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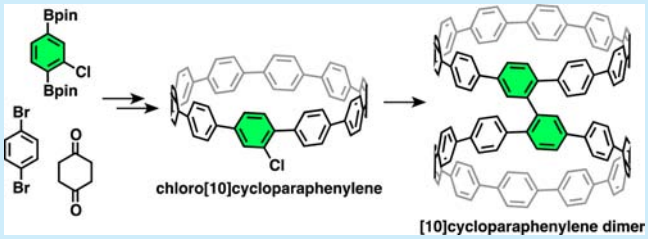
Synthesis and Dimerization of Chloro[10]cycloparaphenylene: A Directly Connected Cycloparaphenylene Dimer

Yuuki Ishii,[†] Sanae Matsuura,[†] Yasutomo Segawa,[†,‡] and Kenichiro Itami*[,†,‡,§]

[†]Graduate School of Science, [‡]JST ERATO, Itami Molecular Nanocarbon Project, and [§]Institute of Transformative Bio-Molecules (WPI-ITbM)Nagoya University, Chikusa, Nagoya 464-8602, Japan

Supporting Information

ABSTRACT: The first synthesis and dimerization of monochlorinated [10]cycloparaphenylene (chloro[10]CPP) are described. By assembling a chlorinated 1,4-diborylbenzene unit with brominated and borylated *cis*-1,4-diphenylcyclohexane units by Suzuki–Miyaura coupling, a triangle-shaped chloro-containing macrocycle was synthesized. The acid-mediated "cyclohexane-to-benzene" aromatization afforded chloro[10]CPP without losing the chloro group. By the action of Ni(0) complex, chloro[10]CPP was converted to a directly connected [10]CPP dimer, which would be an ideal precursor for the "carbon nanobelt".



Bottom-up synthesis of structurally uniform carbon nanotube (CNT) structures is one of the grand challenges in both nanocarbon science and synthetic organic chemistry. Although there have been a number of attempts for the synthesis of ring- and belt-shaped π-conjugated hydrocarbons related to CNT structures,[1] only very short structures have been synthesized. Cycloparaphenylene (CPP),[2] a molecule consisting solely of benzene rings with *para* linkages to each other, represents the shortest segment of armchair CNT (Figure 1). Thus, scientists targeted CPP and considered it an

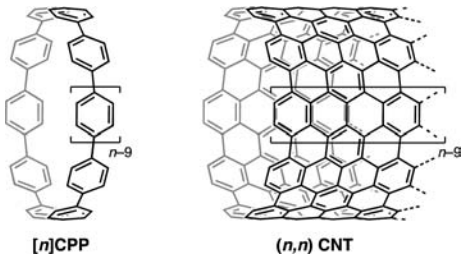


Figure 1. Structures of [*n*]CPP and (*n*,*n*) armchair CNT.

ideal building block of CNT structures. Since 2008, Bertozzi and Jasti,[3] Itami,[4] Jasti,[5] and Yamago[6] have successfully synthesized [*n*]CPPs (*n* = 5–16, 18), where *n* is the number of benzene rings. Structural analysis,[7] photophysical properties,[8] and guest-incorporation abilities[9] of [*n*]CPPs have been investigated. Very recently, our group has achieved a diameter-controlled CNT synthesis using CPPs as templates.[10]

Despite this recent progress in CPP chemistry, however, functionalization of CPPs and synthesis of functionalized CPPs are still limited. Only arylated CPPs, polyaryl[*n*]CPPs,[11] and 1,4-phenylene- or 1,5-naphthylene-bridged [8]CPP dimers[12] have been reported. Introduction of a "foothold" group to CPPs enables us to synthesize various CPP-based structures, thereby bestowing diverse properties and functions. We herein report the synthesis of monochloro[10]CPP and its dimerization reaction to furnish a directly connected [10]CPP dimer for the first time. Because functionalization reactions from C–Cl to C–C or other bonds are already known,[13] chloroCPP can be a suitable platform for a variety of functional CPPs.

Since 2009, our group has accomplished the size-selective synthesis of [7]–[16]CPP by utilizing sequential coupling reactions of L-shaped units (*cis*-1,4-diarylcyclohexane) and linear units (1,4-diborylbenzene or 4,4′-diborylbipheyl) as shown in Figure 2(a). The C–H bonds of CPP are all equal so that selective functionalization of CPP is very difficult. It can be easily predicted that halogenation of CPP furnishes the mixture of haloCPPs, and moreover, isolation of each haloCPP is almost impossible. To avoid this problem, we decided to synthesize chloroCPP from L-shaped units and a chloro-containing linear unit (1,4-diboryl-2-chlorobenzene) (Figure 2b).

The established synthetic route of chloro[10]CPP is shown in Scheme 1. As we already reported,[4e] C-shaped compound **3** can be prepared from two L-shaped units **1** and **2** via a Suzuki–Miyaura cross-coupling reaction. The [9 + 1]-type cyclization, which we used for the selective synthesis of [10]CPP,[4e] was applied to form the cyclic precursor for chloro[10]CPP (**6**). The chloro-containing linear unit (**5**) was synthesized by palladium-catalyzed borylation of bromoarene[14] from 1,4-dibromo-2-chlorobenzene (**4**). Original conditions for our [9 + 1]-type cyclization ($Pd(OAc)_2$, 2-Cy_2P-2′,4′,6′-$^i Pr_3$biphenyl, NaOH, 1,4-dioxane/water, 80 °C) were too reactive so that the chloro group in **4** was also reacted during the cross-coupling.

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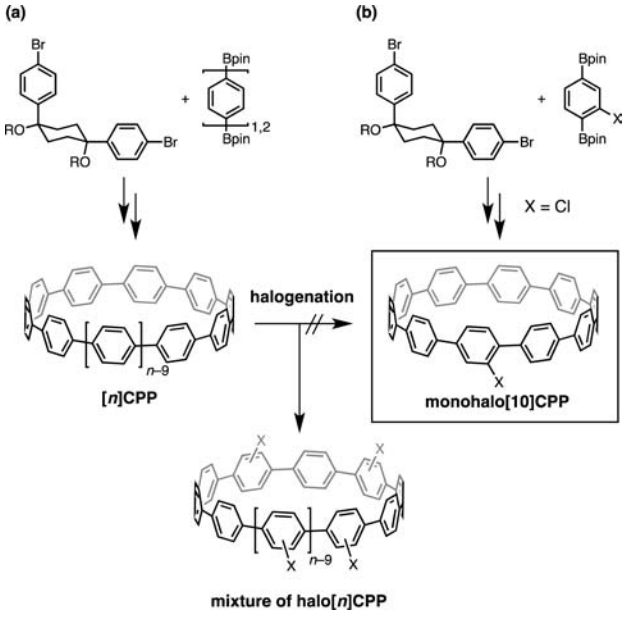
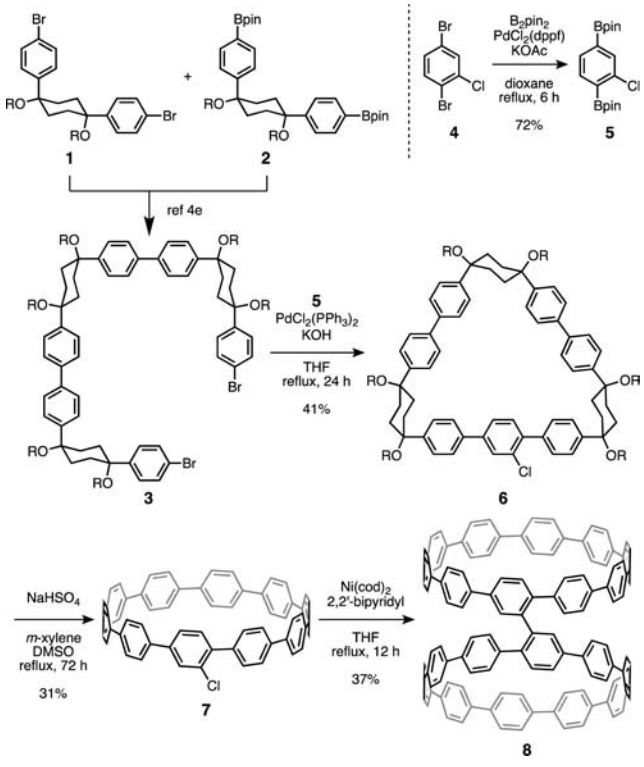


Figure 2. Possible synthetic routes toward halogenated CPPs.

Scheme 1. Synthesis of Chloro[10]CPP (7) and [10]CPP Dimer 8[a]



[a]R = CH_2OMe, Bpin = 4,4,5,5-Me_4-1,3,2-dioxaborolanyl, dppf = 1,1′-$(Ph_2P)_2$ferrocene, cod = 1,5-cyclooctadiene.

We found mild conditions ($PdCl_2(PPh_3)_2$, KOH, THF, reflux, 24 h) retained the chloro group during the cyclization. Under these conditions, triangle-shaped chloro-containing macrocycle **6** was obtained in 41% yield. The macrocycle **6** was then subjected to the acid-mediated aromatization reaction to afford chloro[10]CPP (**7**) without dechlorination. Compound **7** was identified by ^{1}H and ^{13}C NMR spectroscopies and HRMS. Three characteristic ^{1}H NMR signals [δ = 6.98 (d, $^3J_{HH}$ = 8 Hz), 7.10 (dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.78 (d, $^4J_{HH}$ = 2 Hz)] are assigned to three hydrogen atoms of the 2-chloro-1,4-phenylene moiety. To demonstrate further functionalization starting from chloro[10]CPP (**7**), we selected the dimerization reaction. The Yamamoto-type nickel(0)-mediated homocoupling reaction of **7** took place smoothly to afford [10]CPP dimer (**8**) in 37% yield. The NMR spectra and HRMS of **8** fully supported the formation of [10]CPP dimer. This is the first report on the synthesis of directly connected CPP dimer.[15]

Structural analysis of **8** was performed by DFT calculations. The B3LYP method with 6-31G(d) basis set was used for all calculations. The several thus found local minima structures of **8** can be categorized into two types: *close* and *open* as shown in Figure 3.[16] The most stable conformation of **8** belongs to the

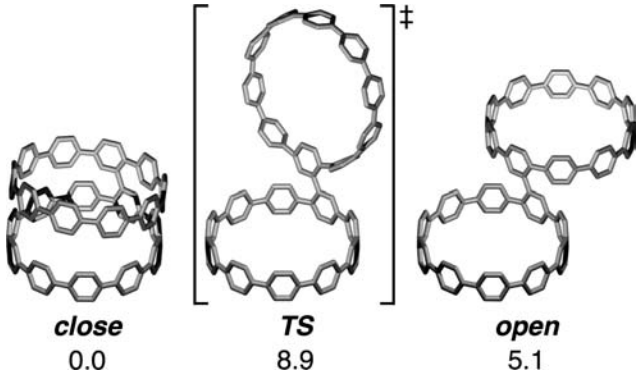


Figure 3. Conformations of **8** and relative Gibbs free energies (kcal·mol^{-1}).

close type, whereas all *open* conformations have 5.1 kcal·mol^{-1} or higher Gibbs free energies (ΔG). Compound **8** can switch between the *close* and *open* conformations through a transition state (TS) where one of the [10]CPP rings revolves around the connecting benzene rings. The lowest TS has 8.9 kcal·mol^{-1} higher energy compared to the lowest *close* conformation. This computational study indicates that **8** forms *close* conformation mainly with rapid isomerization between *close* and *open* conformations.

Absorption and fluorescence spectra of **7** and **8** are shown in Figure 4. Compared to those of [10]CPP, no significant difference was found in both spectra while small red-shift and

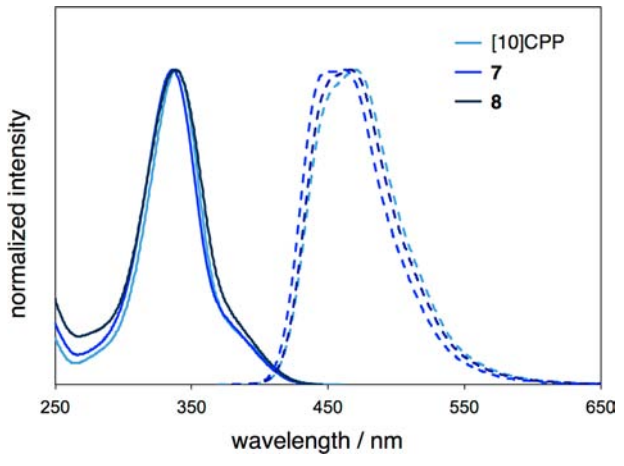


Figure 4. Absorption (solid curves) and fluorescence (broken curves) spectra of [10]CPP, **7**, and **8**.

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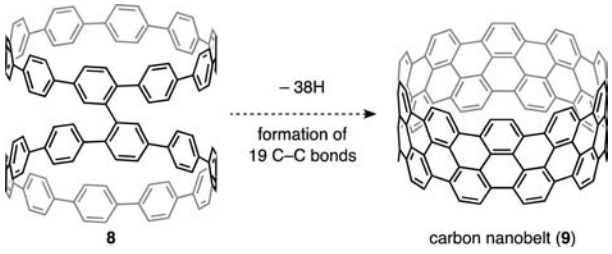
small blue-shift can be seen in the absorption of **8** and fluorescence of **7**, respectively. The fluorescence color of [10]CPP, pale blue, is also the same as those of **7** and **8**. The result indicates that chloro group and dimerization have little influence on the frontier orbitals of [10]CPP.

In summary, we have achieved the selective synthesis of chloro[10]CPP (**7**) in six steps from commercially available materials. This is the first example of halogenated CPP. Conditions of the Suzuki−Miyaura cross-coupling reaction were modified to retain the chloro group during the macrocyclization. Nickel-mediated C−Cl/C−Cl homocoupling of **7** took place to obtain the [10]CPP dimer (**8**) as the first example of the directly connected CPP dimer. Furthermore, **8** would be one of the most promising precursors for carbon nanotube structure. Given that 19 C−C bonds between two [10]CPPs of **8** are all connected (Scheme 2), a very short carbon nanotube structures (**9**), which we name "carbon nanobelt", can be obtained. Conversion of **8** to **9** is ongoing in our group.

Scheme 2. Toward Carbon Nanobelt 9 via [10]CPP Dimer (8)



■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data for all new compounds, and details of computational study. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: itami@chem.nagoya-u.ac.jp.

Notes

The authors declare no competing financial interest.

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(15) The structure of a directly connected [8]CPP dimer was optimized by DFT calculations. See ref 12.

(16) The three structures shown in Figure 3 are modified from optimized structures for clarity. See the Supporting Information for the original optimized structures.