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# Synthesis of 1,4-Cyclohexadiene-Based Acetylenic Macrocycles with Cadiot−Chodkiewicz Coupling. Structure of a Tub-Shaped Tetrameric Container

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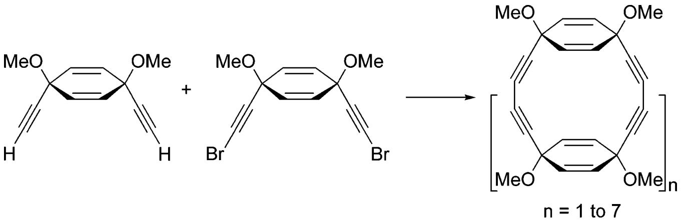

The Cadiot−Chodkiewicz coupling of *cis*-1,4-diethynyl-1,4-dimethoxycyclohexa-2,5-diene and the corresponding ethynyl bromide gave a mixture of acetyenic macrocycles ranging from dimer to octamer in good isolable yields. The trimeric and tetrameric macrocycles have been structurally characterized by single-crystal X-ray crystallography. In the crystal structure of the trimeric macrocycle a molecule of benzene is sandwiched between a pair of macrocyles. The tetrameric macrocycle exhibited a tub-shaped conformation and encapsulated a molecule of ethyl acetate inside the tub.

## Introduction

The design and synthesis of cyclophanes and macrocycles possessing rigidly defined cavities and shape-persistent structures of molecular dimensions is of contemporary interest in the areas of molecular recognition and host−guest chemistry.[1] Acetylenic bridging units are very useful as they impart rigidity to the structure. The size of the cavity can also be controlled by the number of acetylenic units on the bridge.[2] Recent past has witnessed the synthesis of several acetylenic building blocks which are useful as molecular scaffolds for the synthesis of a variety of carbon-rich molecules.[3] Palladium- and copper-mediated cross-coupling reactions of these acetylenic building blocks help in realizing the synthesis of acetylenic cyclophanes and macrocycles.[4] We have introduced *cis*-1,4-diethynylcyclohexa-2,5-diene as an acetylenic building block.[5] We have also demonstrated that this building block can be used for the synthesis of acetylenic macrocycles using the Glaser and Eglinton coupling reactions, albeit in poor yields.[5] Although Glaser and Eglinton coupling reactions are powerful synthetic tools for the synthesis of symmetrical diacetylenes,[6] their utility

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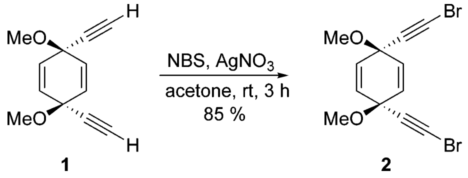
**SCHEME 1. Synthesis of 1,4-Bis(bromoethynyl)-1,4-dimethoxycyclohexa-2,5-diene**



in the synthesis of acetylenic macrocycles and cyclophanes is often limited due to the poor yields of these reactions from polyacetylenic substrates. Formation of acetylenic polymers is a favorable pathway resulting in poor yields of the desired cyclic products. Coupling of a terminal acetylene with a haloacetylene is known as Cadiot−Chodkiewicz coupling[7] and it is generally useful for the synthesis of unsymmetrical diacetylenes. Among the haloacetylenes bromoacetylene has optimal reactivity and gives good yields of the diacetylenes. Cadiot-Chodkiewicz coupling has been widely used in the synthesis of acetyenic cyclophanes,[8] natural[9] and unnatural polyacetylenes.[10] To develop a more efficient method for the synthesis of 1,4-cyclohexadiene-based acetylenic macrocycles, in particular the larger macrocycles, we explored the utility of Cadiot−Chodkiewicz coupling. Herein we report the synthesis of 1,4-cyclohexadiene-based acetylenic macrocycles in excellent isolable yields and material balance on a preparative scale.

## Results and Discussion

**1. Synthesis of Macrocycles 3a−g by the Cadiot−Chodkiewicz Coupling.** Synthesis of 1,4-bis(bromoethynyl)-1,4-dimethoxycyclohexa-2,5-diene (**2**) was accomplished in 85% yield by the bromination of the corresponding diethynyl compound (**1**) with NBS[11] (Scheme 1). A signal at $\delta$ 47.4 ppm in the $^{13}$C NMR spectrum corresponding to the acetylenic carbon bearing the bromine atom[12] and a triplet in a 1:2:1 ratio in the ESI-MS in the molecular ion region corresponding to the protonated molecular ion confirmed the formation of the dibromo derivative **2**.

Cadiot−Chodkiewicz coupling of **1** and **2** proceeded to completion at room temperature within 2 h and gave a complex mixture of products as evident from a series of spots on the TLC of the crude product. Careful chromatographic separation of the crude product afforded the macrocycles **3a−g** in pure form as white crystalline solids (Scheme 2) in good yields and material balance. For example, when the reaction was carried out on a 7 mmol scale (1.3 g of **1**) the combined total isolated yield of the macrocycles **3a−g** after the chromatographic purification was 80%. Therefore we conclude that only a small fraction of the starting materials had undergone polymerization to intractable material. The results are summarized in Table 1.

**SCHEME 2. Synthesis of Macrocycles 3a−g by Cadiot−Chodkiewicz Coupling**

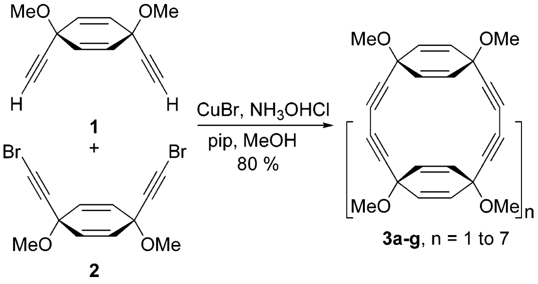


**TABLE 1. Physical and Spectroscopic Data of Macrocyles 3a−g**

| compd | yield (%) | mp (°C) | $^1$H NMR ($\delta$) | $^{13}$C NMR ($\delta$) |
|---|---|---|---|---|
| **3a** | 8 | 205 | 6.09, 3.28 | 130.5, 77.0, 69.6, 68.6, 52.3 |
| **3b** | 10.5 | 180 | 5.93, 3.22 | 128.3, 77.6, 70.2, 66.6, 51.8 |
| **3c** | 32 | 175 | 5.94, 3.23 | 128.2, 77.9, 70.4, 66.6, 51.9 |
| **3d** | 8.3 | 90 | 5.96, 3.24 | 128.5, 78.0, 70.2, 66.7, 51.8 |
| **3e** | 13 | 150−152 | 5.96, 3.26 | 128.7, 78.3, 70.2, 66.9, 52.2 |
| **3f** | 2.5 | 110−112 | 5.96, 3.26 | 128.5, 78.3, 70.6, 67.0, 52.2 |
| **3g** | 6 | 96−98 | 5.96, 3.23 | 128.6, 78.3, 70.4, 66.9, 52.1 |

The major products formed in the reaction were the expected cross-coupling products **3a**, **3c**, **3e**, and **3g** (containing an even number of cyclohexadiene units), namely the dimeric, tetrameric, hexameric, and octameric macrocycles, respectively. It is particularly noteworthy that the tetrameric macrocycle **3c** was obtained as the major product in 33% yield followed by the hexameric macrocycle **3e** in 13% yield after chromatographic purification. Macrocycles containing an odd number of cyclohexadiene units, namely **3b** (trimer), **3d** (pentamer), and **3f** (heptamer), were formed in relatively minor amounts, presumably arising from the homocoupling of the starting materials. With the exception of the pentamer the melting point of the other macrocycles decreased on going from **3a** (dimer) to **3g** (octamer). This is presumably due to the more rigid structure of the lower analogues in comparison to the higher ones, which allows the lower analogues to pack more closely in the crystalline state. We presume that due to the higher flexibility of the larger ring systems some kind of a random coil type arrangement might be present in them in the solid state resulting in poor packing in the solid state and hence lower melting points. Although macrocycles **3a−c** could be crystallized readily to yield good quality single crystals, several attempts to crystallize **3d−g** from various solvents to obtain suitable crystals for the single crystal for X-ray crystallography failed. All the macrocycles were thoroughly characterized by various spectroscopic techniques.

**2. Spectroscopic Characterization of the Macrocycles.** The $^1$H NMR spectra of the macrocycles **3a−g** were nearly invariant. Due to the highly symmetrical nature of the macrocycles only two singlets were observed, one for the ring hydrogens ($\delta$ 5.9−6.0) and the other for the methoxy hydrogens ($\delta$ 3.22−3.28) in the intensity ratio 2:3. For all the macrocycles the $^{13}$C NMR spectra showed 5 peaks, two for the cyclohexadiene ring carbons, two for the acetylenic carbons, and one for the methoxy

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carbon (Table 1). In view of the nearly invariant pattern and the $^1$H and $^{13}$C NMR chemical shifts of these macrocycles it was necessary to ascertain the structure of these macrocycles by mass spectrometry. Electrospray ionization mass spectra of the macrocycles showed the molecular ion peaks as very weak signals. However, upon addition of a small amount of $AgOSO_2CH_3$ the signals due to the monosilver ion complex of these macrocycles could be seen as intense signals. Therefore the macrocycles were characterized as the corresponding silver ion complexes by electrospray ionization mass spectrometry.[13] The characteristic feature of the ESI-MS of the silver complexes of these macrocycles is the cluster of isotope peaks in the molecular ion region.[13] The relative intensities of the cluster of peaks in the molecular ion region corresponding to the isotope peaks matched well with that from the calculated spectra of these complexes. Figure 1 shows the experimental and calculated mass spectra of the hexamer (**3e** + $Ag^+$) and the octamer (**3g** + $Ag^+$). HRMS data of the silver ion complexes further confirmed the molecular composition of these macrocycles.

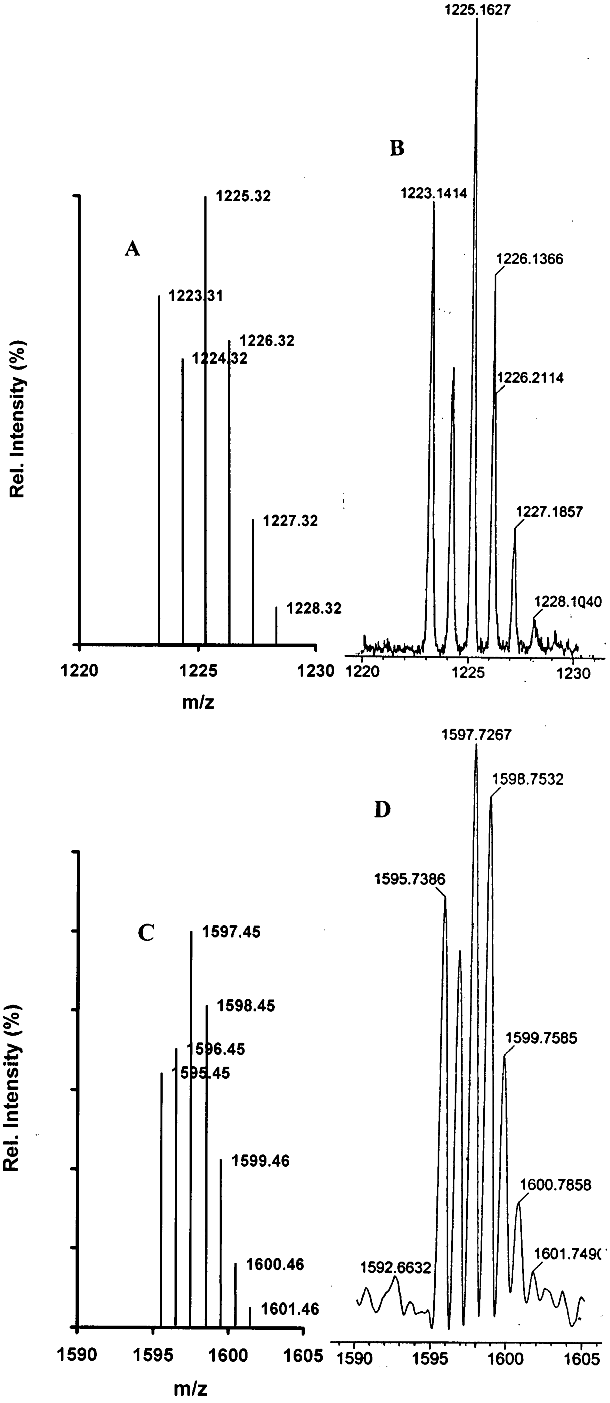

**FIGURE 1.** Calculated (A and C) and experimental ESI-MS (B and D) in the molecular ion region of the $Ag^+$ complexes of hexamer **3e** and octamer **3g**.

**3. Structural Characterization of the Macrocycles in the Crystal.** The structural characterization of the trimer (**3b**) and the tetramer (**3c**) was done with single-crystal X-ray diffraction. The molecular structure of the trimer (**3b**) is shown in Figure 2. The compound was crystallized from benzene. In the crystal a molecule of benzene is sandwiched between a pair of macrocycles (**3b**). The macrocycles within the pair are staggered with respect to each other and are also related to each other through a crystallographic 2-fold axis of symmetry and a plane of symmetry that bisects the benzene ring. The cyclohexadiene rings are nearly planar. Another interesting feature of the structure is that the butadiyne bridges are not straight and have a slight curvature. They are bent in a concave manner toward the trapped benzene molecule.

The molecular structure of the tetramer (**3c**) is shown in Figure 3. Single crystals of **3c** were obtained by crystallization from a mixture of ethyl acetate and hexane. The tetramer has an interesting tub-shaped conformation. The asymmetric unit in the lattice possesses a plane of symmetry. A molecule of ethyl acetate is trapped inside the tub. All the carbon and oxygen atoms of the ethyl acetate molecule lie on the plane of symmetry that bisects the macrocycle. The center-to-center distance of the symmetry related cyclohexadiene units is 10.032 Å while the center-to-center distance between the other pair of cyclohexadiene units is 8.79 Å.

**4. Calculated Energy-Minimized Structure of the Hexamer (3e).** Despite our best efforts we were unable to obtain single crystals of suitable quality to determine the structures of the higher macrocycles. However, in the past we had considerable success in correlating the structure of acetylenic macrocyles determined by X-ray crystallography with that obtained by semiempirical calculations with the AM1 method.[14,15] In view of the shape-persistent rigid nature of this class of macrocycles the experimental and calculated structures generally had excellent agreement, including the macrocycles **3b** and **3c** reported herein.[14,15] The energy-minimized structure of the hexamer (**3e**) (Figure 4), calculated by the AM1 method, is noteworthy. It has an interesting twisted loop structure in the shape of the symbol infinity (∞) or number eight (8). When viewed perpendicular to the two cyclohexadiene rings located at the center of the molecule that are juxtaposed on top of each other the twisted loop structure is evident (Figure 4A). When viewed parallel to the cyclohexadiene rings located at the center of the molecule the crisscrossing of the acetylenic bridges resulting in a zigzag molecular structure is evident (Figure 4B). From this view in fact it is also possible to deduce how the tetramer could have been formed in a tub-shaped conformation. The calculated structure of the hexamer (**3e**) seems to suggest that the higher oligomers of this class of compound might show

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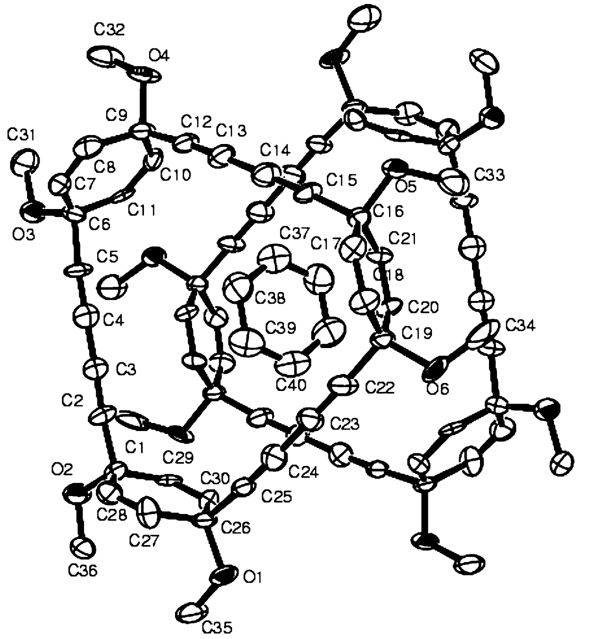

**FIGURE 2.** Structure of trimer **3b** in the crystal with a molecule of benzene sandwiched between two units (hydrogens not shown for clarity).

interesting twisted structures with helical chirality. Acetylenic cyclophanes with twisted structure resulting in helical chirality have been reported.[16]

## Conclusions

Synthesis of 1,4-cyclohexadiene-based acetylenic macrocycles from dimer to octamer has been accomplished in high isolable yields and material balance by Cadiot–Chodkiewicz coupling of the precursors **1** and **2**. The present methodology is much superior to the Glaser–Eglinton coupling method reported earlier in which only the dimer and trimer were obtained in very poor yields. The trimer (**3b**) and the tetramer (**3c**) have been structurally characterized by single-crystal X-ray crystallography. A molecule of benzene is sandwiched between two units of the trimer in the crystal. The tetramer has an interesting tub-shaped conformation and a molecule of ethyl acetate is trapped inside the tub. The calculated energy-minimized structure of the hexamer (**3e**) shows an interesting twisted loop type structure in the shape of the symbol infinity.

## Experimental Section

**Synthesis of *cis*-1,4-Bis(bromoethynyl)-1,4-dimethoxycyclohexa-2,5-diene (2).** To a solution of *cis*-1,4-diethynyl-1,4-dimethoxycyclohexa-2,5-diene (**1**)[5] (2.0 g, 10.6 mmol) in degassed acetone (50 mL) were added NBS (13.2 g, 74.5 mmol) and $AgNO_3$ (1.44 g, 8.5 mmol) with stirring at room temperature under nitrogen atmosphere. After 3 h TLC indicated the complete disappearance of **1**. The solid was filtered and solvent was removed under vacuum in the rotary evaporator. The crude product was poured into ice cold water (200 mL) and extracted with ether (3 × 50 mL). The combined ether extracts were washed with saturated brine solution (2 × 100 mL) and dried over anhydrous $Na_2SO_4$. On removal of solvent the crude product was obtained as a yellow solid that was purified by column chromatography on silica gel with ether–hexane mixture (1:9 v/v) as eluant to yield the title compound (**2**) (3.1 g, 85%) as a yellow solid. IR (KBr) 2194 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 5.96 (s, 4H), 3.21 (s, 6H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 128.8, 78.1, 67.1, 57.7, 47.4 (C–Br); ESI-MS ($C_{12}H_{11}O_2Br_2$) 345, 347, 349 ($M^+$+1, 1:2:1); HRMS calcd for $C_{12}H_{11}O_2{}^{79}Br_2$ ($M^+ + 1$) 344.9126, found 344.9124; HRMS calcd for $C_{12}H_{10}O_2{}^{79}Br_2Na$ ($M^+ + Na$) 366.8945, found 366.8927.

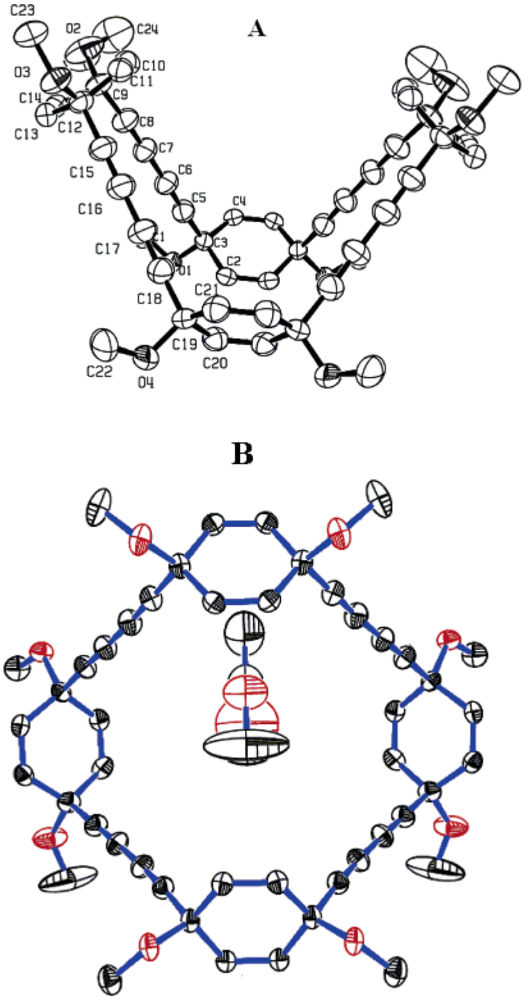

**FIGURE 3.** Structure of tetramer **3c** in the crystal. View A shows the tub-shaped conformation of the molecule (ethyl acetate and hydrogens not shown for clarity). View B is along the crystallographic plane of symmetry of the molecule and it shows the location of ethyl acetate in the tub (hydrogens not shown for clarity).

**Synthesis of Macrocycles 3a–g by Cadiot–Chodkiewicz Coupling of 1 and 2.** To a stirred solution of a mixture containing **1** (1.3 g, 7.0 mmol), piperidine (1.73 mL, 17.5 mmol), CuBr (0.1 g, 0.7 mmol), and hydroxylamine hydrochloride (0.097 g, 1.4 mmol) in methanol (300 mL) under nitrogen atmosphere at room temperature was added a degassed solution of **2** (2.4 g, 7.0 mmol) in methanol (30 mL) over a period of 1.5 h. The mixture was stirred for 2 h after which the disappearance of the starting materials was confirmed by TLC. Solvent was removed under reduced pressure in the rotary evaporator and the crude product was poured into ice

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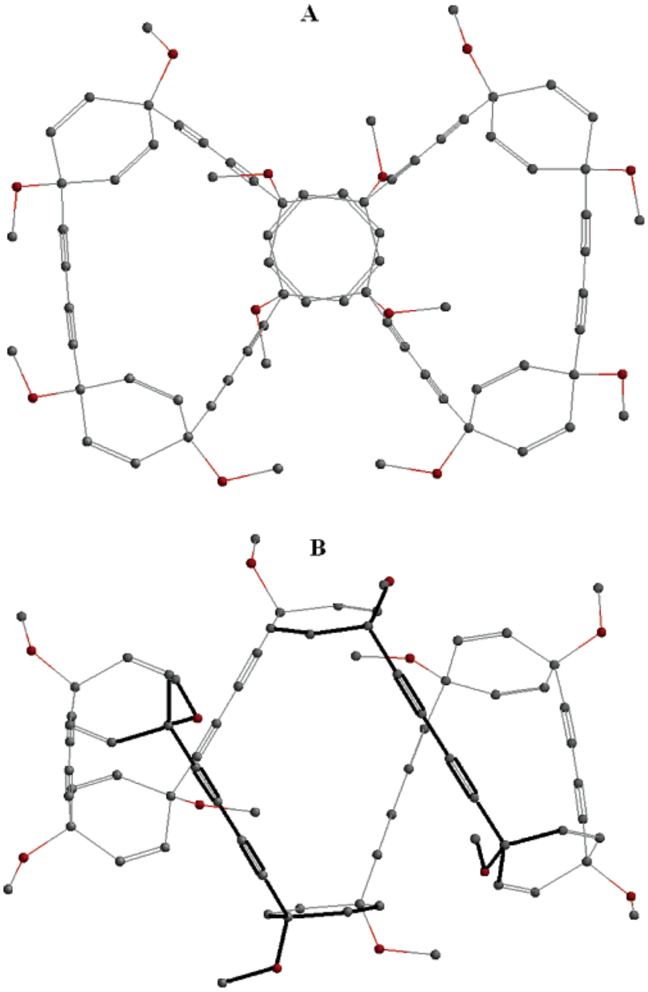

**FIGURE 4.** Calculated energy minimized structure of hexamer **3e**. The thick lines are bonds closer to the viewer (hydrogens not shown for clarity).

cold water (100 mL), then extracted with ethyl acetate and the organic extract was washed with saturated brine solution (150 mL). The organic layer was dried over anhydrous $Na_2SO_4$ and solvent was removed. The crude product was separated by column chromatography on silica gel with ethyl acetate−hexane mixture (5:95 v/v) as the eluant. The macrocycles **3a** to **3g** were eluted in the increasing order of their size. Removal of solvent from pure fractions yielded the individual macrocycles in pure form as colorless solids. The macrocycles were characterized by various spectroscopic techniques. **Dimer 3a**:[5a] 0.2 g (8%), mp 205 °C dec; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 6.09 (s, 8H), 3.28 (s, 12H), $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 130.5, 77.0, 69.6, 68.6, 52.3. **Trimer 3b**:[5a] 0.27 g (10.5%), mp 180 °C dec; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 5.93 (s, 12H), 3.22 (s, 18H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 128.3, 77.6, 70.2, 66.6, 51.8; ESI-MS (rel intensity) ($C_{36}H_{30}O_6Ag$, M+Ag$^+$) 665 (72), 666 (15), 667 (100), 668 (22), 669 (16); HRMS calcd for $C_{36}H_{30}O_6Ag$ 665.1093, found 665.1112. **Tetramer 3c**: 0.81 g (32%), mp 175 °C dec; IR (KBr) 2145 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 5.94 (s, 16H), 3.23 (s, 24H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 128.2, 77.9, 70.4, 66.6, 51.9; ESI-MS (rel intensity) ($C_{48}H_{40}O_8Ag$, M + Ag$^+$) 851 (90), 852 (40), 853 (100), 854 (50), 855 (15); HRMS calcd for $C_{48}H_{40}O_8Ag$ 851.1774, found 851.1802; HRMS calcd for $C_{48}H_{40}O_8Na$ 767.2621, found 767.2636. **Pentamer 3d**: 0.22 g (8.3%), mp 90 °C; IR (KBr) 2149 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 5.96 (s, 20H), 3.24 (s, 30H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 128.5, 78.0, 70.2, 66.7, 51.8; ESI-MS (rel intensity) ($C_{60}H_{50}O_{10}Ag$, M + Ag$^+$) 1037 (70), 1038 (50), 1039 (100), 1040 (50), 1041 (20); HRMS calcd for $C_{60}H_{50}O_{10}Ag$ 1037.2455, found 1037.2451; HRMS calcd for $C_{60}H_{50}O_{10}Na$ 953.3302, found 953.3331. **Hexamer 3e:** 0.34 g (13%), mp 150−152 °C dec; IR (KBr) 2153 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 5.96 (s, 24H), 3.26 (s, 36H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 128.7, 78.3, 70.2, 66.9, 52.2; ESI-MS (rel intensity) ($C_{72}H_{60}O_{12}Ag$, M + Ag$^+$) 1223 (65), 1224 (50), 1225 (100), 1226 (55), 1227 (30); HRMS calcd for $C_{72}H_{60}O_{12}Ag$ 1223.3136, found 1223.3112. **Heptamer 3f**: 0.063 g (2.5%), mp 110−112 °C; IR (KBr) 2149 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 5.96 (s, 28H), 3.26 (s, 42H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 128.5, 78.3, 70.6, 67.0, 52.2; ESI-MS (rel intensity) ($C_{84}H_{70}O_{14}Ag$, M + Ag$^+$) 1409 (70), 1410 (65), 1411 (100), 1412 (60), 1413 (40), 1414 (10); HRMS calcd for $C_{84}H_{70}O_{14}Ag$ 1409.3817, found 1409.3792. **Octamer 3g**: 0.15 g (6%), mp 96−98 °C; IR (KBr) 2150 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 5.96 (s, 32H), 3.23 (s, 48H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 128.6, 78.3, 70.4, 66.9, 52.1; ESI-MS (rel intensity) ($C_{96}H_{80}O_{16}$-Ag, M + Ag$^+$) 1595 (75), 1596 (70), 1597 (100), 1598 (90), 1599 (50), 1600 (15); HRMS calcd for $C_{96}H_{80}O_{16}Ag$ 1595.4497, found 1595.4481.

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**Supporting Information Available:** Crystal structure data for compounds **3b** and **3c**, $^1$H and $^{13}$C NMR spectra of **2** and **3a**−**g**, and total energies and Cartesian coordinates of structure **3e** optimized at AM1. This material is available free of charge via the Internet at http://pubs.acs.org.

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