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Selective and Gram-Scale Synthesis of [8]Cycloparaphenylene

Tatsuya Kawanishi,[†] Kosuke Ishida,[‡] Eiichi Kayahara,[‡] and Shigeru Yamago[‡]**

[†]Oji R&D Center, Tokyo Chemical Industry Co., LTD., Toshima, Kita-ku, Tokyo 114-0003, Japan

[‡]Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

KEYWORDS. Cycloparaphenylene, Macrocycles, Platinum, Tin, Reductive aromatization

ABSTRACT. A selective and large-scale synthesis of [8]cycloparaphenylene (CPP) was achieved in seven steps starting from commercially available 4-bromo-4'-hydroxybiphenyl and 4,4'-dibromobiphenyl. The key unsymmetrical tetraring unit, 4-bromophenyl and 4'-bromobiphenyl-substituted *cis*-1,4-bis(triethylsiloxy)-2,5-cyclohexadiene-1,4-diyl (**5fA**), was synthesized on an ~50 g scale by stereoselective *cis*-addition of 4-bromo-4'-lithiobiphenyl to 4-(4-bromophenyl)-4-hydroxy-2,5-cyclohexadien-1-one, which was synthesized on an ~100 g scale. Platinum-mediated selective dimerization of the four-ring unit **5fB** and subsequent reductive aromatization of the cyclohexadiene-diyl by H_2SnCl_4 gave 2 g of [8]CPP in 8.8% overall yield.

Introduction

Hoop-shaped π-conjugated macrocycles have garnered immense interest due to their unique topological structure, physical properties, and potential applications in molecular electronics.[1-4] [*N*]Cycloparaphenylenes ([*N*]CPPs, Figure 1), which consist of para-linked *N* phenylene units forming a cyclic structure corresponding to the simplest structural unit of armchair carbon nanotubes (CNTs), occupy the central position among such macrocycles after the first synthesis of [9], [12], and [18]CPPs by Bertozzi and Jasti in 2008.[5] With the significant endeavors by Itami,[6] Yamago,[7] Jasti,[8] and others,[9-17] CPPs with different sizes ([5]-[16], [18], [20], and [21]CPPs), [18-21,22-25,26-33] various CPP derivatives,[12, 13, 15, 16, 34-46] and structurally related cyclic conjugated macrocycles[10, 14, 47-51] have also been synthesized to date. Moreover, the unique properties of CPPs, such as photophysical properties,[52, 53] redox properties,[26, 54-62] and host–guest chemistry,[63-71] have been intensively studied. Furthermore, applications of these conjugated macrocycles to organic devices have emerged.[17, 46, 72, 73] With these advances in CPP chemistry and materials science, the demand for the availability of CPPs in quantity has been increasing. While large-scale synthesis (>0.5 g scale) of [5],[30] [6],[31] [8],[19] [10],[19, 32] and [12]CPPs[22] has already been reported, the development of a more efficient synthetic route is still lacking.

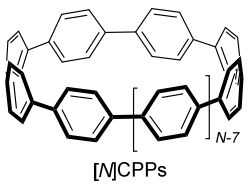


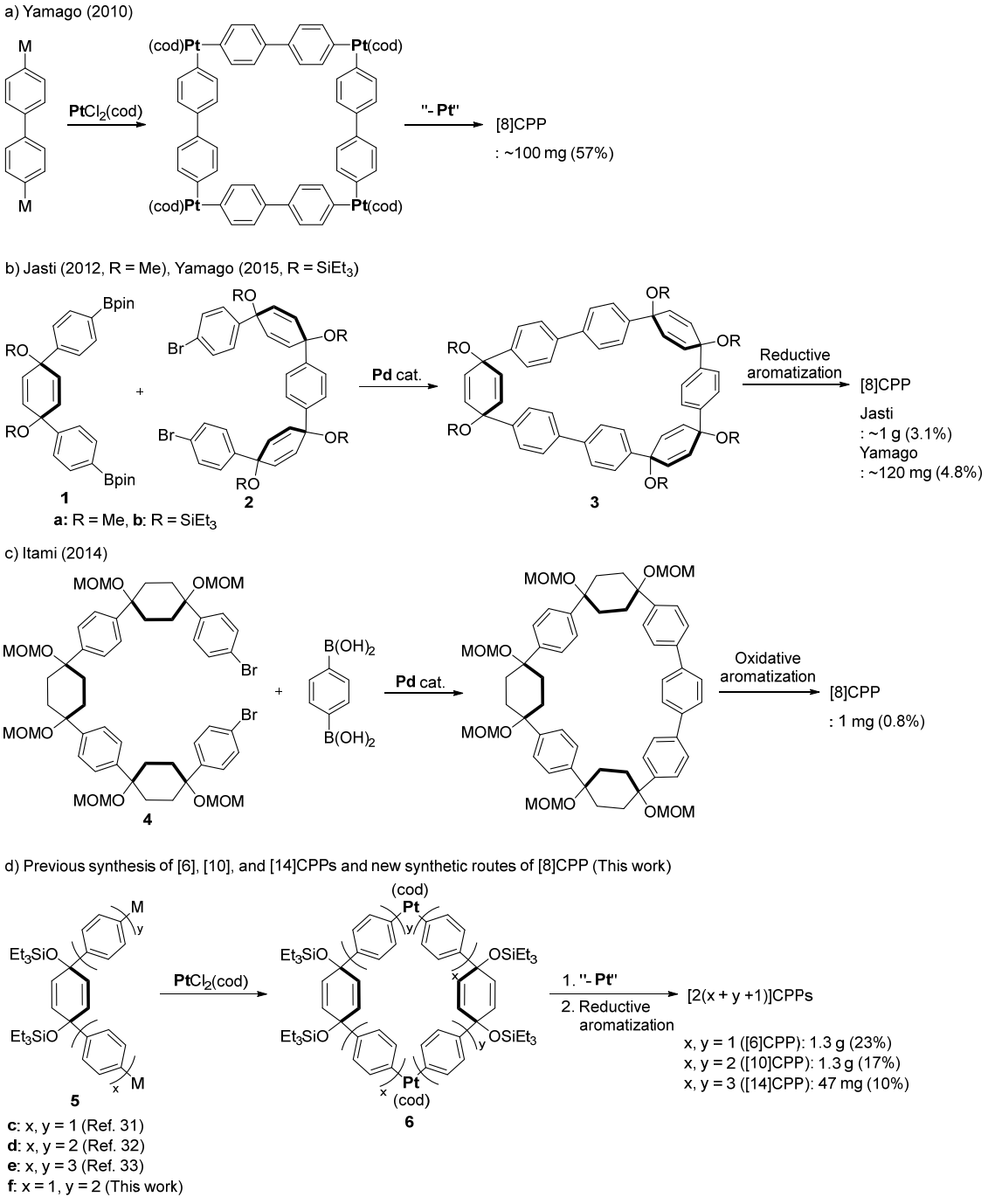
Figure 1. Structure of [*N*]CPPs.

[8]CPP is a unique CPP with characteristic yellow-green fluorescence with a moderate quantum yield (8%).[7] CPPs larger than [9]CPPs emit blue fluorescence with high quantum yields,[52] but

[7]CPP emits orange fluorescence with a very low quantum yield (0.7%).[8] No fluorescence was observed for [6] and [5]CPPs.[20, 21, 28, 29] Furthermore, a recent time-resolved spectroscopic study revealed that [8]CPP possesses the longest life time of the S_1 state among [5]-[12]CPPs.[74] These results suggest that [8]CPP is located at the inflection point in the photophysical properties of CPPs. Therefore, increasing the availability of [8]CPP would further stimulate the elucidation of its interesting properties and lead to the development of [8]CPP-based materials through, for example, its chemical functionalization.

[8]CPP was synthesized for the first time by Yamago by using the platinum-mediated cyclotetramerization of 4,4'-bistrimethylstannylbiphenyl (Scheme 1a).[7] The overall yield was 57% after the optimization,[75] but the requirement for four equivalents of platinum and the low solubility of the platinum intermediate limited the large-scale synthesis. Jasti reported the gram-scale synthesis of [8]CPP based on the coupling reaction of three-ring unit **1a** and five-ring unit **2a** (R = Me) having *cis*-1,4-dimethoxy-2,5-cyclohexadiene-1,4-diyl groups to yield macrocycle **3a** (Scheme 1b).[3] Reductive aromatization of the dimethoxy-2,5-cyclohexadiene-1,4-diyl moieties in **3a** by sodium naphthalenide afforded [8]CPP. More than 1 g of [8]CPP was obtained in 3.1% overall yield from the commercially available 4-bromo-4'-hydroxybiphenyl. Yamago reported the modification of this method using bis(triethylsilyloxy [TES]) derivatives **1b** and **2b** (R = $SiEt_3$) as the coupling partners and applying H_2SnCl_4-mediated reductive aromatization of **3b** to give [8]CPP in 4.8% overall yield.[30] Itami also reported the coupling reaction of seven-ring unit **4** and 1,4-phenylenediboronic acid followed by oxidative dehydration, but the scale and yield were low (<1 % overall yield, Scheme 1c).[25]

Here, we report a new and scalable synthesis of [8]CPP (Scheme 1d). The method is based on our gram-scale synthesis of [6]CPP through the platinum-mediated dimerization of **5c** (x, y =



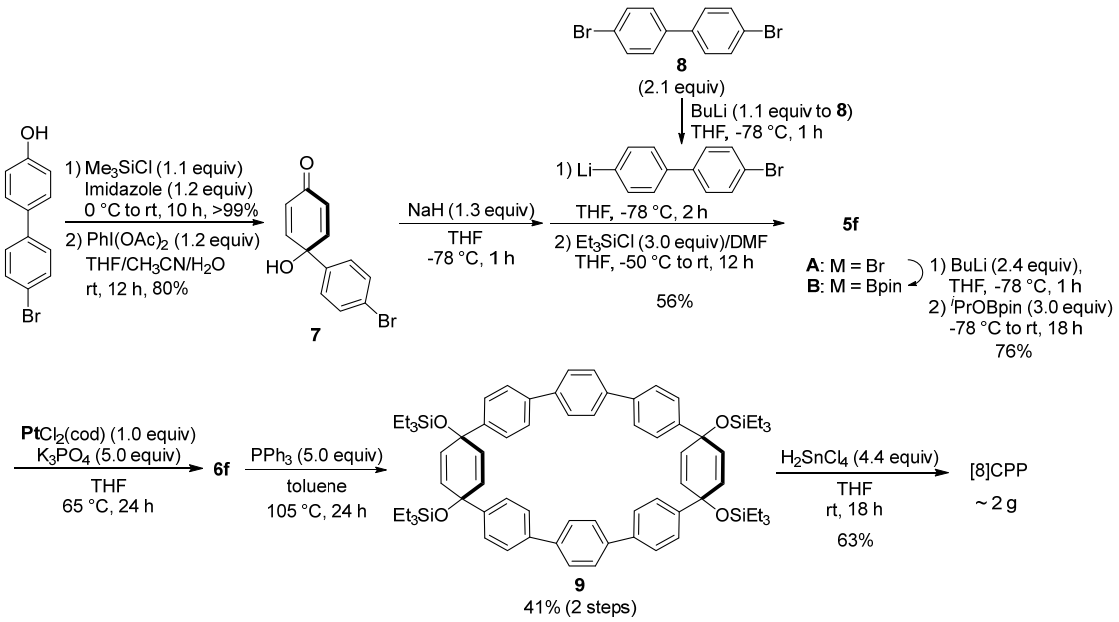
Scheme 1. a-c) Previous synthetic routes of [8]CPP. d) Previous synthesis of [6], [10], and [14]CPPs and new synthetic route for [8]CPP. cod = 1,5-cyclooctadiene, pin = pinacolato, MOM = methoxymethyl.

1). [31] Although one-step cyclization of **5c** by Yamamoto coupling employing a Ni(0) complex gave a mixture of cyclic dimer **6c**, trimer, and tetramer, the reaction of **5c** and $PtCl_2$(cod) (cod = 1,5-cyclooctadiene) selectively and exclusively afforded dimer **6c**, from which the reductive elimination of platinum and reductive aromatization of the 1,4-cyclohexadiene groups by H_2SnCl_4 yielded gram quantities of [6]CPP. The method was recently applied to the synthesis of [10]CPP[32] and [14]CPP[33] through the platinum-mediated selective dimerization of **5d** (x, y = 2) and **5e** (x, y = 3), respectively. The method is highly reliable for the synthesis of cyclic dimers of **5** derivatives, and various substituted [10]CPP derivatives have been synthesized by this method on the gram scale.[32] However, the method is applicable for the synthesis of [2(2x +1)]CPPs only when the numbers of phenylene units x and y are equal. If we can use an unsymmetrical precursor with different values of x and y, the method would become more versatile. Here, we report the synthesis [8]CPP based on the dimerization of unsymmetrical precursor **5f** (x = 1, y = 2) as a proof of principle of this synthetic route. Furthermore, the generality of this method was evaluated by synthesizing fluorene-embedded [8]CPP.

Results and Discussion

The synthesis started from commercially available 4-bromo-4'-hydroxybiphenyl, which was transformed to 4-(4-bromophenyl)-4-hydroxy-2,5-cyclohexadien-1-one (**7**)[19] in two steps on a 100 g scale by modifying the method reported by Jasti[19] (Scheme 2). Then, **7** was converted to TES-protected **5fA** (M = Br) in one pot in 56% yield through protection of the hydroxyl group of **7** as a sodium salt by treatment with NaH (1.3 equiv), addition of 4-bromo-4′-lithiobiphenyl prepared in situ from 4,4′-dibromobiphenyl (**8**, 2.1 equiv) and BuLi (2.2 equiv), and trapping of the resulting bis-alkoxide with TES chloride (3.0 equiv). NMR analyses suggest the exclusive formation of the *cis* isomer (>90% selectivity). 4-Bromo-4′-lithiobiphenyl was generated from 4-bromo-4′-

iodobiphenyl in a previous report,[32] and we found that dibromo precursor **8**, which has higher availability than 4-bromo-4'-iodobenzene, was successfully used with equal efficiency. Then, **5fA** was converted into bis-boronate **5fB** (X = B[pin]) through a twofold bromine-borane exchange reaction. Nearly 40 g of **5fB** was isolated by silica gel chromatography in 76% yield.



Scheme 2. Synthesis of [8]CPP

The feasibility of the new synthetic route was first examined on a small scale. Thus, a mixture of **5fB** (0.20 mmol) and $PtCl_2(cod)$ (1.0 equiv) in the presence of K_3PO_4 (5.0 equiv) in THF was heated at 65 °C for 20 h, and the desired cyclic dimer **6f** was isolated in 62% yield by preparative gel permeation chromatography (GPC). While nearly 20% of linear oligomers were separated, no cyclic oligomers other than **6f** were detected. The structure of **6f** was estimated at first by ^1H NMR measured in $CDCl_3$; the protons of the cyclohexadiene groups appeared at δ = 5.81 and 5.99 ppm as two doublets ($^3J_{H\text{-}H}$ = 10.0 Hz), and those of the paraphenyl groups were observed at δ = 6.99, 7.08, 7.18, 7.29, 7.33, and 7.33 ppm as doublets ($^3J_{H\text{-}H}$ = 8.0-8.4 Hz). The olefinic protons of the

cod ligand were observed at 5.21 and 5.08 ppm as singlets with a ^{195}Pt satellite ($^{2}J_{Pt\text{-}H}$ = 43 and 56 Hz, respectively), and the methylene protons appeared at approximately 2.54 ppm as broad peaks. In the ^{13}C NMR spectrum, twelve and four signals corresponding to the carbon atoms of the paraphenyl and cyclohexadiene groups, respectively, were observed. The observed spectra are consistent with the C_{2h} structure of **6f**. In the electrospray ionization time-of-flight mass spectra (ESI-TOF MS), the molecular ion mass of **6f** was observed as sodium ion adducts.

The reductive elimination of platinum from **6f** in the presence of PPh_3 (5.0 equiv) afforded cyclic dimer **9** in 77% yield after silica gel chromatography. The highly symmetric D_{2h} structure of **9** was suggested by ^{1}H NMR spectroscopy; the protons of the cyclohexadiene and the central paraphenyl rings in the terphenyl bridge appear at 6.33 and 7.16 ppm, respectively, as singlets, and those of the paraphenylene rings connected to the 1,4-cyclohexadiene groups appear at 6.95 and 7.00 ppm ($^{3}J_{H\text{-}H}$ = 8.8 Hz) as two doublets. The observed high magnetic field resonance of the latter signals is due to the deshielding effect of the facing paraphenyl rings. Indeed, the optimized structure of the free alcohol form of **9** by density functional theory (DFT) calculations at the rings connecting to the 1,4-cyclohexadiene groups are located 3.51 and 4.42 Å from the centroid

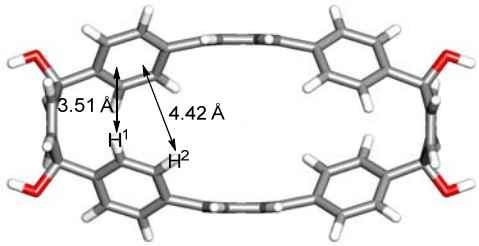


Figure 2. Optimized structure of the free alcohol form of **9** calculated by DFT calculation at the B3LYP/6-31G(d) level of theory. Gray, white, and red represent carbon, hydrogen, and oxygen atoms.

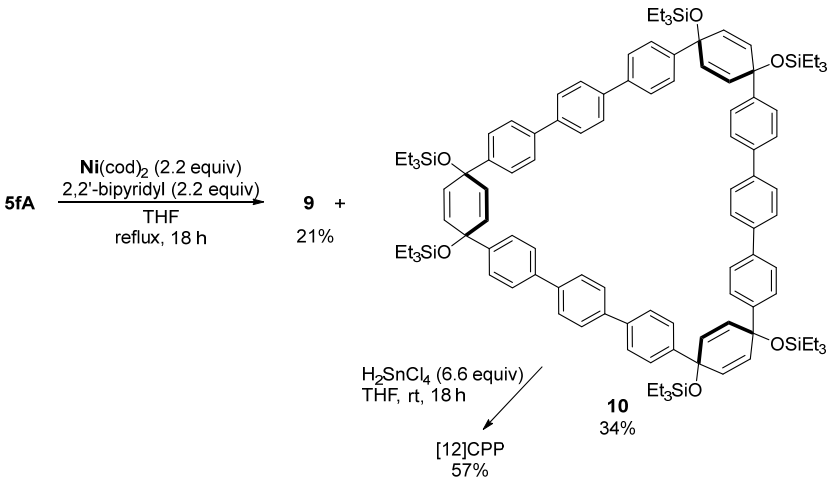
B3LYP/6-31G(d) level of theory suggests that the two protons (H^1 and H^2) of the paraphenylene of the facing paraphenyl group, respectively (Figure 2). These distances are consistent with the deshielding effect of H^1 and H^2 observed in the ^1H NMR.

Next, the same reaction was repeated on a large scale by starting from 50.0 g of **5fB** (60.9 mmol) and $PtCl_2$(cod) (22.8 g, 60.9 mmol) in the presence of K_3PO_4 (64.7 g, 0.305 mol) in THF (4.0 L) at 65 °C for 46 h. The crude reaction mixture containing **6f** was directly used for the next step without purification, and the reductive elimination of platinum at 105 °C by adding PPh_3 gave 10.7 g of **9** in 31% yield (two steps).

Reductive aromatization of **9** (5.80 g, 5.12 mmol) was successfully carried out by employing H_2SnCl_4 (4.4 equiv)[30] prepared in situ from $SnCl_2$ and HCl (2.0 equiv) in THF at room temperature for 18 h, and 1.97 g of [8]CPP was isolated by silica gel chromatography in 67% yield. The overall yield was 8.8% in 7 steps with 6 pots from the commercially available 4-bromo-4'-hydroxybiphenyl. While purification of the intermediate and final product by silica gel chromatography was still needed, this synthetic route significantly improved the previous gram-scale synthesis of [8]CPP.

To clarify the advantage of platinum-mediated dimerization, one-step cyclization of **5fA** was investigated under the Ni(0)-mediated Yamamoto coupling reaction condition by treatment with $Ni(cod)_2$ and 2,2'-bipyridyl (Scheme 3). Cyclic trimer **10** was formed as the major product in 34% yield, and the desired dimer **9** was obtained in only 21% yield. As **10** and **9** could be separated by preparative GPC and **10** could be transformed to [12]CPP in high yield by H_2SnCl_4-mediated reductive aromatization, the method can be utilized for the random synthesis of [8] and [12]CPPs. Despite the usefulness of the random synthesis for increase the availability of CPPs with different

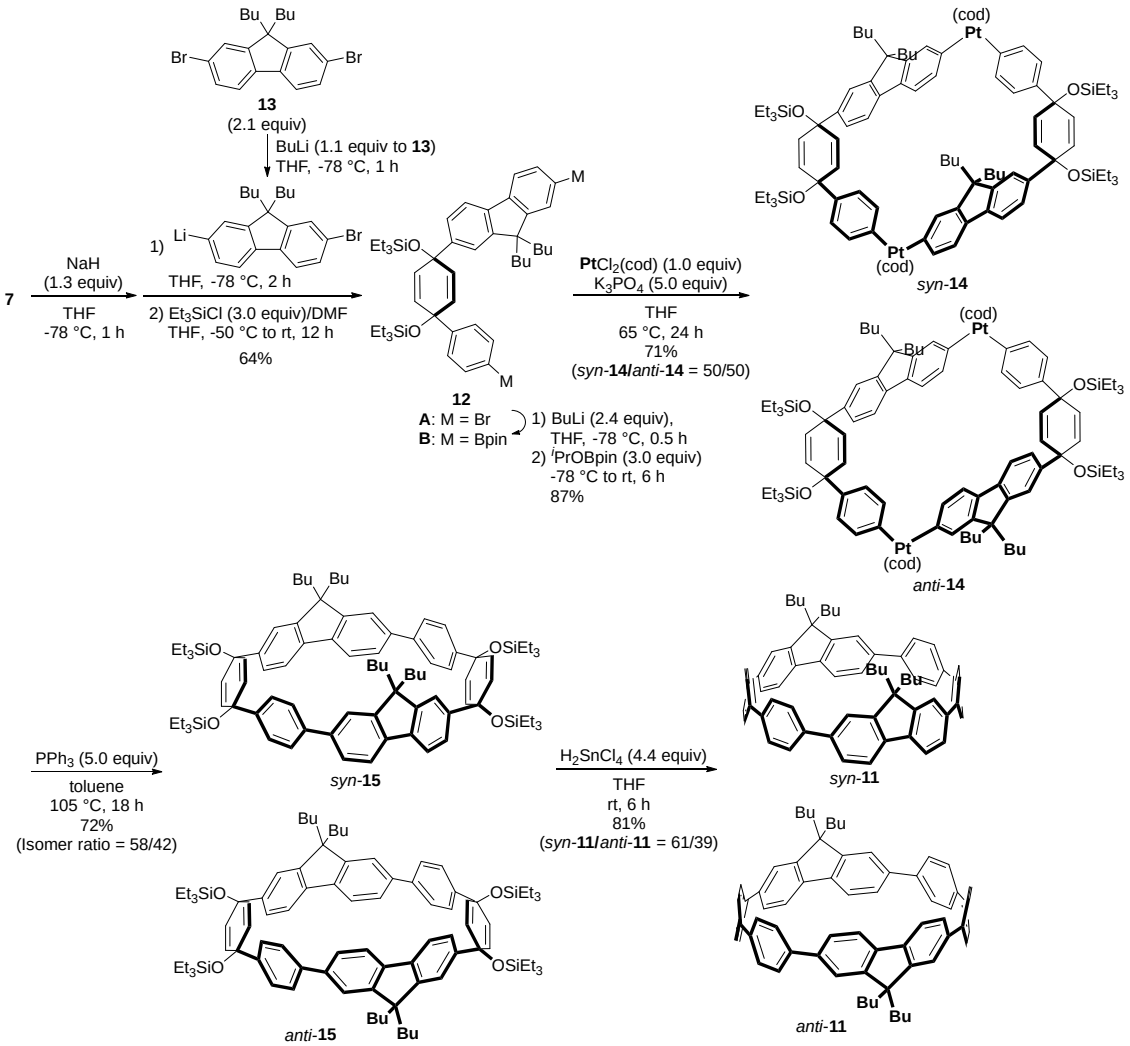
size, however, the method is limited to the small scale synthesis due to the use of preparative GPC for the separation. Therefore, the platinum-mediated method is suitable for obtaining [8]CPP with high efficiency and selectivity.



Scheme 3. One-step cyclization of **5fA**

Finally, the generality of the new protocol was examined by the synthesis of fluorene-embedded [8]CPP **11** (Scheme 4). The asymmetric unit **12** was synthesized by the addition of 2-bromo-9,9-dibutyl-7-lithio-9H-fluorene, which was in situ generated from 2,7-dibromo-9,9-dibutyl-9H-fluorene (**13**) and BuLi, to a sodium salt of **7** and subsequent TES protection gave **12A** with high *cis* selectivity in 64% yield. After bromine-borane transformation from **12A** to **12B**, the reaction of **12B** and $PtCl_2$(cod) in the presence of K_3PO_4 gave the bis-platinum complex **14** in 71% yield along with ca. 15% of linear oligomers. **14** consists of a 50:50 mixture of *syn* and *anti* rotamers with respect to the relative orientation of the fluorene unit. Highly selective synthesis of **14** is in sharp contrast to our previous attempts to synthesize CPPs through a rectangular shaped platinum complex having platinum atom at each corner,[26] which resulted in low yield of the desired product. The difference most likely comes from the rigid structure of 1,4-cyclohexadiene unit in **14**

compared to the platinum atom for making curvature required for the synthesis of cyclic complexes. The mixture of *syn* and *anti* isomers of **14** was subjected to the reductive elimination of platinum giving a 58:42 mixture of two rotamers of cyclic dimer **15**. Reductive aromatization of **15** by H_2SnCl_4 afforded the desired **11** as a 61:39 mixture of *syn* and *anti* isomers in 81% combined yield. The *syn/anti* ratio of both **15** and **11** did not change after heating at 150 °C for 12 h in CD_2Cl_4.



Scheme 4. Synthesis of fluorene-embedded [8]CPP **11**

The stability of the *syn* and *anti* isomers of **15** and **11** was estimated by the DFT calculation for

the model compounds of **15**, tetraol (OH group instead of OTES group) of bis-dimethylfluorene-embedded derivative, and **11**, bis-dimethylfluorene derivative, at the B3LYP/6-31G* level of theory. The results indicates that the *anti* isomer is slightly thermodynamically more stable than the *syn* isomer by 6.1 kJ mol^{-1} for **15**, whereas the *syn* isomer is significantly more stable than the *anti* isomer by 15 kJ mol^{-1} for **11**. The results would suggest that the enrichment of the *syn* isomer in **11** is due to the isomerization during the transformation from **15** to **11** or the difference in the efficiency of conversion from *anti* and *syn* isomers of **15** to the corresponding isomers of **11**. Further studies are needed to clarify this point.

In summary, [8]CPP was synthesized on a gram scale in 7 steps through the platinum-mediated dimerization of unsymmetrical four-ring unit **5fB** and H_2SnCl_4-mediated reductive aromatization. We believe that the current method opens new possibilities to design and synthesize various CPP derivatives and structurally diverse macrocycles in a highly selective and efficient manner.

Experimental Section

General. All reactions involving air- and moisture-sensitive compounds were carried out in a dry reaction vessel under nitrogen atmosphere. An oil bath was used to elevate the temperature of reactions. Preparative GPC was performed on JAIGEL 1H, 2H, and 2.5H polystyrene columns (Japan Analytical Industry Co., Ltd.) with $CHCl_3$ as the eluent. ^1H (400 MHz) and $^{13}C\{^1H\}$ (100 MHz) NMR spectra were obtained for a $CDCl_3$ solution of the samples and are reported as δ in units of parts per million (ppm) from an internal tetramethylsilane or a residual solvent peak. The electrospray ionization (ESI)-TOF MS spectrum was recorded on a spectrometer in positive or negative mode. A sample was injected as a CH_2Cl_2/methanol or acetonitrile solution. The matrix-

assisted laser-desorption ionization (MALDI)-TOF MS spectrum was obtained on a spectrometer in positive reflection mode at an acceleration voltage of 20 kV. Samples were prepared from a THF solution by mixing a sample (1 mg mL^{-1}) and dithranol (10 mg mL^{-1}) in a 1:1 ratio. Infrared (IR) spectroscopy was reported in cm^{-1}. Melting point (mp) was measured and was uncorrected.

Materials. Unless otherwise noted, commercially available materials were used without purification. Chlorotrimethylsilane was distilled just before use. The water content in the solvents was determined by a Karl-Fisher water titrater. Compound **7** was synthesized by modifying the literature method.[19] $PtCl_2$(cod) and **13**[76] were synthesized according to literature procedures.[77]

Synthesis of 4-(4-bromophenyl)-4-hydroxycyclohexa-2,5-dien-1-one (7). To a slurry of 4-bromo-4'-hydroxybiphenyl (100 g, 401 mmol) and imidazole (32.8 g, 481 mol) in CH_2Cl_2 (150 mL) was added chlorotrimethylsilane (55.8 mL, 441 mmol) over 30 min at 0 °C, and the resulting mixture was slowly warmed to room temperature. After stirring for 10 h at 0 °C, the reaction mixture was quenched with a saturated aqueous $NaHCO_3$ solution and extracted with CH_2Cl_2. The combined organic layers were washed with saturated brine solution and dried over Na_2SO_4, filtered and concentrated to give 4-bromo-4'-[(trimethylsilyl)oxy]-1,1'-biphenyl quantitatively (129 g) as a colorless solid. [Acetyloxy(phenyl)-λ^3-iodanyl] acetate ($PhI(OAc)_2$, 155 g, 481 mmol) and the above-obtained biphenyl were alternatively added to a mixture of THF (2.00 L), CH_3CN (500 mL) and H_2O (500 mL) over the course of 3 h at room temperature. After stirring for an additional 12 h at room temperature, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution and extracted with CH_2Cl_2. The combined organic layer was washed with a saturated aqueous NaCl solution, dried over Na_2SO_4, filtered and concentrated under reduced pressure to give a crude mixture. The residue was washed with dibutyl ether to give **7** as a colorless solid in 80% yield (84.9 g). The NMR spectra were consistent with literature data.[19]

Synthesis of [1-[4-bromo-(1,1'-biphenyl)-4'-yl]-4-(4-bromophenyl)-4-triethylsilyloxycyclohexa-2,5-dien-1-yl]oxy-triethylsilane (5fA). A solution of **7** (30.0 g, 0.113 mol) in 240 mL of THF was added slowly to a slurry of sodium hydride (5.88 g, 0.147 mol, 60% in mineral oil) in 300 mL of THF over 0.5 h at -78 °C through a dropping funnel, and the resulting mixture was stirred for 1 h at the same temperature. In a separate flask, BuLi (156 mL, 1.6 M in hexane, 0.249 mol) was added slowly to a solution of 4,4'-dibromobiphenyl (74.1 g, 0.238 mol) in THF (750 mL) at -78 °C using a dropping funnel. After stirring for 1 h at the same temperature, the resulting 4-bromo-4′-lithiobiphenyl was added through a cannula to the above-prepared solution containing **7** at -78 °C. After stirring for 2 h at the same temperature, DMF (120 mL) and TES chloride (51.2 g, 0.340 mol) were added to the solution at approximately -50 °C. After stirring overnight at room temperature, the reaction mixture was quenched with crushed ice and a saturated aqueous $NaHCO_3$ solution and extracted with ethyl acetate. The combined organic layer was washed with a saturated aqueous NaCl solution, dried over Na_2SO_4, filtered and concentrated under reduced pressure to give a crude mixture. Purification by silica gel chromatography (hexane/toluene = 100/0, 20/1 to 9/1) afforded **5fA** as a colorless gummy oil in 56% yield (46.2 g).

^{1}H NMR ($CDCl_3$, 400 MHz) 0.62 (q, 6H, *J* = 7.8 Hz, $SiEt_3$), 0.63 (q, 6H, *J* = 7.8 Hz, $SiEt_3$), 0.95 (t, 9H, *J* = 7.8 Hz, $SiEt_3$), 0.96 (t, 9H, *J* = 7.8 Hz, $SiEt_3$), 5.98 (d, 2H, *J* = 10.0 Hz, -CH=CH-), 6.04 (d, 2H, *J* = 10.0 Hz, -CH=CH-), 7.24 (d, 2H, *J* = 8.8 Hz, -Ar), 7.39 (d, 2H, *J* = 8.0 Hz, -Ar), 7.40 (d, 2H, *J* = 8.4 Hz, -Ar), 7.46 (d, 2H, *J* = 8.4 Hz, -Ar), 7.48 (d, 2H, *J* = 8.4 Hz, -Ar), 7.56 (d, 2H, *J* = 8.3 Hz, -Ar); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) 6.39, 6.42, 7.04, 7.04, 71.1, 71.2, 121.2, 121.5, 126.3, 126.7, 127.7, 128.6, 131.15, 131.19, 131.7, 131.8, 138.9, 139.6, 145.1, 145.3; HRMS (ESI-

TOF) *m/z*: $[M + Cs]^+$ Calcd for $C_{36}H_{46}Br_2O_2Si_2Cs$ 857.0458, found 857.0483; IR (KBr) 726, 878, 1003, 1070, 1241, 1351, 1412, 1456, 1601, 2877, 2956.

Synthesis of [1-[4'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1'-biphenyl-4-yl]-4-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-4-triethylsilyloxycyclohexa-2,5-dien-1-yl]oxy-triethylsilane (5fB). To a solution of **5fA** (45.2 g, 62.2 mmol) in THF (600 mL) was added BuLi (93.4 mL, 1.60 M in hexane, 0.149 mol) through a dropping funnel at -78 °C over 0.5 h. After stirring for 1 h at this temperature, a solution of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (^{i}PrOB(pin), 34.7 g, 0.187 mol) in THF (80 mL) was slowly added through a dropping funnel at -78 °C, and the resulting mixture was slowly warmed to room temperature. After stirring for 18 h at this temperature, the reaction mixture was quenched with H_2O and extracted with ethyl acetate. The combined organic layer was washed with saturated aqueous NaCl solution, dried over Na_2SO_4, filtered and concentrated under reduced pressure to give a crude mixture. Purification by silica gel chromatography (hexane/ethyl acetate = 20/1 to 9/1) afforded **5fB** as a faint yellow solid in 76% yield (38.6 g).

^{1}H NMR ($CDCl_3$, 400 MHz) 0.59 (q, 6H, *J* = 7.8 Hz, $SiEt_3$), 0.65 (q, 6H, *J* = 7.8 Hz, $SiEt_3$), 0.93 (t, 9H, *J* = 7.8 Hz, $SiEt_3$), 0.97 (t, 9H, *J* = 7.8 Hz, $SiEt_3$), 1.35 (s, 12H, -Bpin), 1.37 (s, 12H, -Bpin), 6.01 (s, 4H, -CH=CH-), 7.41 (d, 4H, *J* = 8.2 Hz, -Ar), 7.53 (d, 2H, *J* = 8.2 Hz, -Ar), 7.61 (d, 2H, *J* = 7.8 Hz, -Ar), 7.75 (d, 2H, *J* = 7.8 Hz, -Ar), 7.88 (d, 2H, *J* = 8.2 Hz, -Ar); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) 6.41, 6.41, 7.0, 7.1, 24.9, 71.4, 71.5, 83.7, 83.8, 125.2, 126.2, 126.4, 126.9, 131.3, 131.6, 134.7, 135.2, 139.7, 143.5, 145.4, 149.2; HRMS (ESI-TOF) *m/z*: $[M + Cs]^+$ Calcd for $C_{48}H_{70}B_2O_6Si_2Cs$ 953.3952, found 953.3975; IR (KBr) 881, 1271, 1456, 1609, 2824, 2924, 3030, 3078; mp 75.0-76.2 °C.

Small scale synthesis of bis[μ-[[(1,1'-biphenyl)-4,4'-diyl]-1,4-bis[(triethylsilyl)oxy]-2,5-cyclohexadiene-1,4-diyl][1,4-phenylene]]bis[(1,2,5,6-η)-1,5-cyclooctadiene]diplatinum (6f). A suspension of **5fB** (246 mg, 0.300 mmol), $PtCl_2$(cod) (112 mg, 0.300 mmol), and K_3PO_4 (318 mg, 1.50 mmol) in THF (60 mL) was heated at 65 °C for 24 h. Water was added, and the resulting mixture was extracted with CH_2Cl_2 (50 mL). The combined organic layer was washed with a saturated aqueous NaCl solution, dried over Na_2SO_4, filtered and concentrated under reduced pressure to give a crude mixture, which was purified by recycling preparative GPC using chloroform as the eluent to give **6f** as a colorless solid in 62% yield (162 mg). A mixture of linear oligomers was also separated, and the amount was 51.1 mg (~20%).

^{1}H NMR ($CDCl_3$, 400 MHz) 0.54 (q, 12H, J = 8.0 Hz, $SiEt_3$), 0.60 (q, 12H, J = 8.0 Hz, $SiEt_3$), 0.87 (t, 18H, J = 7.8 Hz, $SiEt_3$), 0.92 (t, 18H, J = 7.8 Hz, $SiEt_3$), 2.54 (brs, 16H, cod), 5.08 (s, 4H, $^2J_{Pt\text{-}H}$ = 43 Hz, cod), 5.21 (s, 4H, $^2J_{Pt\text{-}H}$ = 56 Hz, cod), 5.81 (d, 4H, J = 10 Hz, -CH=CH-), 5.98 (d, 4H, J = 10 Hz, -CH=CH-), 6.98 (d, 4H, J = 8.0 Hz, $^3J_{Pt\text{-}H}$ = 68 Hz, -Ar), 7.07 (d, 4H, J = 8.4 Hz, -Ar), 7.18 (d, 4H, J = 8.0 Hz, -Ar), 7.29 (d, 4H, J = 8.8 Hz, -Ar), 7.33 (d, 4H, J = 6.0 Hz, -Ar), 7.33 (d, 4H, J = 6.0 Hz, $^3J_{Pt\text{-}H}$ = 64 Hz, -Ar); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) 6.45, 6.46, 7.0, 7.1, 29.8, 29.9, 71.4, 72.0, 104.2 (d, $^2J_{Pt\text{-}C}$ = 66 Hz), 104.7 (d, $^2J_{Pt\text{-}C}$ = 66 Hz), 125.5, 125.6, 125.7, 126.0, 126.1, 131.2 (d, $^1J_{Pt\text{-}C}$ = 212 Hz), 131.5 (d, $^1J_{Pt\text{-}C}$ = 212 Hz), 134.0, 135.1, 135.2, 139.7, 143.6, 154.1 (d, $^1J_{Pt\text{-}C}$ = 229 Hz), 155.1 (d, $^1J_{Pt\text{-}C}$ = 253 Hz); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{88}H_{116}O_4Si_4Pt_2Na$ 1760.7123, found 1760.7147; IR (KBr) 521, 732, 806, 1074, 1479, 1583, 1794, 2876; dp > 174 °C.

Small scale synthesis of triethyl-[[14,17,30-tris(triethylsilyloxy)-nonacyclo[28.2.2.2^{2,5}.2^{6,9}.2^{10,13}.2^{14,17}.2^{18,21}.2^{22,25}.2^{26,29}]octatetraconta-2,4,6,8,10,12,15,18,20,22,24,26,28,31,33,35,37,39,41,43,45,47-docosaenyl]oxy]silane (9). A

solution of **6f** (87.1 mg, 50.0 μmol) and PPh_3 (65.6 mg, 250 μmol) in toluene (5 mL) was heated at 105 °C for 24 h. The resulting solution was concentrated under reduced pressure to give a crude mixture. Purification by silica gel chromatography (hexane/CH_2Cl_2=4/1 to 2/1) afforded **9** as a colorless solid in 77% yield (44 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) 0.64 (q, 24H, *J* = 7.8 Hz, $SiEt_3$), 0.97 (t, 36H, *J* = 7.8 Hz, $SiEt_3$), 6.33 (s, 8H, -CH=CH-), 6.95 (d, 8H, *J* = 8.8 Hz, -Ar), 7.00 (d, 8H, *J* = 8.4 Hz, -Ar), 7.16 (s, 8H, -Ar); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) 6.4, 7.0, 72.5, 126.6, 126.7, 127.7, 133.6, 139.8, 140.2, 142.4; HRMS (MALDI-TOF) *m/z*: $[M]^+$ Calcd for $C_{72}H_{92}O_4Si_4$ 1132.6073, found 1132.6091; IR (KBr) 812, 840, 1004, 1184, 1238, 1381, 1487, 2453, 2955; mp 194-199 °C.

Large-scale synthesis of 9. A suspension of **5fB** (50.0 g, 60.9 mmol), $PtCl_2$(cod) (22.8 g, 60.9 mmol), and K_3PO_4 (64.7 g, 0.305 mol) in THF (4.0 L) was heated at 65 °C for 46 h. After the resulting mixture was quenched with H_2O, THF was removed under reduced pressure, and the resulting mixture was extracted with CH_2Cl_2 (2.0 L × 2). The combined organic layer was washed with a saturated aqueous NaCl solution, dried over Na_2SO_4, filtered and concentrated under reduced pressure to give a crude mixture, which was used for the next step without further purification. A solution of the crude mixture and PPh_3 (39.9 g, 0.152 mol) in toluene (1.25 L) was heated at 105 °C for 24 h. The resulting solution was concentrated under reduced pressure, and purification of the resulting crude mixture by silica gel chromatography (hexane/CH_2Cl_2=4/1 to 2/1) afforded **9** as a pale yellow solid in 31% yield (10.7 g, for 2 steps).

Synthesis of [8]CPP. To a solution of $SnCl_2 \cdot 2H_2O$ (5.08 g, 22.5 mmol) in THF (500 mL) was added conc. HCl (3.75 mL, 12 N, 45.0 mmol) at room temperature. After stirring for 0.5 h at this temperature, the resulting solution was added to a solution of **9** (5.80 g, 5.12 mmol) in THF (80

mL). After stirring for 18 h at room temperature, the reaction mixture was quenched with crushed ice and a 10% aqueous NaOH solution and extracted with CH_2Cl_2 (400 mL x 2). The combined organic layer was washed with saturated aqueous NaCl solution, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by passing over a short silica gel plug with CH_2Cl_2 as the eluent. The resulting solid was dispersed in MeOH, filtered, and washed with MeOH to give [8]CPP (1.97 g, 63%) as a yellow solid. The NMR and MS spectra were consistent with the literature data.[7]

Synthesis of triethyl-[[14,17,30,33,46-penta[(triethylsilyl)oxy]-tridecacyclo[44.2.2.2^{2,5}.2^{6,9}.2^{10,13}.2^{14,17}.2^{18,21}.2^{22,25}.2^{26,29}.2^{30,33}.2^{34,37}.2^{38,41}.2^{42,45}]doheptaconta2,4,6,8,10,12,15,18,20,22,24,26,28,31,34,36,38,40,42,44,47,49,51,53,55,57,59,61,63,65,67,69,71-tritriacontaenyl]oxy]silane (10). $Ni(cod)_2$ (303 mg, 1.10 mmol) and 2,2'-bipyridyl (172 mg, 1.10 mmol) were dissolved in THF (50 mL), and the mixture was stirred at 50 °C for 0.5 h under a nitrogen atmosphere. The resulting mixture was added to a solution of **5fA** (363 mg, 0.500 mmol) in THF (50 mL), and the resulting mixture was refluxed for 18 h. The reaction mixture was passed through a pad of Celite using ethyl acetate as the eluent and was concentrated under reduced pressure to give a crude mixture. The residue was purified by recycling preparative GPC using chloroform as the eluent, giving **9** (59.5 mg, 21%) and **10** (96.2 mg, 34%) as off-white solids.

10: ^{1}H NMR ($CDCl_3$, 400 MHz) 0.65 (q, 36H, J = 8.0 Hz, -$SiEt_3$), 0.97 (t, 54H, J = 8.0 Hz, -$SiEt_3$), 6.05 (s, 12H, -CH=CH-), 7.47 (d, 12H, J = 8.4 Hz, -Ar), 7.58 (d, 12H, J = 8.8 Hz, -Ar), 7.67 (s, 12H, -Ar); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) 6.5, 7.1, 71.5, 126.4, 126.7, 127.3, 131.5, 139.4, 139.6, 145.3 ppm; HRMS (MALDI-TOF) *m/z*: $[M + Ag]^+$ Calcd for $C_{108}H_{138}O_6Si_6Ag$ 1806.8193, found 1806.8172; IR (KBr) 748, 864, 959, 1179, 1238, 1389, 1458, 1487, 2875, 2953, 3032; dp > 272 °C.

Synthesis of [12]CPP. To a solution of $SnCl_2 \cdot 2H_2O$ (43.8 mg, 194 μmol) in THF (5 mL) was added conc. HCl (32.3 μL, 12 N, 388 μmol) at room temperature. After stirring for 0.5 h at this temperature, the resulting solution was added to a suspension of **10** (50 mg, 29.4 μmol) in THF (10 mL). After stirring for 18 h at room temperature, the reaction mixture was quenched with crushed ice and a 10% aqueous NaOH solution and extracted with CH_2Cl_2 (400 mL x 2). The combined organic layer was washed with a saturated aqueous NaCl solution, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by passing over a short silica gel plug with CH_2Cl_2 as the eluent. The resulting solid was dispersed in MeOH, filtered, and washed with MeOH to give [12]CPP (15.3 mg, 57%) as a light yellow solid. The NMR and MS spectra were consistent with the literature data.[5]

Synthesis of [1-(7-bromo-9,9-dibutyl-9H-fluoren-2-yl)-4-(4-bromophenyl)-4-triethylsilyloxycyclohexa-2,5-dien-1-yl]oxy-triethylsilane (12A). A solution of **7** (798 mg, 3.00 mmol) in 5 mL of THF was added slowly to a slurry of sodium hydride (156 mg, 3.90 mmol, 60% in mineral oil) in 5 mL of THF over 0.5 h at -78 °C through a cannula, and the resulting mixture was stirred for 1 h at the same temperature. In a separate flask, BuLi (4.20 mL, 1.56 M in hexane, 6.60 mmol) was added slowly to a solution of **13** (2.61 g, 6.00 mmol) in THF (15 mL) at -78 °C using a syringe. After stirring for 1 h at the same temperature, the resulting 2-bromo-9,9-dibutyl-7-lithio-9H-fluorene was added through a cannula to the above-prepared solution containing **7** at -78 °C. After stirring for 2 h at the same temperature, DMF (1.00 mL) and TES chloride (1.50 mL, 9.00 mmol) were added to the solution at approximately -50 °C. After stirring overnight at room temperature, the reaction mixture was quenched with crushed ice and a saturated aqueous $NaHCO_3$ solution and extracted with ethyl acetate. The combined organic layer was washed with a saturated aqueous NaCl solution, dried over Na_2SO_4, filtered and concentrated under reduced pressure to

give a crude mixture. Purification by silica gel chromatography (hexane/ethyl acetate = 100/0 to 95/5) afforded **12A** as a colorless solid in 64% yield (1.64 g).

^{1}H NMR ($CDCl_3$, 400 MHz) 0.48-0.63 (m, 10H, Bu), 0.66 (q, 6H, *J* = 7.8 Hz, $SiEt_3$), 0.68 (q, 6H, *J* = 7.8 Hz, $SiEt_3$), 0.91 (t, 9H, *J* = 8.0 Hz, $SiEt_3$), 0.96 (t, 9H, *J* = 8.0 Hz, $SiEt_3$), 1.08 (quin, 4H, *J* = 7.6 Hz, Bu), 1.79-1.99 (m, 4H, Bu), 5.93 (d, 2H, *J* = 10.4 Hz, -CH=CH-), 6.10 (d, 2H, *J* = 10.0 Hz, -CH=CH-), 7.21 (d, 2H, *J* = 8.4 Hz, -Ar), 7.31 (dd, 1H, *J* = 8.0, 1.6 Hz, -Ar), 7.35 (dd, 1H, *J* = 8.0, 1.6 Hz, -Ar), 7.35 (d, 2H, *J* = 8.8 Hz, -Ar), 7.42-7.47 (m, 2H, -Ar), 7.53 (d, 1H, *J* = 8.8 Hz, -Ar), 7.57 (d, 1H, *J* = 8.4 Hz, -Ar); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) 6.4, 6.5, 6.99, 7.00, 13.8, 23.0, 25.9, 40.0, 55.3, 71.1, 71.3, 119.5, 120.1, 120.9, 121.0, 125.0, 126.1, 127.5, 129.9, 131.1, 131.7, 139.3, 139.7, 145.3, 145.6, 150.5, 153.1; HRMS (ESI-TOF) *m/z*: $[M + Cs]^+$ Calcd for $C_{45}H_{62}Br_2O_2Si_2Cs$ 983.1689, found 983.1703; IR (KBr) 734, 739, 968, 1009, 1067, 1107, 1240, 1402, 1456, 2874, 2955; mp 68.3-69.4 °C.

Synthesis of [1-[7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dibutyl-9H-fluoren-2-yl]-4-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-4-triethylsilyloxycyclohexa-2,5-dien-1-yl]oxy-triethylsilane (12B). To a solution of **12A** (851 mg, 1.00 mmol) in THF (2 mL) was added BuLi (1.50 mL, 1.58 M in hexane, 2.40 mmol) using a syringe at -78 °C over 0.5 h. After stirring for 1 h at this temperature, a solution of *i*-PrOB(pin) (620 μL, 3.00 mmol) was slowly added using a syringe at -78 °C, and the resulting mixture was slowly warmed to room temperature. After stirring for 6 h at this temperature, the reaction mixture was quenched with H_2O and extracted with ethyl acetate. The combined organic layer was washed with saturated aqueous NaCl solution, dried over Na_2SO_4, filtered and concentrated under reduced pressure to give a crude mixture. The crude mixture was washed with cold MeOH to give **12B** (821 mg, 87%) as a colorless solid.

^{1}H NMR ($CDCl_3$, 400 MHz) 0.57 (q, 6H, *J* = 8.0 Hz, $SiEt_3$), 0.64 (q, 6H, *J* = 7.8 Hz, $SiEt_3$), 0.64 (t, 6H, *J* = 7.6 Hz, Bu), 0.92 (t, 9H, *J* = 8.0 Hz, $SiEt_3$), 0.95 (t, 9H, *J* = 8.0 Hz, $SiEt_3$), 0.98 (quin, 4H, *J* = 7.2 Hz, Bu), 1.06 (quin, 4H, *J* = 7.6 Hz, Bu), 1.32 (s, 12H, -Bpin), 1.39 (s, 12H, -Bpin), 1.80-2.05 (m, 4H, Bu), 5.97 (d, 2H, *J* = 10.0 Hz, -CH=CH-), 6.07 (d, 2H, *J* = 10.0 Hz, -CH=CH-), 7.30 (d, 1H, *J* = 9.2 Hz, -Ar), 7.37 (d, 2H, *J* = 8.0 Hz, -Ar), 7.41 (s, 1H, -Ar), 7.60 (d, 1H, *J* = 8.0 Hz, -Ar), 7.67 (d, 1H, *J* = 8.0 Hz, -Ar), 7.71 (d, 2H, *J* = 8.4 Hz, -Ar), 7.72 (s, 1H, -Ar), 7.79 (d, 1H, *J* = 7.2 Hz, -Ar); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) 6.4, 6.5, 7.0, 7.0, 13.8, 23.0, 24.8, 24.9, 25.9, 40.0, 55.1, 71.52, 71.53, 83.6, 83.7, 119.0, 119.7, 120.3, 124.7, 125.1, 128.1, 128.8, 131.3, 131.6, 133.7, 134.7, 140.1, 143.9, 145.8, 149.2, 150.2, 151.4; HRMS (MALDI-TOF) *m/z*: [M + Cs]$^+$ Calcd for $C_{57}H_{86}B_2O_6Si_2Cs$ 1077.5204, found 1077.5218; IR (KBr) 731, 862, 962, 1007, 1080, 1146, 1360, 1611, 2934, 2957; mp 78.2-79.8 °C.

Synthesis of bis[μ-[[9,9-dibutyl-9*H*-fluorene-2,7-diyl]-1,4-bis[(triethylsilyl)oxy]-2,5-cyclohexadiene-1,4-diyl][1,4-phenylene]]bis[(1,2,5,6-η)-1,5-cyclooctadiene]diplatinum (14). A suspension of **12B** (212 mg, 0.400 mmol), $PtCl_2$(cod) (150 mg, 0.400 mmol), and K_3PO_4 (424 mg, 2.00 mmol) in THF (80 mL) was heated at 65 °C for 24 h. Water was added, and the resulting mixture was extracted with ethyl acetate (50 mL). The combined organic layer was washed with a saturated aqueous NaCl solution, dried over Na_2SO_4, filtered and concentrated under reduced pressure to give a crude mixture, which was purified by recycling preparative GPC using chloroform as the eluent to give **14** as a colorless solid in 71% yield (282 mg). The ratio of two isomers (*syn*-**14**/*anti*-**14**) was determined to be 50:50 as judged by a comparison of the integrals of protons at cyclohexadiene-diyl moieties (δ = 5.72, 5.82, 5.95, and 6.00 ppm) in the ^{1}H NMR analysis. A mixture of linear oligomers was also separated in ca. 15% (59.6 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) 0.43 (t, 12H, *J* = 7.6 Hz, Bu), 0.45 (t, 12H, *J* = 7.6 Hz, Bu), 0.55 (q, 24H, *J* = 8.0 Hz, $SiEt_3$), 0.64 (q, 24H, *J* = 8.0 Hz, $SiEt_3$), 0.83 (t, 36H, *J* = 8.0 Hz, $SiEt_3$), 0.92 (t, 36H, *J* = 8.0 Hz, $SiEt_3$), 0.85-0.99 (m, 32H, *J* = 8.0 Hz, $SiEt_3$), 1.55-2.02 (m, 16H, Bu), 2.31-2.80 (m, 32H, cod), 4.85 (brs, 4H, cod), 5.17 (brs, 4H, $^2J_{Pt-H}$ = 42 Hz, cod), 5.28 (brs, 4H, cod), 5.37 (brs, 4H, cod), 5.72 (d, 4H, *J* = 9.2 Hz, -CH=CH-), 5.82 (d, 4H, *J* = 10 Hz, -CH=CH-), 5.95 (d, 4H, *J* = 10 Hz, -CH=CH-), 6.00 (d, 4H, *J* = 10 Hz, -CH=CH-), 6.78 (d, 4H, *J* = 8.0 Hz, -Ar), 7.00 (d, 8H, *J* = 8.0 Hz, -Ar), 7.02 (d, 4H, *J* = 8.0 Hz, -Ar), 7.10 (d, 4H, *J* = 8.0 Hz, -Ar), 7.17 (dd, 4H, *J* = 7.6, 3.6 Hz, -Ar), 7.21 (s, 4H, -Ar), 7.26-7.32 (m, 8H, -Ar), 7.34 (d, 4H, *J* = 7.6 Hz, -Ar), 7.43 (d, 4H, *J* = 8.0 Hz, -Ar); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) 6.4, 6.5, 6.6, 7.0, 7.08, 7.11, 13.9, 22.9, 23.0, 26.0, 29.75, 29.78, 39.8, 40.1, 54.5, 54.6, 70.9, 71.2, 71.5, 72.0, 103.7, 104.0, 104.4, 104.6, 118.0, 118.1, 118.3, 118.5, 119.6, 120.4, 124.2, 124.5, 124.7, 124.8, 125.0, 129.7, 130.1, 130.5, 130.8, 131.1, 131.5, 132.0, 132.1, 132.3, 132.5, 133.5, 134.9, 135.9, 136.1, 139.7, 140.8, 141.3, 143.9, 144.0, 149.7, 149.8, 149.9, 150.2, 153.2, 153.6, 155.6, 156.6; (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{106}H_{148}O_4Si_4Pt_2Na$ 2009.9660, found 2009.9642; IR (KBr) 735, 812, 866, 962, 1005, 1070, 1238, 1456, 2873, 2953; dp > 186 °C.

Synthesis of fluorene-embedded cyclic dimer (15). A solution of **14** (87.1 mg, 100 μmol) and PPh_3 (131 mg, 500 μmol) in toluene (10 mL) was heated at 105 °C for 18 h. The resulting solution was concentrated under reduced pressure to give a crude mixture. Purification by silica gel chromatography (hexane/CH_2Cl_2=9/1 to 4/1) afforded **15** as a colorless solid in 72% yield (99.5 mg). The ratio of two isomers was determined to be 58:42 as judged by a comparison of the integrals of protons at cyclohexadiene-diyl moieties (δ = 5.78, 5.88-6.16, and 6.38 ppm) in the ^{1}H NMR analysis.

Isomer 1: ^{1}H NMR ($CDCl_3$, 400 MHz) 0.38 (t, 6H, *J* = 6.4 Hz, Bu), 0.58 (q, 12H, *J* = 8.0 Hz, $SiEt_3$), 0.67 (q, 12H, *J* = 8.0 Hz, $SiEt_3$), 0.88 (t, 18H, *J* = 8.0 Hz, $SiEt_3$), 0.97 (t, 18H, *J* = 8.0 Hz, $SiEt_3$), 0.76-1.06 (m, 16H, Bu), 1.33-2.01 (m, 8H, Bu), 5.88-6.16 (m, 8H, -CH=CH-), 6.82 (d, 4H, *J* = 8.0 Hz, -Ar), 6.91-7.08 (m, 10H), 7.53-7.62 (m, 6H, -Ar), Isomer 2: ^{1}H NMR ($CDCl_3$, 400 MHz) 0.38 (t, 6H, *J* = 6.4 Hz, Bu), 0.52 (q, 12H, *J* = 8.0 Hz, $SiEt_3$), 0.66 (q, 12H, *J* = 8.0 Hz, $SiEt_3$), 0.61-0.68 (m, 6H, Bu), 0.88 (t, 18H, *J* = 8.0 Hz, $SiEt_3$), 0.97 (t, 18H, *J* = 8.0 Hz, $SiEt_3$), 0.76-1.06 (m, 16H, Bu), 1.33-2.01 (m, 8H, Bu), 5.78 (d, 4H, *J* = 10 Hz, -CH=CH-), 6.38 (d, 4H, *J* = 10 Hz, -CH=CH-), 6.87 (d, 4H, *J* = 8.0 Hz, -Ar), 6.96 (s, 2H), 6.97 (d, 8H, *J* = 8.0 Hz, -Ar), 7.66 (d, 4H, *J* = 8.4 Hz, -Ar), 7.70 (s, 2H, -Ar); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) 6.40, 6.44, 6.5, 6.90, 6.94, 7.1, 13.1, 13.2, 13.8, 13.9, 22.7, 23.1, 25.9, 26.3, 38.5, 40.1, 53.6, 54.8, 69.8, 71.3, 71.4, 72.5, 119.4, 120.3, 120.4, 121.3, 121.7, 122.2, 124.0, 125.7, 125.8, 126.2, 126.3, 126.5, 126.7, 126.8, 128.5, 129.6, 131.3, 131.5, 135.1, 138.5, 138.7, 138.9, 139.0, 139.3, 139.6, 140.6, 141.4, 142.8, 143.3, 143.8, 144.57, 144.64, 145.2, 151.3, 151.65, 151.73, 153.1; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{90}H_{124}O_4Si_4Na$ 1403.8474, found 1403.8489; IR (KBr) 743, 818, 972, 1005, 1078, 1238, 1414, 1460, 2911, 2954; mp 126-129 °C.

Fluorene-embedded [8]CPP (11). To a solution of $SnCl_2 \cdot 2H_2O$ (29.8 mg, 132 μmol) in THF (1 mL) was added conc. HCl (22 μL, 12 N, 264 μmol) at room temperature. After stirring for 0.5 h at this temperature, the resulting solution was added to a solution of **15** (41.5 mg, 30 μmol) in THF (3 mL). After stirring for 6 h at room temperature, the reaction mixture was quenched with water and a 10% aqueous NaOH solution and extracted with CH_2Cl_2 (5 mL x 2). The combined organic layer was washed with saturated aqueous NaCl solution, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by passing over a short silica gel plug with CH_2Cl_2 as the eluent. The resulting solid was dispersed in MeOH, filtered, and washed

with MeOH to give **11** (20.8 mg, 81%) as a yellow solid. The ratio of two isomers (*syn*-**11**/*anti*-**11**) was determined to be 61:39 as judged by a comparison of the integrals of protons at the 1 and 8 positions of fluorene units (*syn*-**11**: δ = 6.85 ppm, *anti*-**11**: δ = 6.64 and 6.89 ppm) in the ^{1}H NMR analysis.

^{1}H NMR ($CDCl_3$, 400 MHz) -0.91 ~ -0.75 (m, 6H, Bu), -0.69 (t, 3H, *J* = 7.6 Hz, Bu), -0.68 (t, 3H, *J* = 7.2 Hz, Bu), -0.16-0.13 (m, 12H, Bu), 0.74-0.85 (m, 16H, Bu), 1.11-1.32 (m, 16H, Bu), 1.59-1.81 (m, 16H, Bu), 6.64 (s, 2H, -Ar of *anti*-**15**), 6.85 (d, 4H, *J* = 1.6 Hz, -Ar of *syn*-**15**), 6.89 (d, 2H, *J* = 1.6 Hz, -Ar of *syn*-**15**), 7.18 (d, 1H, *J* = 2.0 Hz, -Ar of *anti*-**15**), 7.28-7.51 (m, 28H, -Ar), 7.52 (s, 2H, -Ar of *anti*-**15**), 7.54 (s, 8H, -Ar of *syn*-**15**), 7.55-7.57 (m, 5H, -Ar), 7.58 (d, 2H, *J* = 1.2 Hz, -Ar of *anti*-**15**), 7.59 (d, 2H, *J* = 1.6 Hz, -Ar of *anti*-**15**), 7.61 (d, 1H, *J* = 1.6 Hz -Ar of *anti*-**15**); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) 12.1, 12.5, 13.96, 13.96, 21.4, 21.9, 23.17, 23.17, 23.76, 23.79, 27.39, 27.41, 35.0, 35.1, 42.2, 42.5, 56.7, 121.88, 121.96, 122.03, 123.3, 123.7, 126.7, 127.2, 127.4, 127.6, 128.0, 128.1, 128.2, 128.7, 129.2, 136.4, 137.1, 137.2, 137.3, 137.7, 137.9, 138.1, 138.5, 138.9, 139.7, 139.9, 140.0, 140.2, 140.8, 152.5, 152.9; HRMS (MALDI-TOF) *m/z*: $[M]^+$ Calcd for $C_{66}H_{64}$ 856.5008, found 856.5021.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXXXXXXXXXXXXXXX.

Synthetic and computational data (PDF)

AUTHOR INFORMATION

Corresponding Authors

*kayahara@scl.kyoto-u.ac.jp

* yamago@scl.kyoto-u.ac.jp

ORCID

Eiichi Kayahara: 0000-0003-1663-5273

Shigeru Yamago: 0000-0002-4112-7249

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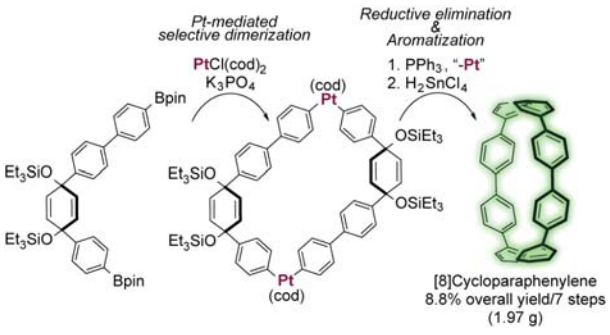
REFERENCES



1. Schröder, A.; Mekelburger, H.-B.; Vögtle, F., Belt-, ball-, and tube-shaped molecules. *Top. Curr. Chem.* **1994,** *172*, 179-201.

2. Tahara, K.; Tobe, Y., Molecular Loops and Belts. *Chem. Rev.* **2006,** *106* (12), 5274-5290.

3. Kawase, T.; Kurata, H., Ball-, Bowl-, and Belt-Shaped Conjugated Systems and Their Complexing Abilities: Exploration of the Concave-Convex π-π Interaction. *Chem. Rev.* **2006,** *106* (12), 5250-5273.

4. Evans, P.; Jasti, R., Molecular Belts. *Top. Curr. Chem.* **2013**, 1-42.

5. Jasti, R.; Bhattacharjee, J.; Neaton, J. B.; Bertozzi, C. R., Synthesis, Characterization, and Theory of [9]-, [12]-, and [18]Cycloparaphenylene: Carbon Nanohoop Structures. *J. Am. Chem. Soc.* **2008,** *130* (52), 17646-17647.

6. Takaba, H.; Omachi, H.; Yamamoto, Y.; Bouffard, J.; Itami, K., Selective Synthesis of [12]Cycloparaphenylene. *Angew. Chem. Int. Ed.* **2009,** *48* (33), 6112-6116.

7. Yamago, S.; Watanabe, Y.; Iwamoto, T., Synthesis of [8]Cycloparaphenylene from a Square-Shaped Tetranuclear Platinum Complex. *Angew. Chem. Int. Ed.* **2010,** *49* (4), 757-759.

8. Sisto, T. J.; Golder, M. R.; Hirst, E. S.; Jasti, R., Selective Synthesis of Strained [7]Cycloparaphenylene: An Orange-Emitting Fluorophore. *J. Am. Chem. Soc.* **2011,** *133* (40), 15800-15802.

9. Hitosugi, S.; Nakanishi, W.; Yamasaki, T.; Isobe, H., Bottom-up synthesis of finite models of helical (n,m)-single-wall carbon nanotubes. *Nat Commun* **2011,** *2*, 492.

10. Nishiuchi, T.; Feng, X.; Enkelmann, V.; Wagner, M.; Müllen, K., Three-Dimensionally Arranged Cyclic p-Hexaphenylbenzene: Toward a Bottom-Up Synthesis of Size-Defined Carbon Nanotubes. *Chem. Eur. J.* **2012,** *18* (52), 16621-16625.

11. Batson, J. M.; Swager, T. M., Towards a Perylene-Containing Nanohoop. *Synlett* **2013,** *24* (EFirst), 2545-2549.

12. Tran-Van, A.-F.; Huxol, E.; Basler, J. M.; Neuburger, M.; Adjizian, J.-J.; Ewels, C. P.; Wegner, H. A., Synthesis of Substituted [8]Cycloparaphenylenes by [2 + 2 + 2] Cycloaddition. *Org. Lett.* **2014,** *16* (6), 1594-1597.

13. Huang, C.; Huang, Y.; Akhmedov, N. G.; Popp, B. V.; Petersen, J. L.; Wang, K. K., Functionalized Carbon Nanohoops: Synthesis and Structure of a [9]Cycloparaphenylene Bearing Three 5,8-Dimethoxynaphth-1,4-diyl Units. *Org. Lett.* **2014,** *16* (10), 2672-2675.

14. Jiang, H.-W.; Tanaka, T.; Mori, H.; Park, K. H.; Kim, D.; Osuka, A., Cyclic 2,12-Porphyrinylene Nanorings as a Porphyrin Analogue of Cycloparaphenylenes. *J. Am. Chem. Soc.* **2015,** *137* (6), 2219-2222.

15. Myśliwiec, D.; Kondratowicz, M.; Lis, T.; Chmielewski, P. J.; Stępień, M., Highly Strained Nonclassical Nanotube End-caps. A Single-Step Solution Synthesis from Strain-Free, Non-Macrocyclic Precursors. *J. Am. Chem. Soc.* **2015,** *137* (4), 1643-1649.

16. Miyauchi, Y.; Johmoto, K.; Yasuda, N.; Uekusa, H.; Fujii, S.; Kiguchi, M.; Ito, H.; Itami, K.; Tanaka, K., Concise Synthesis and Facile Nanotube Assembly of a Symmetrically Multifunctionalized Cycloparaphenylene. *Chem. Eur. J.* **2015,** *21* (52), 18900-18904.

17. Zhang, B.; Trinh, M. T.; Fowler, B.; Ball, M.; Xu, Q.; Ng, F.; Steigerwald, M. L.; Zhu, X. Y.; Nuckolls, C.; Zhong, Y., Rigid, Conjugated Macrocycles for High Performance Organic Photodetectors. *J. Am. Chem. Soc.* **2016,** *138* (50), 16426-16431.

18. Darzi, E. R.; Sisto, T. J.; Jasti, R., Selective Syntheses of [7]–[12]Cycloparaphenylenes Using Orthogonal Suzuki–Miyaura Cross-Coupling Reactions. *J. Org. Chem.* **2012,** *77* (15), 6624-6628.

19. Xia, J.; Bacon, J. W.; Jasti, R., Gram-scale synthesis and crystal structures of [8]- and [10]CPP, and the solid-state structure of C60@[10]CPP. *Chem. Sci.* **2012,** *3* (10), 3018-3021.

20. Xia, J.; Jasti, R., Synthesis, Characterization, and Crystal Structure of [6]Cycloparaphenylene. *Angew. Chem. Int. Ed.* **2012,** *51* (10), 2474-2476.

21. Evans, P. J.; Darzi, E. R.; Jasti, R., Efficient room-temperature synthesis of a highly strained carbon nanohoop fragment of buckminsterfullerene. *Nat. Chem.* **2014,** *6* (5), 404-408.

22. Segawa, Y.; Miyamoto, S.; Omachi, H.; Matsuura, S.; Šenel, P.; Sasamori, T.; Tokitoh, N.; Itami, K., Concise Synthesis and Crystal Structure of [12]Cycloparaphenylene. *Angew. Chem. Int. Ed.* **2011,** *50* (14), 3244-3248.

23. Segawa, Y.; Šenel, P.; Matsuura, S.; Omachi, H.; Itami, K., [9]Cycloparaphenylene: Nickel-mediated Synthesis and Crystal Structure. *Chem. Lett.* **2011,** *40* (4), 423-425.

24. Ishii, Y.; Nakanishi, Y.; Omachi, H.; Matsuura, S.; Matsui, K.; Shinohara, H.; Segawa, Y.; Itami, K., Size-selective synthesis of [9]-[11] and [13]cycloparaphenylenes. *Chem. Sci.* **2012,** *3* (7), 2340-2345.

25. Sibbel, F.; Matsui, K.; Segawa, Y.; Studer, A.; Itami, K., Selective synthesis of [7]- and [8]cycloparaphenylenes. *Chem. Commun.* **2014,** *50* (8), 954-956.

26. Iwamoto, T.; Watanabe, Y.; Sakamoto, Y.; Suzuki, T.; Yamago, S., Selective and Random Syntheses of [n]Cycloparaphenylenes (n = 8-13) and Size Dependence of Their Electronic Properties. *J. Am. Chem. Soc.* **2011,** *133* (21), 8354-8361.

27. Kayahara, E.; Sakamoto, Y.; Suzuki, T.; Yamago, S., Selective Synthesis and Crystal Structure of [10]Cycloparaphenylene. *Org. Lett.* **2012,** *14* (13), 3284-3287.

28. Kayahara, E.; Iwamoto, T.; Suzuki, T.; Yamago, S., Selective Synthesis of [6]-, [8]-, and [10]Cycloparaphenylenes. *Chem. Lett.* **2013,** *42* (6), 621-623.

29. Kayahara, E.; Patel, V. K.; Yamago, S., Synthesis and Characterization of [5]Cycloparaphenylene. *J. Am. Chem. Soc.* **2014,** *136* (6), 2284-2287.

30. Patel, V. K.; Kayahara, E.; Yamago, S., Practical Synthesis of [n]Cycloparaphenylenes (n=5, 7–12) by H2SnCl4-Mediated Aromatization of 1,4-Dihydroxycyclo-2,5-diene Precursors. *Chem. Eur. J.* **2015,** *21* (15), 5742-5749.

31. Kayahara, E.; Patel, V. K.; Xia, J.; Jasti, R.; Yamago, S., Selective and Gram-Scale Synthesis of [6]Cycloparaphenylene. *Synlett* **2015,** *26* (11), 1615-1619.

32. Kayahara, E.; Sun, L.; Onishi, H.; Suzuki, K.; Fukushima, T.; Sawada, A.; Kaji, H.; Yamago, S., Gram-Scale Syntheses and Conductivities of [10]Cycloparaphenylene and Its Tetraalkoxy Derivatives. *J. Am. Chem. Soc.* **2017,** *139* (51), 8480-18483.

33. Kayahara, E.; Cheng, Y.; Yamago, S., Short-step Synthesis of Large Cycloparaphenylenes. *Chem. Lett.* **2018,** *47* (9), 1108-1111.

34. Omachi, H.; Segawa, Y.; Itami, K., Synthesis and Racemization Process of Chiral Carbon Nanorings: A Step toward the Chemical Synthesis of Chiral Carbon Nanotubes. *Org. Lett.* **2011,** *13* (9), 2480-2483.

35. Xia, J.; Golder, M. R.; Foster, M. E.; Wong, B. M.; Jasti, R., Synthesis, Characterization, and Computational Studies of Cycloparaphenylene Dimers. *J. Am. Chem. Soc.* **2012,** *134* (48), 19709-19715.

36. Yagi, A.; Segawa, Y.; Itami, K., Synthesis and Properties of [9]Cyclo-1,4-naphthylene: A π-Extended Carbon Nanoring. *J. Am. Chem. Soc.* **2012,** *134* (6), 2962-2965.

37. Matsui, K.; Segawa, Y.; Itami, K., Synthesis and Properties of Cycloparaphenylene-2,5-pyridylidene: A Nitrogen-Containing Carbon Nanoring. *Org. Lett.* **2012,** *14* (7), 1888-1891.

38. Iwamoto, T.; Kayahara, E.; Yasuda, N.; Suzuki, T.; Yamago, S., Synthesis, Characterization, and Properties of [4]Cyclo-2,7-pyrenylene: Effects of Cyclic Structure on the Electronic Properties of Pyrene Oligomers. *Angew. Chem. Int. Ed.* **2014,** *53* (25), 6430-6434.

39. Kayahara, E.; Qu, R.; Kojima, M.; Iwamoto, T.; Suzuki, T.; Yamago, S., Ligand-Controlled Synthesis of [3]- and [4]Cyclo-9,9-dimethyl-2,7-fluorenes through Triangle- and Square-Shaped Platinum Intermediates. *Chem. Eur. J.* **2015,** *21* (52), 18939-18943.

40. Kuroda, Y.; Sakamoto, Y.; Suzuki, T.; Kayahara, E.; Yamago, S., Tetracyclo(2,7-carbazole)s: Diatropicity and Paratropicity of Inner Regions of Nanohoops. *J. Org. Chem.* **2016,** *81* (8), 3356-3363.

41. Li, S.; Huang, C.; Thakellapalli, H.; Farajidizaji, B.; Popp, B. V.; Petersen, J. L.; Wang, K. K., Syntheses and Structures of Functionalized [9]Cycloparaphenylenes as Carbon Nanohoops Bearing Carbomethoxy and N-Phenylphthalimido Groups. *Org. Lett.* **2016,** *18* (9), 2268-2271.

42. Li, S.; Aljhdli, M.; Thakellapalli, H.; Farajidizaji, B.; Zhang, Y.; Akhmedov, N. G.; Milsmann, C.; Popp, B. V.; Wang, K. K., Synthesis and Structure of a Functionalized [9]Cycloparaphenylene Bearing Three Indeno[2,1-a]fluorene-11,12-dione-2,9-diyl Units. *Org. Lett.* **2017,** *19* (15), 4078-4081.

43. Kayahara, E.; Zhai, X.; Yamago, S., Synthesis and physical properties of [4]cyclo-3,7-dibenzo[b,d]thiophene and its S,S-dioxide. *Can. J. Chem.* **2017,** *95* (4), 351-356.

44. Van Raden, J. M.; Louie, S.; Zakharov, L. N.; Jasti, R., 2,2′ -Bipyridyl-Embedded Cycloparaphenylenes as a General Strategy To Investigate Nanohoop-Based Coordination Complexes. *J. Am. Chem. Soc.* **2017,** *139* (8), 2936-2939.

45. Della Sala, P.; Capobianco, A.; Caruso, T.; Talotta, C.; De Rosa, M.; Neri, P.; Peluso, A.; Gaeta, C., An Anthracene-Incorporated [8]Cycloparaphenylene Derivative as an Emitter in Photon Upconversion. *J. Org. Chem.* **2018,** *83* (1), 220-227.

46. Huang, Q.; Zhuang, G.; Jia, H.; Qian, M.; Cui, S.; Yang, S.; Du, P., Photoconductive Curved-Nanographene/Fullerene Supramolecular Heterojunctions. *Angew. Chem. Int. Ed.* **2019,** *58* (19), 6244-6249.

47. Hitosugi, S.; Nakanishi, W.; Yamasaki, T.; Isobe, H., Bottom-up synthesis of finite models of helical (n,m)-single-wall carbon nanotubes. *Nat. Commun.* **2011,** *2*, 492.

48. Kayahara, E.; Iwamoto, T.; Takaya, H.; Suzuki, T.; Fujitsuka, M.; Majima, T.; Yasuda, N.; Matsuyama, N.; Seki, S.; Yamago, S., Synthesis and physical properties of a ball-like three-dimensional π-conjugated molecule. *Nat. Commun.* **2013,** *4*, 2694-2700.

49. Matsui, K.; Segawa, Y.; Namikawa, T.; Kamada, K.; Itami, K., Synthesis and properties of all-benzene carbon nanocages: a junction unit of branched carbon nanotubes. *Chem. Sci.* **2013,** *4* (1), 84-88.

50. Ball, M.; Fowler, B.; Li, P.; Joyce, L. A.; Li, F.; Liu, T.; Paley, D.; Zhong, Y.; Li, H.; Xiao, S.; Ng, F.; Steigerwald, M. L.; Nuckolls, C., Chiral Conjugated Corrals. *J. Am. Chem. Soc.* **2015,** *137* (31), 9982-9987.

51. Senthilkumar, K.; Kondratowicz, M.; Lis, T.; Chmielewski, P. J.; Cybińska, J.; Zafra, J. L.; Casado, J.; Vives, T.; Crassous, J.; Favereau, L.; Stępień, M., Lemniscular [16]Cycloparaphenylene: A Radially Conjugated Figure-Eight Aromatic Molecule. *J. Am. Chem. Soc.* **2019,** *141* (18), 7421-7427.

52. Fujitsuka, M.; Cho, D. W.; Iwamoto, T.; Yamago, S.; Majima, T., Size-dependent fluorescence properties of [n]cycloparaphenylenes (n = 8-13), hoop-shaped [small pi]-conjugated molecules. *Phys. Chem. Chem. Phys.* **2012,** *14* (42), 14585-14588.

53. Segawa, Y.; Fukazawa, A.; Matsuura, S.; Omachi, H.; Yamaguchi, S.; Irle, S.; Itami, K., Combined experimental and theoretical studies on the photophysical properties of cycloparaphenylenes. *Org. Biomol. Chem.* **2012,** *10* (30), 5979-5984.

54. Kayahara, E.; Kouyama, T.; Kato, T.; Takaya, H.; Yasuda, N.; Yamago, S., Isolation and Characterization of the Cycloparaphenylene Radical Cation and Dication. *Angew. Chem. Int. Ed.* **2013,** *52* (51), 13722-13726.

55. Zabula, A. V.; Filatov, A. S.; Xia, J.; Jasti, R.; Petrukhina, M. A., Tightening of the Nanobelt upon Multielectron Reduction. *Angew. Chem. Int. Ed.* **2013,** *52* (19), 5033-5036.

56. Fujitsuka, M.; Tojo, S.; Iwamoto, T.; Kayahara, E.; Yamago, S.; Majima, T., Radical Ions of Cycloparaphenylenes: Size Dependence Contrary to the Neutral Molecules. *J. Phys. Chem. Lett.* **2014,** *5* (13), 2302-2305.

57. Toriumi, N.; Muranaka, A.; Kayahara, E.; Yamago, S.; Uchiyama, M., In-Plane Aromaticity in Cycloparaphenylene Dications: A Magnetic Circular Dichroism and Theoretical Study. *J. Am. Chem. Soc.* **2015,** *137* (1), 82-85.

58. Talipov, M. R.; Jasti, R.; Rathore, R., A Circle Has No End: Role of Cyclic Topology and Accompanying Structural Reorganization on the Hole Distribution in Cyclic and Linear Poly-p-phenylene Molecular Wires. *J. Am. Chem. Soc.* **2015,** *137* (47), 14999-15006.

59. Kayahara, E.; Kouyama, T.; Kato, T.; Yamago, S., Synthesis and Characterization of [n]CPP (n = 5, 6, 8, 10, and 12) Radical Cation and Dications: Size-Dependent Absorption, Spin, and Charge Delocalization. *J. Am. Chem. Soc.* **2016,** *138* (1), 338-344.

60. Kayahara, E.; Fukayama, K.; Nishinaga, T.; Yamago, S., Size Dependence of [n]Cycloparaphenylenes (n=5–12) in Electrochemical Oxidation. *Chem. Asian J.* **2016,** *11* (12), 1793-1797.

61. Masumoto, Y.; Toriumi, N.; Muranaka, A.; Kayahara, E.; Yamago, S.; Uchiyama, M., Near-Infrared Fluorescence from In-Plane-Aromatic Cycloparaphenylene Dications. *J. Phys. Chem. A* **2018,** *122* (23), 5162-5167.

62. Spisak, S. N.; Wei, Z.; Darzi, E.; Jasti, R.; Petrukhina, M. A., Highly strained [6]cycloparaphenylene: crystallization of an unsolvated polymorph and the first mono- and dianions. *Chem. Comm.* **2018,** *54* (56), 7818-7821.

63. Iwamoto, T.; Watanabe, Y.; Sadahiro, T.; Haino, T.; Yamago, S., Size-Selective Encapsulation of C60 by [10]Cycloparaphenylene: Formation of the Shortest Fullerene-Peapod. *Angew. Chem. Int. Ed.* **2011,** *50* (36), 8342-8344.

64. Iwamoto, T.; Watanabe, Y.; Takaya, H.; Haino, T.; Yasuda, N.; Yamago, S., Size- and Orientation-Selective Encapsulation of C70 by Cycloparaphenylenes. *Chem. Eur. J.* **2013,** *19* (42), 14061–14068.

65. Iwamoto, T.; Slanina, Z.; Mizorogi, N.; Guo, J.; Akasaka, T.; Nagase, S.; Takaya, H.; Yasuda, N.; Kato, T.; Yamago, S., Partial Charge Transfer in the Shortest Possible Metallofullerene Peapod, La@C82 ⊂ [11]Cycloparaphenylene. *Chem. Eur. J.* **2014,** *20* (44), 14403-14409.

66. Nakanishi, Y.; Omachi, H.; Matsuura, S.; Miyata, Y.; Kitaura, R.; Segawa, Y.; Itami, K.; Shinohara, H., Size-Selective Complexation and Extraction of Endohedral Metallofullerenes with Cycloparaphenylene. *Angew. Chem. Int. Ed.* **2014,** *53* (12), 3102-3106.

67. Ueno, H.; Nishihara, T.; Segawa, Y.; Itami, K., Cycloparaphenylene-Based Ionic Donor‐Acceptor Supramolecule: Isolation and Characterization of Li+@C60⊂[10]CPP. *Angew. Chem. Int. Ed.* **2015,** *54* (12), 3707-3711.

68. Hashimoto, S.; Iwamoto, T.; Kurachi, D.; Kayahara, E.; Yamago, S., Shortest Double-Walled Carbon Nanotubes Composed of Cycloparaphenylenes. *ChemPlusChem* **2017,** *82* (7), 1015-1020.

69. Jérémy, R.; Sebastian, B.; Georgios, R.; Sebastian, A.; Denis, J.; Nikos, T.; Chris, E.; A., W. H., Electronic Communication between two [10]cycloparaphenylenes and Bis(azafullerene) (C59N)2 Induced by Cooperative Complexation. *Angew. Chem. Int. Ed.* **2018,** *57* (23), 6930-6934.

70. Xu, Y.; Kaur, R.; Wang, B.; Minameyer, M. B.; Gsänger, S.; Meyer, B.; Drewello, T.; Guldi, D. M.; von Delius, M., Concave–Convex π–π Template Approach Enables the Synthesis of [10]Cycloparaphenylene–Fullerene [2]Rotaxanes. *J. Am. Chem. Soc.* **2018,** *140* (41), 13413-13420.

71. Xu, Y.; Wang, B.; Kaur, R.; Minameyer, M. B.; Bothe, M.; Drewello, T.; Guldi, D. M.; von Delius, M., A Supramolecular [10]CPP Junction Enables Efficient Electron Transfer in Modular Porphyrin‐[10]CPP⊃Fullerene Complexes. *Angew. Chem. Int. Ed.* **2018,** *57* (36), 11549-11553.

72. Ball, M.; Zhong, Y.; Fowler, B.; Zhang, B.; Li, P.; Etkin, G.; Paley, D. W.; Decatur, J.; Dalsania, A. K.; Li, H.; Xiao, S.; Ng, F.; Steigerwald, M. L.; Nuckolls, C., Macrocyclization in the Design of Organic n-Type Electronic Materials. *J. Am. Chem. Soc.* **2016,** *138* (39), 12861-12867.

73. Liu, Y.-Y.; Lin, J.-Y.; Bo, Y.-F.; Xie, L.-H.; Yi, M.-D.; Zhang, X.-W.; Zhang, H.-M.; Loh, T.-P.; Huang, W., Synthesis and Crystal Structure of Highly Strained [4]Cyclofluorene: Green-Emitting Fluorophore. *Org. Lett.* **2016,** *18* (2), 172-175.

74. Fujitsuka, M.; Lu, C.; Zhuang, B.; Kayahara, E.; Yamago, S.; Majima, T., Size-Dependent Relaxation Processes of Photoexcited [n]Cycloparaphenylenes (n = 5–12): Significant Contribution of Internal Conversion in Smaller Rings. *J. Phys. Chem. A* **2019,** *123* (22), 4737-4742.

75. Yamago, S.; Kayahara, E.; Iwamoto, T., Organoplatinum-Mediated Synthesis of Cyclic π-Conjugated Molecules: Towards a NewOrga of Three-Dimensional Aromatic Compounds. *Chem. Rec.* **2014,** *14* (1), 84-100.

76. Lin, N.; Liu, X. Y.; Diao, Y. Y.; Xu, H.; Chen, C.; Ouyang, X.; Yang, H.; Ji, W., Switching on Fluorescent Emission by Molecular Recognition and Aggregation Dissociation. *Adv. Funct. Mater.* **2012,** *22* (2), 361-368.

77. Hill, G. S.; Irwin, M. J.; Levy, C. J.; Rendina, L. M.; Puddephatt, R. J.; Andersen, R. A.; McLean, L., Platinum(II) Complexes of Dimethyl Sulfide. *Inorg. Synth.* **2007,** *32*, 149-153.