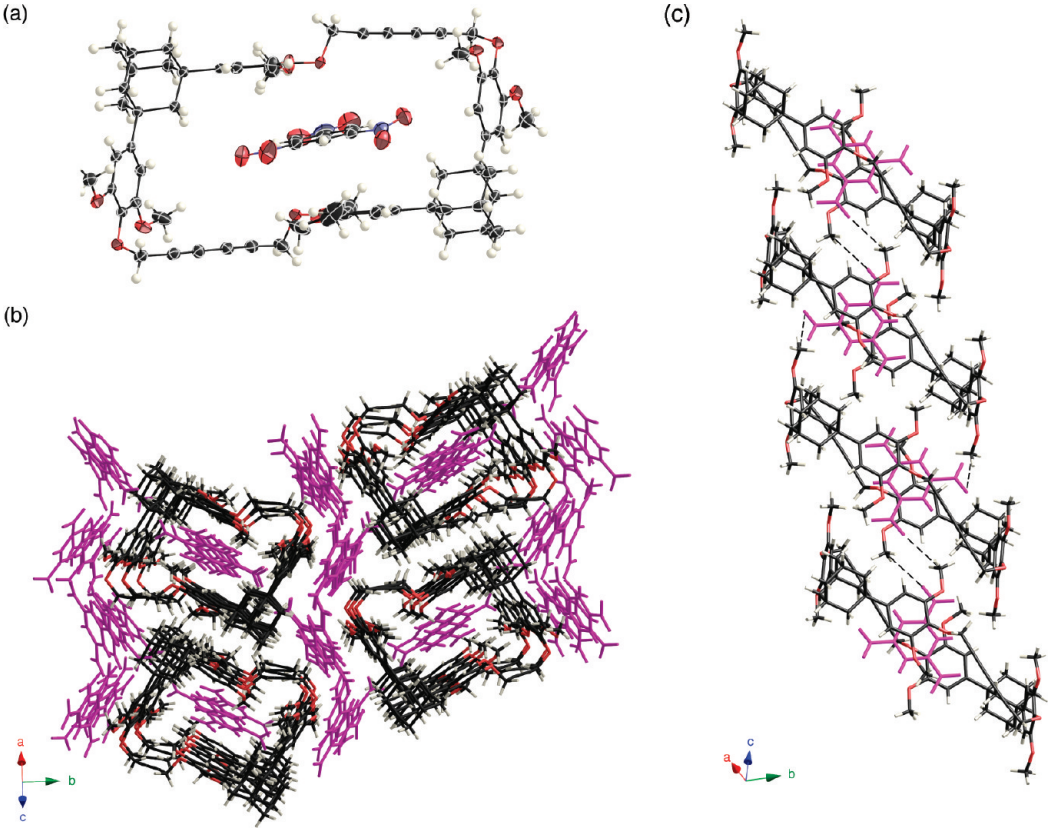


FIGURE 2. (a) Crystal structure of complex **1**·**4** in the thermal ellipsoid model. Guest molecules located outside of the cavity are omitted for clarity. Side view (b) and top view (c) of the tubular structure in the packing diagram of complex **1**·**4**. The guest molecules **4** are colored magenta. Hydrogen bonds are indicated by black dashes.

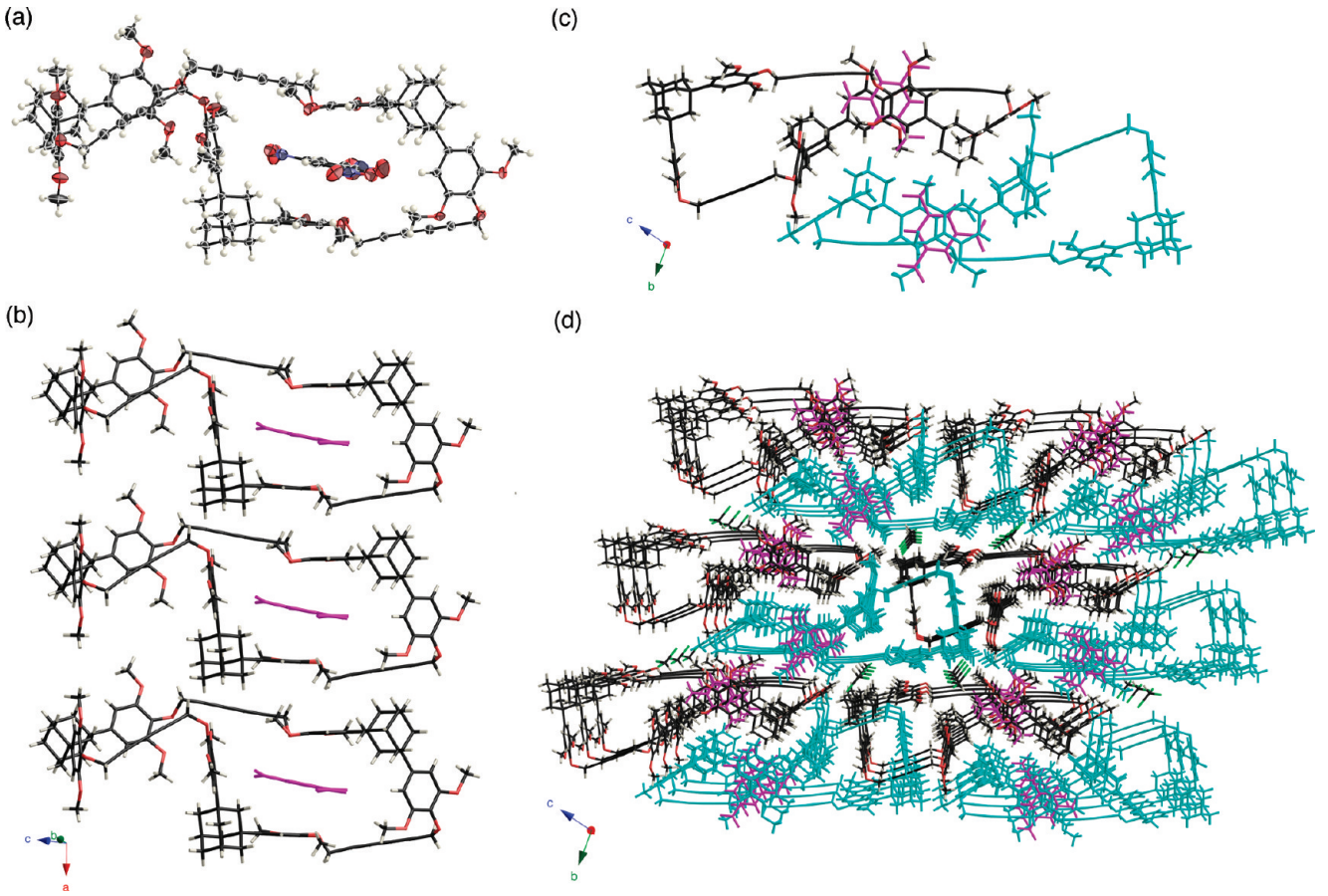


FIGURE 3. (a) Crystal structure of the complex **2**·**4** in the thermal ellipsoid model. The chloroform molecules outside of the cavity have been omitted for clarity. Side view (b) and top view (c) of the columnar structure in the packing diagram of complex **2**·**4**. Overall view of the packing structure including the chloroform molecules (d). The guest molecules **4** are colored magenta. The molecules of neighboring columns are colored cyan.

of **1** and three molecules of **4** in the asymmetric unit. The crystal structure showed that the macrocyclic framework is also a rectangular shape, where the measured distance between the centroids of opposing rings are 15.72 and 7.59 Å, respectively (Figure 2a). However, the shape is slightly distorted in comparison to crystal **1** because two aromatic ring moieties of **1** are stacked on the π-face of **4** with donor−acceptor interactions in a parallel fashion. These distances are slightly longer than the van der Waals diameters of two aromatic rings, but the maximum contacts of the aromatic rings required for a CT-type electronic interaction are realized. The distance between the phenyl ring of **1** and **4** is 3.57 and 4.15 Å (measured from the center of the ring to the center of the ring), and the dihedral angle of a cofacial pair is slightly tilted at 8.3° and 8.6°. This complex stacks regularly to form a tubular structure via intermolecular multiple C−H···O interactions (the C···O distance ranged from 3.16 to 3.53 Å) between the methoxy protons and the oxygen atoms of the nitro groups in neighboring enclathrated **4** (Figure 2b,c). These results displayed that the packing of the host framework in the host−guest complex can be controlled by the guest molecule. Guest **4** entrapped in the 1D array existed in two different orientations, which were alternately aligned within the tubular structure. The tubular structures were observed to assemble into a 2D layered aggregation through C−H···O interactions between the methoxy groups of the aromatic ring moieties (the C···O distance ranged from 3.43 to 4.06 Å). Interestingly, two molecules of **4** were located at the exterior of the macrocycle and formed a charge-transfer complex with residual aromatic ring moieties of **1**. Consequently, the 3D network formed was composed of two different types of layers, in which the host layer (including the guest) and the guest layer were stacked in an alternating fashion.

Single crystals of complex **2**·**4** were also obtained as pale yellow blocks by vapor diffusion of hexane into a chloroform solution containing **2** and **4** in 1:6 molar ratio. The crystal of complex **2**·**4** crystallized in the triclinic system, space group $P\bar{1}$, and included one molecule each of **2**, **4**, and chloroform in the asymmetric unit. In the crystals of complex **2**·**4**, the shape of **2** is significantly distorted, where the distances between the centroids of opposing rings were 11.96, 22.57, and 8.99 Å, respectively (Figure 3a). The guest **4** was gripped by macrocycle **2** in such a way that the electron-poor **4** formed a triple donor−acceptor π-stack with the electron-rich aromatic ring systems of the macrocycle. The distance between the aromatic ring of **2** and **4** is 3.70 and 3.59 Å (measured from the center of the ring to the center of the ring), and the dihedral angle of a cofacial pair is tilted at 8.4° and 12.7°. The host−guest complex packs into a columnar structure in the crystal along the *a* axis (Figure 3b−d). Multiple C−H···O interactions (the C···O distance ranged

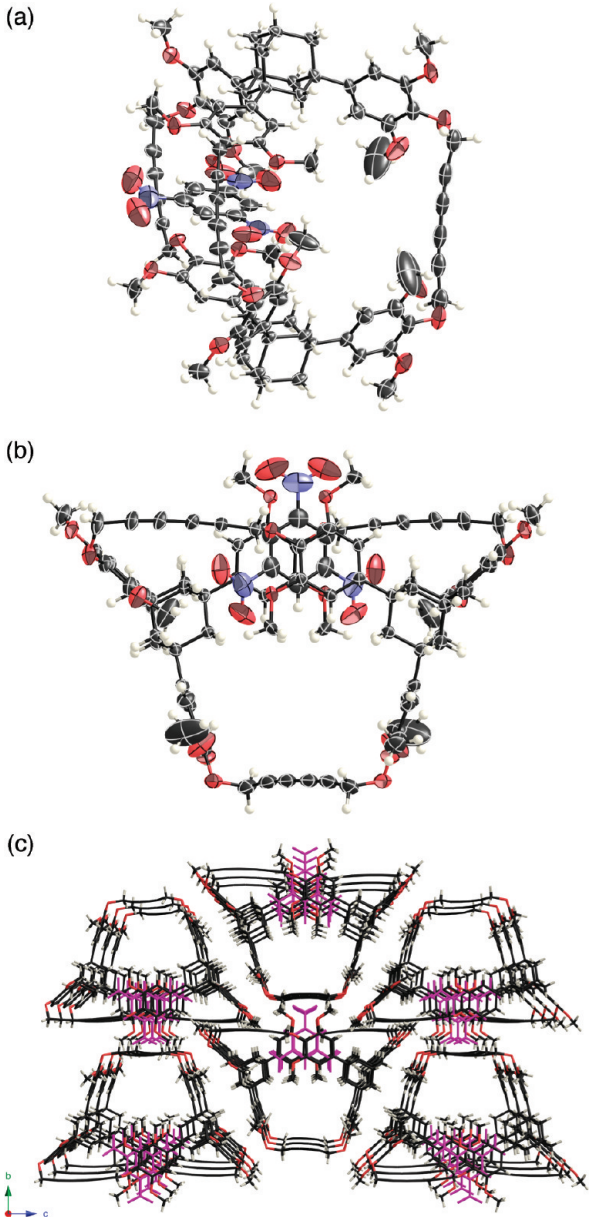


FIGURE 4. Side view (a) and top view (b) of the crystal structure of the complex **3**·**4** in the thermal ellipsoid model. Hydrogen atoms and chloroform molecules are omitted for clarity. (c) Packing diagram of the complex **3**·**4**. The guest molecules are colored cyan. The chloroform molecules are omitted for clarity.

from 3.26 to 3.66 Å) between the methylene protons of the adamantane parts and the oxygen atoms and protons of the methoxy groups were observed.

Single crystals of complex **3**·**4** were also obtained as pale yellow blocks by vapor diffusion of hexane into a chloroform solution containing **2** and **4** in 1:4 molar ratio.[19] The crystal of complex **3**·**4** crystallized in the monoclinic system, space group $C2/c$, and included one molecule each of **3**, **4**, and chloroform in the unit cell. The top view of the crystal structure showed that the distortion of the capsule framework of **3** was slightly increased in comparison to the structure of **3** alone (Figure 4a,b). This is because two aromatic ring moieties of **3** are stacked on the π-face of **4** with donor−acceptor interactions occurring in a parallel fashion. The distance between the phenyl ring of **3** and **4** is 3.55 Å (measured from the center of the ring to the center of the ring), and the dihedral angle of a cofacial pair is tilted at 14.2°. Cage molecules stack regularly to form a columnar structure by intermolecular C−H···π interactions between the phenyl ring and the methylene protons of the linker unit (the distance measured from the center of the ring to the carbon atom of the methylene group is 3.57 Å) that is aligned with the a axis (Figure 4c). Interestingly, a microporous structure was observed along the a axis in the one-dimensional array.[20]

Conclusions

In conclusion, we have achieved macrocyclization of di- and trisubstituted adamantane bearing acetylenic aromatic ring parts by copper-mediated oxidative coupling and isolated two types of macrocycles and cryptand-like macrobicyclic cage with a cavity, respectively. Crystallographic analyses of the macrocycles and cage and their charge-transfer complexes were realized. X-ray diffraction experiments of the host−guest complexes revealed that the macrocycles and cage receptor was found to encapsulate the electron-poor guest molecule via charge-transfer interactions. Furthermore, guest molecules had an influence on the packing of the host molecules, resulting in the generation of crystalline solids such as columns, tubes, 2D layers, and 3D networks composed of two different types. We believe that macrocycles and cage represent a versatile scaffold for a new family of supramolecular architectures. The synthesis of the corresponding larger host frameworks and their inclusion phenomenon with other electron-deficient guest molecules are the subject of the current studies.

Experimental Section

1,3-Bis(4-propargyloxy-3,5-dimethoxyphenyl)adamantine. A mixture of 1,3-bis(4-hydroxy-3,5-dimethoxyphenyl)adamantane (2.20 g, 5.00 mmol), propargyl bromide (0.98 mL, 13.0 mmol), and potassium carbonate (1.79 g, 13.0 mmol) in dry DMF (50 mL) was stirred for 12 h at room temperature under an argon atmosphere. The reaction mixture was poured into water and then extracted with chloroform. The extract was washed with water and brine and dried over Na_2SO_4. Evaporation of solvent followed by silica gel column chromatography (eluent: $CHCl_3$) afford the title compound as a white solid (2.40 g, 4.65 mmol) in 93% yield. Mp 137−138 °C. FT-IR (ATR, cm^{-1}) 3279, 2907, 1586, 1507, 1448, 1122, 823. ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ 6.60 (s, 4H), 4.68 (d, J = 2.4 Hz, 4H), 3.87 (s, 12H), 2.45 (t, J = 2.4 Hz, 2H), 2.33 (s, 2H), 2.00−1.78 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 152.9, 147.0, 135.8, 102.3, 79.5, 74.6, 59.8, 56.1, 49.4, 42.1, 37.5, 35.7, 29.4. MS (FAB, m/z) calcd for $C_{32}H_{37}O_6$ ($M + H^+$) 517.25, found 517.7. Elemental Anal. Calcd for $C_{32}H_{36}O_6 \cdot 0.05CHCl_3$: C, 73.66; H, 6.95. Found: C, 73.82; H, 6.99.

Macrocycles 1 and 2. A solution of the 1,3-bis(4-propargyloxy-3,5-dimethoxyphenyl)adamantane (0.21 g, 0.40 mmol), copper(I) chloride (1.98 g, 20.0 mmol), and *N*,*N*,*N*′,*N*′-tetra-

(19) The determination of the formation constant of the CT complexes between **3** and **4** with use of the Benesi−Hildebrand method and a nonlinear curve-fitting procedure was attempted. The magnitude of the association constants was ca. 10 M^{-1}.

(20) Although solvent molecules (chloroform or water) may be included in the void space, they could not be easily identified due to disorder.

methylethylenediamine (TMEDA) (3.00 mL, 20.0 mmol) in dry CH_2Cl_2 (800 mL) was stirred for 12 h at room temperature. The reaction mixture was washed with water and brine and dried over anhydrous Na_2SO_4. Evaporation of the solvent followed by silica gel column chromatography (eluent: $CHCl_3$) and gel permeation chromatography (JAIGEL 1H+2H, $CHCl_3$) afford **1** (145 mg, 0.14 mmol, 71%) and **2** (36.1 mg, 23.3 μmol, 18%) as a white powder, respectively. **1**: mp > 300 °C dec. FT-IR (ATR, cm^{-1}) 2159, 1559, 1507, 1457, 1112, 795. ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ 6.58 (s, 8H), 4.74 s, 8H), 3.83 (s, 24H), 2.34 (s, 4H), 2.07−1.77 (m, 24H). ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 153.0, 147.2, 133.1, 102.3, 75.1, 70.8, 60.1, 56.2, 50.5, 42.0, 37.6, 35.8, 29.5. MS (FAB, *m*/*z*) calcd for $C_{64}H_{69}O_{12}$ ($M + H^+$) 1029.47, found 1029.3. Elemental Anal. Calcd for $C_{64}H_{68}O_{12}\cdot 0.2CHCl_3$: C, 73.22; H, 6.53. Found: C, 73.50; H, 6.87. **2**: mp > 300 °C dec. FT-IR (ATR, cm^{-1}) 2160, 1583, 1506, 1452, 1124, 794. ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ 6.51 (s, 12H), 4.66 (s, 12H), 3.76 (s, 36H), 2.26 (s, 6H), 1.92−1.71 (m, 36H). ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 153.0, 147.3, 133.4, 102.3, 75.3, 70.8, 60.4, 56.2, 49.4, 42.3, 37.6, 35.8, 29.5. MS (FAB, *m*/*z*) calcd for $C_{96}H_{103}O_{18}$ ($M + H^+$) 1543.71, found 1543.4. Elemental Anal. Calcd for $C_{96}H_{102}O_{18}\cdot 0.33CHCl_3$: C, 73.06; H, 6.51. Found: C, 72.82; H, 6.85.

1,3,5-Tris(4-hydroxy-3,5-dimethoxyphenyl)adamantane. A mixture of 1,3,5-adamantanetriol (3.31 g, 18.0 mmol) and 2,6-dimethoxyphenol (21.14 g, 81.0 mmol) in trifluoroacetic acid (100 mL) and 1,2-dichloroethane (100 mL) in the presence of a catalytic amount of trifluoromethanesulfonic acid was stirred at 90 °C for 12 h under an argon atmosphere. The solvents were removed under reduced pressure, then the reaction mixture was washed with H_2O, saturated aqueous $NaHCO_3$, H_2O, and brine and dried over Na_2SO_4. Evaporation of solvent followed by silica gel column chromatography (eluent: $CHCl_3$) afford the title compound as a white solid (8.00 g, 13.5 mmol) in 75% yield. Mp 220−221 °C. FT-IR (ATR, cm^{-1}) 3498, 2929, 1604, 1517, 1408, 1211, 1107, 794, 747. ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ 6.65 (s, 6H), 5.43 (s, 3H), 3.91 (s, 18H), 2.55 (s, 1H), 2.08−1.98 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 146.8, 141.4, 133.2, 102.2, 56.5, 48.7, 41.7, 38.4, 30.2. MS (FAB, *m*/*z*) calcd for $C_{34}H_{41}O_9$ ($M + H^+$) 593.27, found 593.6. Elemental Anal. Calcd for $C_{34}H_{40}O_9$: C, 68.90; H, 6.80. Found: C, 68.63; H, 6.83.

1,3,5-Tri(4-propargyloxy-3,5-dimethoxyphenyl)adamantane. A mixture of 1,3,5-tri(4-hydroxy-3,5-dimethoxyphenyl)adamantane (1.48 g, 2.50 mmol), propargyl bromide (0.74 mL, 9.75 mmol), and potassium carbonate (1.35 g, 9.75 mmol) in dry DMF (50 mL) was stirred for 12 h at room temperature under an argon atmosphere. The reaction mixture was poured into water and then extracted with $CHCl_3$. The extract was washed with H_2O and brine, then dried over Na_2SO_4. Evaporation of solvent followed by silica gel column chromatography (eluent: $CHCl_3$) afford the title compound as a white solid (1.57 g, 2.23 mmol) in 89% yield. Mp 184−185 °C. FT-IR (ATR, cm^{-1}) 3258, 2925, 2117, 1662, 1587, 1508, 1184, 1121, 999. ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ 6.64 (s, 6H), 4.70 (d, J = 2.8 Hz, 6H), 3.88 (s, 18H), 2.56 (s, 3H), 2.45 (t, J = 2.4, 4.8 Hz, 3H), 2.10−1.99 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 153.2, 146.4, 134.2, 102.6, 79.6, 74.7, 60.0, 56.4, 48.34, 41.5, 38.7, 30.1. MS (FAB, *m*/*z*) calcd for $C_{43}H_{47}O_9$ ($M + H^+$) 707.31, found 707.7. Elemental Anal. Calcd for $C_{43}H_{46}O_9\cdot 0.2CHCl_3$: C, 71.01; H, 6.37. Found: C, 71.28; H, 6.48.

Cage 3. A solution of the 1,3,5-tri(4-propargyloxy-3,5-dimethoxyphenyl)adamantane (0.56 g, 0.80 mmol), copper(I) chloride (2.78 g, 24.0 mmol), and *N*,*N*,*N*′,*N*′-tetramethylethlene diamine (3.60 mL, 24.0 mmol) in dry CH_2Cl_2 (320 mL) was stirred for 12 h at room temperature under air. The reaction mixture was washed with water and brine, then dried over anhydrous Na_2SO_4. Evaporation of the solvent followed by silica gel column chromatography (eluent: $CHCl_3$) and gel permeation chromatography (JAIGEL 1H+2H, $CHCl_3$) afford **3** (56 mg, 40.0 μmol, 10%) as a white powder. Mp > 300 °C dec. FT-IR (ATR, cm^{-1}) 2927, 2849, 2161, 1585, 1507, 1457, 1409, 1123, 982, 752. ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C) δ 6.64 (s, 12H), 4.79 (s, 12H), 3.77 (s, 36H), 2.57 (s, 2H), 2.17−1.98 (m, 24H). ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C) δ 153.4, 146.5, 133.6, 102.7, 75.3, 70.6, 60.0, 56.4, 48.1, 41.6, 38.7, 30.1. MS (FAB, *m*/*z*) calcd for $C_{86}H_{87}O_{18}$ ($M + H^+$) 1407.58, found 1408.4. Elemental Anal. Calcd for $C_{86}H_{86}O_{18}\cdot 0.33CHCl_3$: C, 71.64; H, 6.01. Found: C, 71.65; H, 6.30.

Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectroscopic data (PDF) and crystallographic analysis data. This material is available free of charge via the Internet at http://pubs.acs.org.