

Synthesis and Characterization of [5]Cycloparaphenylene

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S Supporting Information

ABSTRACT: The synthesis of highly strained [5]-cycloparaphenylene ([5]CPP), a structural unit of the periphery of C₆₀ and the shortest possible structural constituent of the sidewall of a (5,5) carbon nanotube, was achieved in nine steps in 17% overall yield. The synthesis relied on metal-mediated ring closure of a triethylsilyl (TES)-protected masked precursor **1c** followed by removal of the TES groups and subsequent reductive aromatization. UV-vis and electrochemical studies revealed that the HOMO-LUMO gap of [5]CPP is narrow and is comparable to that of C₆₀, as predicted by theoretical calculations. The results suggest that [5]CPP should be an excellent lead compound for molecular electronics.

Considerable interest has recently been focused on hoop-shaped π -conjugated molecules because of their great potential in molecular electronics.^{1–8} In particular, cycloparaphenylenes (CPPs) (Figure 1a) which consist of phenylene

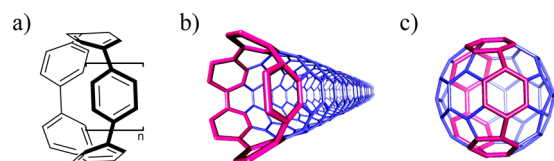


Figure 1. Structures of (a) cycloparaphenylenes ($n = 1$ for [5]CPP), (b) a (5,5) armchair CNT, and (c) C₆₀. The [5]CPP units in the CNT and C₆₀ are highlighted in red.

units that are para-linked in a cyclic manner, have attracted increasing attention in this area^{9–14} for not only their aesthetic structure having radially extended unique π orbitals originating from the curvature but also their applications in electronic and optoelectronic materials, as CPPs are the smallest structural units of the sidewalls of armchair carbon nanotubes (CNTs) (Figure 1b) and structural constituents of fullerenes (Figure 1c).^{15–23} Their use as seeds for the synthesis of structurally uniform CNTs has also been suggested.^{5,24} In addition, the concave cavities of CPPs can act as hosts for π -conjugated molecules with convex surfaces, such as fullerenes,^{25,26} and such host-guest chemistry is useful for studying concave-convex π - π interactions and fabricating hierarchically ordered π materials.

Despite their simple structure, however, the synthesis of CPPs has been a significant challenge because of the difficulty in constructing the highly strained cyclic structure. After desperate endeavors over more than a half century, the synthesis of CPPs

was achieved recently by three groups including our own. Jasti, Bertozzi, and co-workers reported the synthesis of [9]-, [12]-, and [18]CPP featuring the use of a *cis*-1,4-dimethoxycyclohexa-2,5-diene moiety as a masked paraphenylene unit.²⁷ Jasti and co-workers extended this synthetic strategy to realize the selective synthesis of [n]CPP ($n = 6–12$).^{28–31} Particularly noteworthy was the synthesis of [6]CPP by coupling of doubly masked pentaparaphenylene unit **1a** with 1,4-bis(pinacolyboryl)benzene followed by reductive aromatization (Figure 2a).³¹ While the overall yield was low (0.2%), [6]CPP is the smallest CPP synthesized to date. Itami and co-workers subsequently reported the selective synthesis of [12]CPP utilizing a *cis*-cyclohexan-2,5-diol unit as a masked paraphenylene.³² Extension

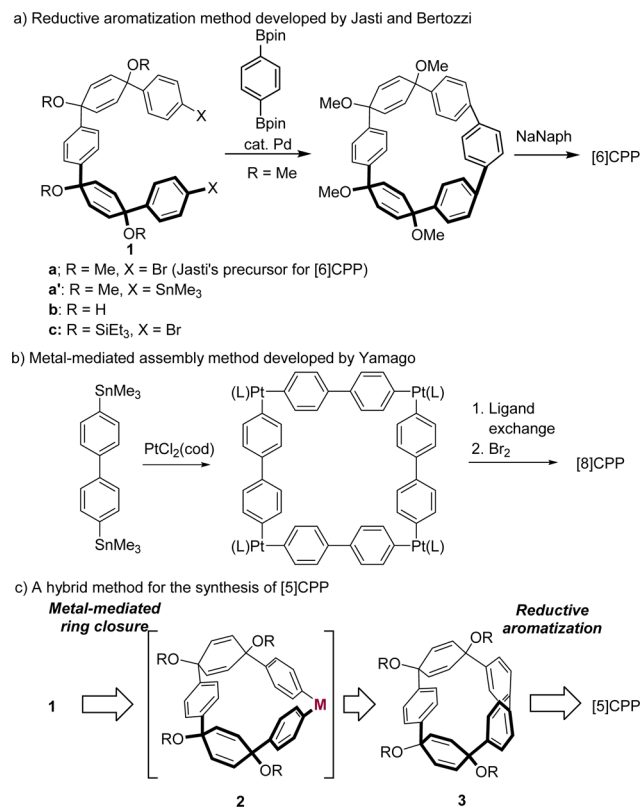


Figure 2. Synthetic routes to (a) [6]CPP by Jasti and (b) [8]CPP by Yamago and (c) a new synthetic route to [5]CPP.

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of this method led them to synthesize $[n]$ CPP ($n = 7-16$) in a size-selective manner.³³⁻³⁷

We reported a synthesis of [8]CPP based on platinum-mediated assembly of 4,4'-biphenyl units to form a square-shaped cyclic platinum complex followed by reductive elimination of the platinum (Figure 2b).³⁸ [8]CPP was the smallest CPP reported at the time (2010). In sharp contrast to the methods developed by Bertozzi, Jasti, and Itami, our method relied on the cis-coordinated bis(aryl)platinum species to serve as the precursor for the cyclic structure. The method was extended to the synthesis of [12]CPP and the random synthesis of $[n]$ CPP ($n = 8-13$).³⁹ An extension of this method led to the selective synthesis of [6]-, [8]-, and [10]CPP.^{40,41} As [6]CPP was obtained in reasonable overall yield (10%), this method would be suitable for the synthesis of highly strained CPPs.

Theoretical studies by our group suggested that in sharp contrast to linear oligoparaphenylenes, for CPPs the HOMO-LUMO energy gap (HOMO and LUMO refer to highest occupied and lowest unoccupied molecular orbitals, respectively) becomes narrower as the number of phenylene rings decreases because of the increase and decrease of the HOMO and LUMO energies, respectively.³⁹ Therefore, CPPs of small ring size should display a range of intriguing electronic properties compared with larger CPPs. In particular, the calculated HOMO-LUMO energy gap of [5]CPP, which is a constituent of the equatorial belt of C_{60} (Figure 1c), is 2.71 eV, which is almost identical to that of C_{60} (2.88 eV), suggesting that [5]CPP would be an excellent lead compound for molecular electronics. However, the synthesis of [5]CPP has not been reported to date.

Obviously, the challenge of synthesizing smaller CPPs arises from the strain energy, which increases exponentially with decreasing ring size. For example, the strain energy of [6]CPP was computed to be 407 kJ mol⁻¹, but that of [5]CPP jumped up to 491 kJ mol⁻¹.³⁹ Furthermore, by analogy to the reactivity of C_{60} , [5]CPP would be highly reactive toward various reagents and be unstable under certain conditions. Therefore, it was unclear whether [5]CPP would be stable under the reaction conditions used for the synthesis.

Considering these factors in mind, we accepted the challenge of synthesizing [5]CPP by taking advantage of our own and Jasti's synthetic routes (Figure 2c). We envisioned that **1** would directly cyclize to **3** via organometallic intermediate **2** if, for example, a platinum complex ($M = Pt$) were employed. Upon formation of **3**, reductive aromatization of the masked paraphenylene unit should give [5]CPP. We report here the first synthesis of [5]CPP via this route. The cyclization of **1a** to **3a** proceeded in high yield. However, the reductive aromatization of **3a** did not give [5]CPP under various conditions. Therefore, we developed a new precursor **1c** having triethylsilyl (TES) protecting groups. After the cyclization, removal of the TES groups followed by reductive aromatization of the resulting free-hydroxyl precursor afforded [5]CPP for the first time in nine steps in 17% overall yield.

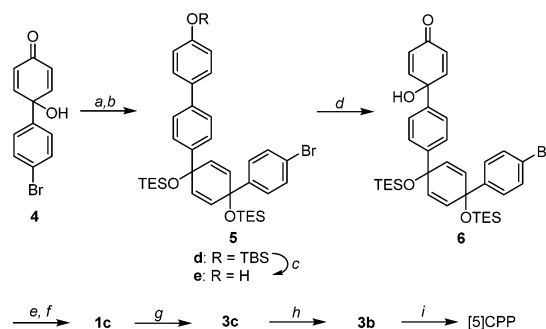
At first, Jasti's compound **1a** ($R = Me$, $X = Br$) was used as the starting material.³¹ **1a** was transformed to the corresponding stannane **1a'** ($R = Me$, $X = SnMe_3$) in 93% yield by treatment with BuLi (2.2 equiv) in THF at $-78^\circ C$ followed by addition of Me_3SnCl (2.5 equiv). Next, **1a'** was treated with $PtCl_2(cod)$ (0.50 equiv; $cod = 1,5$ -cyclohexadiene) at $60^\circ C$ for 20 h and PPh_3 (2.2 equiv) at $95^\circ C$ for 18 h. The desired product **3a** ($R = Me$) was obtained in 52% yield after purification by silica gel chromatography and preparative gel-permeation chromatography. **3a** was also synthesized in one step from **1a** in 63% yield

under Ni(0)-mediated Yamamoto coupling conditions^{42,43} by employing $Ni(cod)_2$ (2.0 equiv) and 2,2'-bipyridine (bpy) (2.0 equiv) in refluxing THF for 15 h. Despite the high efficiency of the cyclization reaction, however, attempts at reductive aromatization of **3a** to [5]CPP using various reducing agents were unsuccessful.

This result was probably due to the low reactivity of methoxy group in **3a**, and we expected that **3b** having free hydroxyl groups ($R = H$) would be sufficiently reactive and become a suitable precursor for [5]CPP. As several attempts to deprotect **1a** to give **1b** or **3a** to give **3b** under standard conditions were unsuccessful because of the extremely acid-sensitive character of **1a** and **3a**, we synthesized TES-protected **1c** as a precursor of **3b** by following the synthesis of **1a** as reported by Jasti.³¹

4-Bromophenyl-4-hydroxycyclohexadienone (**4**) was treated with sodium hydride (1.3 equiv) and then with in situ-prepared 4-lithio-4'-(*tert*-butyldimethylsilyloxy)biphenyl (2.1 equiv), and the resulting product was treated with TESCl (3.0 equiv) to afford **5d** (Scheme 1). The *tert*-butyldimethylsilyl (TBS)

Scheme 1. Synthesis of [5]CPP^a



^aReagents and conditions: (a) (1) NaH (1.3 equiv), THF, $-78^\circ C$, 0.5 h; (2) $LiC_{12}H_8OTBS$ (2.1 equiv), THF, $-78^\circ C$, 2 h. (b) TESCl (3.0 equiv), imidazole (4.0 equiv), DMF, room temperature (rt) to $40^\circ C$, 9 h. (c) $LiOH \cdot H_2O$ (2.5 equiv), DMF, rt, 11 h, 92% (three steps). (d) $PhI(OAc)_2$ (1.5 equiv), THF/ CH_3CN/H_2O , rt, 2.5 h. (e) (1) NaH (1.3 equiv), THF, $-78^\circ C$, 0.5 h; (2) LiC_6H_4Br (2.1 equiv), THF, $-78^\circ C$, 2.5 h. (f) TESCl (3.0 equiv), imidazole (4.0 equiv), DMF, rt to $40^\circ C$, 10 h, 53% (three steps). (g) $Ni(cod)_2$ (2.0 equiv), bpy (2.0 equiv), THF, reflux, 15 h, 63%. (h) TBAF (4.2 equiv), THF, rt, 2 h, 94%. (i) $SnCl_2 \cdot H_2O$ (10 equiv), THF, $60^\circ C$, 6 h, 58%.

protecting group in **5d** was selectively removed by employing $LiOH \cdot H_2O$ (2.5 equiv), providing phenol **5e**. It is worth noting that the preparation of **5e** from **4** was conducted in excellent overall yield (92%) on a large scale (>20 g). Treatment of **5e** with $PhI(OAc)_2$ (1.5 equiv) afforded hydroxy ketone **6**, which was successively treated with sodium hydride (1.3 equiv), 4-bromophenyllithium (2.1 equiv), and TESCl (3.0 equiv) to afford **1c** in 53% yield over the three steps. Treatment of **1c** with $Ni(cod)_2$ (2.0 equiv) and bpy (2.0 equiv) in refluxing THF for 15 h afforded the cyclized product **3c** in 63% isolated yield. Removal of the TES groups was successfully carried out by treatment with tetrabutylammonium fluoride to afford tetraol **3b** quantitatively.

Reductive aromatization of **3b** was successfully carried out by employing $SnCl_2 \cdot H_2O$ (10 equiv) in THF at $60^\circ C$ for 6 h, and [5]CPP was formed and isolated in 58% yield as a dark-purple solid. [5]CPP was found to be stable under air and soluble in many common solvents, including toluene, THF, $CHCl_3$, CH_2Cl_2 , and acetone. $SnCl_2$ reduction is usually carried out in acidic media, but the same reaction under acidic conditions did

not give [5]CPP at all. Therefore, the neutral conditions were essential to obtain [5]CPP.

The product was fully characterized by NMR spectroscopy and mass spectrometry. In the ^1H NMR spectrum in CDCl_3 at 25°C , [5]CPP showed one singlet at 7.85 ppm, which is consistent with the highly symmetrical structure of [5]CPP. The result also suggests that the paraphenylene units rotate freely at room temperature on the time scale of the NMR measurement. The singlet signal was shifted upfield by 0.22 and 0.37 ppm compared with the corresponding protons of [6]- and [7]CPP (7.63 and 7.48 ppm, respectively). The observed shift is probably derived from ring strain, as observed in the size dependence of the chemical shift in cyclophanes.^{14,44–47} The ^{13}C NMR spectrum showed two signals at 126.61 and 131.97 ppm. In the MALDI-TOF mass spectrum, a molecular ion peak was observed at m/z 380.1136 with an isotopic distribution pattern identical to the calculated value based on the natural-abundance isotopic ratio.

The solution of [5]CPP in CHCl_3 exhibited a dark-purple color and had the strongest maximum absorption at $\lambda_{\text{max}} = 335$ nm with absorption coefficient $\epsilon = 6.82 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ (Figure 3). A weak absorption having $\lambda_{\text{max}} = 502$ nm with $\epsilon = 652 \text{ M}^{-1}$

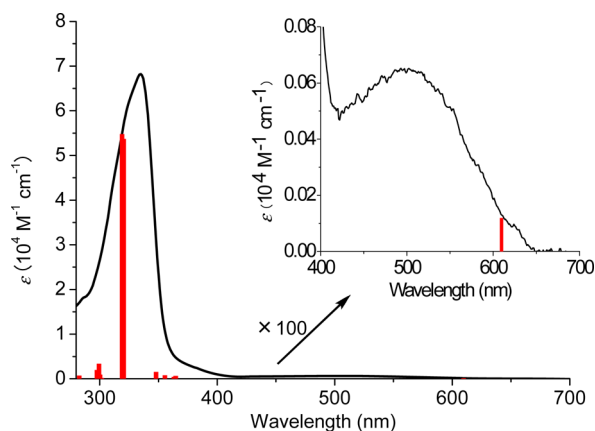


Figure 3. UV-vis spectrum of [5]CPP in CHCl_3 along with the oscillator strengths (red bars) obtained by TD-DFT calculations.

cm^{-1} was also observed. The λ_{max} value of the strongest absorption was almost same as those observed for other CPPs.^{17,5–11} No fluorescence was observed when [5]CPP was excited at <400 nm, and this result is also consistent with the observed behavior of [7]- and [6]CPP, which exhibit negligible or no fluorescence.^{28,31,41}

Time-dependent density functional theory (TD-DFT) calculations at the B3LYP/6-31G* level indicated that the strongest absorption at $\lambda_{\text{max}} = 335$ nm can be assigned as the transitions from the nearly degenerate HOMO–1 or HOMO–2 to the LUMO and from the HOMO to the nearly degenerate LUMO+1 or LUMO+2 at 319 and 320 nm with oscillator strengths (f) of 0.6319 and 0.6446, respectively. The results are consistent with the assignments for other CPPs.^{17,5–11} The weak absorption at $\lambda_{\text{max}} = 502$ nm was assigned as the almost-forbidden HOMO–LUMO transition at 610 nm with $f = 0.0014$.^{17,5–11} The HOMO–LUMO gap of [5]CPP was calculated to be 2.47 or 1.91 eV (238 or 184 kJ mol^{-1}) by taking the observed peak ($\lambda = 502$ nm) or the absorption onset ($\lambda = 649$ nm), respectively. It is worth noting that these values are smaller than that for C_{60} .

Electrochemical analysis of [5]CPP was performed in 0.1 mol L^{-1} Bu_4NPF_6 solutions in 1,1,2,2-tetrachloroethane (TCE) or THF (Figure 4). Cyclic voltammetry (CV) by scanning in the

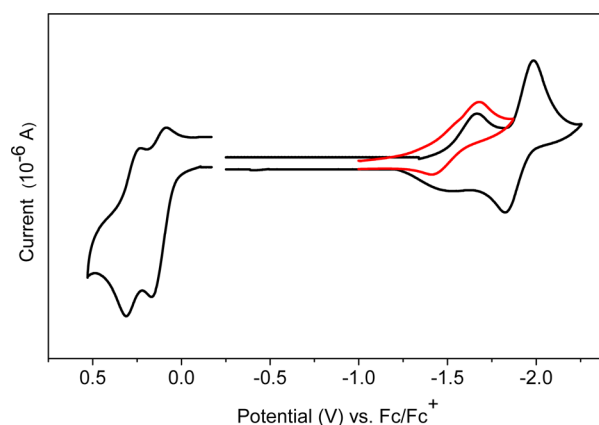


Figure 4. Cyclic voltammograms of [5]CPP in $\text{C}_2\text{H}_2\text{Cl}_4$ (for oxidation) or THF (for reduction) containing 0.1 mol L^{-1} Bu_4NPF_6 at room temperature at a scan rate of 0.1 V/s (for oxidation) or 0.05 V/s (for reduction). The red curve represents the voltammogram obtained upon scanning potential between -1.0 and -1.87 V .

positive direction in TCE exhibited two chemically reversible oxidation processes with half-wave potentials ($E_{1/2}$) of 0.13 and 0.27 V vs ferrocene/ferrocenium (Fc/Fc^+). The same measurement in THF also gave two oxidation waves with $E_{1/2} = 0.10$ and 0.30 V vs Fc/Fc^+ , but the reversibility was considerably decreased (Figure S1 in the Supporting Information). The observation of two oxidation waves is consistent with the formation of the radical cation and dication of the CPP.²²

Scanning in the negative direction in THF to -1.87 V vs Fc/Fc^+ gave a pseudoreversible reduction wave at $E_{1/2} = -1.59 \text{ V}$ vs Fc/Fc^+ (Figure 4, red curve). Further scanning gave a second pseudoreversible reduction at $E_{1/2} = -1.91 \text{ V}$ vs Fc/Fc^+ . The reversibility of the first wave significantly decreased under this condition, suggesting that the reduced compound is unstable. The HOMO–LUMO energy gap was estimated to be 1.69 eV from the first oxidation and reduction potentials measured in THF. This value is in good agreement with that obtained from the absorption onset of the UV-vis spectrum, but it is much smaller than that obtained from the theoretical calculation and also that of C_{60} obtained electrochemically (2.34 eV).⁴⁸ This difference is most likely derived from inaccuracy of the oxidation potential measured in THF. While further studies are needed to obtain an accurate value of the energy gap, all of the data are consistent with a low HOMO–LUMO gap in [5]CPP.

In summary, [5]CPP was synthesized for the first time by metal-mediated ring closure of TES-protected masked precursor **1c** followed by removal of the TES groups and subsequent reductive aromatization. The use of hydroxyl groups instead of methoxy groups considerably increased the efficiency of the reductive aromatization, which enabled the use of a weak reducing agent (SnCl_2) at ambient temperature. The conditions are in sharp contrast to the previous synthesis of larger CPPs by Bertozzi and Jasti using a methoxy-protected precursor, which required a strong reducing agent such as sodium naphthalenide at low temperature. The TES protection method would be applicable to the synthesis of larger CPPs under mild conditions, and such a synthetic route should be suitable for large-scale preparation. UV-vis and electrochemical studies revealed that the narrow HOMO–LUMO gap of [5]CPP is comparable to that of C_{60} , as predicted by theoretical calculations. The results suggest that [5]CPP should be an excellent lead compound for molecular electronics. Furthermore, since [5]CPP is expected to

have high chemical reactivity, chemical modification of [5]CPP for the synthesis of functionalized CPPs would be of great interest.

■ ASSOCIATED CONTENT

● Supporting Information

Synthesis and characterization of all new compounds, electrochemical analysis, and results of the TD-DFT calculations on [5]CPP. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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