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Palladium-free Synthesis of [10]Cycloparaphenylene

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ABSTRACT

A palladium-free, short-step synthesis of [10]cycloparaphenylene ([10]CPP) has been developed. The key macrocyclization step was performed by a nickel-mediated homocoupling of a newly designed U-shaped unit **2**. Surprisingly, the rectangular macrocycle **3** was obtained in high yield compared with previous macrocyclization reactions in CPP syntheses. X-ray crystallography as well as DFT calculation revealed unstrained structure of the macrocycle **3**.

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1. Introduction

Fully π -conjugated macrocyclic molecules are of great interest because of their unique optical and electronic properties.¹ In recent years, much attention has been paid to cycloparaphenylenes (CPPs), which consist of solely benzene rings connected at *para* positions, due to their structural appearance and radial π -conjugation systems.² Since the first synthesis of CPPs in 2008, the groups of Bertozzi/Jasti, Itami, and Yamago reported the synthesis of various sizes of CPPs.^{3–5}

Because the structure of [n]CPP, where *n* is the number of benzene rings, represents the shortest sidewall segment of (*n,n*) armchair carbon nanotubes, CPPs are considered as ideal templates for the growth of carbon nanotubes. Recently we have reported the synthesis of carbon nanotubes by using CPPs as templates, where the diameter of resulting carbon nanotubes correspond to that of CPP.⁶ Adding to the structural feature of CPPs, characteristic size-dependent optical and electronic properties of CPPs owing to their radial π -conjugation have been uncovered.⁷ It was also reported that [10]- and [11]CPP are useful host molecules for sphere-shaped guest molecules such as fullerenes and metallofullerenes. Yamago, Jasti, and Itami reported the formation of C₆₀@[10]CPP, Li⁺@C₆₀@[10]CPP, C₇₀@[10]CPP, C₇₀@[11]CPP, and Ln@C₈₂@[11]CPP with high binding constants (Figure 1).^{4f,8}

Figure 1. Structures of [n]CPP (left) and Li⁺@C₆₀@[10]CPP (right).

In the synthesis of CPPs, high ring-strain of CPPs^{7a} needs to be released in the macrocyclization step. As shown in Figure 2, three groups utilized their strain-releasing strategies for the synthesis of CPPs. Bertozzi/Jasti used a cyclohexadiene unit as a benzene-convertible bent unit (Figure 2a). Itami used a cyclohexane unit, which can be converted into a benzene ring by acid-mediated aromatization reaction (Figure 2b). In Yamago's method, *cis*-platinum coordination was applied for construction of biphenyl units (Figure 2c). The first selective synthesis of CPP was reported by Itami in 2009, where the macrocyclic precursor for [12]CPP was synthesized by sequential palladium-catalyzed Suzuki–Miyaura cross-coupling.^{3a} To date, in almost all of the synthetic routes reported by Itami, Jasti, and Yamago groups, expensive transition metals such as palladium or platinum are needed in the synthesis. Since the first nickel-mediated synthesis of [9]- and [12]CPP by Itami,^{3c} there have been few examples which accomplished the synthesis of CPPs without palladium nor platinum, for example, [7]CPP by Itami^{3f} and [5]CPP by Yamago.^{4j} As for [10]CPP, Itami,^{3c} Jasti,^{4f,4g} and Yamago^{4h,4i} reported the selective synthesis, but in all cases palladium or platinum was used despite the usefulness of [10]CPP as a host molecule. Thus, the size-selective and economically sound

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synthesis of [10]CPP has become increasingly important in order to ensure its further application as materials.

2. Results and discussion

The established palladium-free synthesis of [10]CPP is shown in Scheme 2. The MOM-protected 4-(4-bromophenyl)-4-hydroxycyclohexanone (**1**)^{3f} (MOM = methoxymethyl) was used for the synthesis of U-shaped unit **2**. At first, two-fold halogen-lithium exchange reaction of 1,4-dibromobenzene with four equivalent of *tert*-butyllithium was performed and the thus-generated 1,4-dilithiobenzene was sequentially reacted with ketone **1**. Resulting reaction mixture was subjected to MOM protection reaction to afford the U-shaped unit **2** in 36% yield. Homocoupling reaction of **2** mediated by Ni(cod)₂/bpy (cod = 1,5-cyclooctadiene, bpy = 2,2'-bipyridyl) was attempted in diluted conditions (6 mM of **2** in THF). Surprisingly, macrocycle **3** was obtained in very high yield (81%) along with trace amount of cyclic trimer as judged by MALDI-TOF MS. Finally, the macrocycle **3** was converted into [10]CPP by acid-mediated aromatization reaction in 26% yield, which was comparable to previously reported yields of the aromatization steps. Considering that the ketone **1** was synthesized in 66% yield (two steps),^{3f} the total yield of [10]CPP from commercially available chemicals was 5%, which was higher than our previous method for [10]CPP (2%).^{3e}

Figure 2. Synthetic strategies of CPPs. (a) Bertozzi/Jasti's method. (b) Itami's method. (c) Yamago's method.

We herein report an alternative synthetic route to [10]CPP without using palladium. Scheme 1 shows our previous work on the synthesis of [10]CPP. The macrocycle **B**, which was the precursor for [10]CPP, was synthesized by sequential Suzuki–Miyaura cross-coupling reactions *via* a C-shaped intermediate **A**. We designed a new macrocyclic precursor **D**, which might be obtained by nickel-mediated homocoupling of a U-shaped unit **C**. The "U + U" homocoupling reaction was previously used for the synthesis of [14]CPP and [16]CPP.^{3e} The U-shaped unit **C** can be synthesized by lithiation and nucleophilic addition of bromoarenes.

Scheme 2. Palladium-free synthesis of [10]CPP.

To gain insight into the high-yielding macrocyclization process (**2**→**3**), structural investigation of the macrocycle **3** was performed. First, X-ray crystallography of a single crystal of **3** was attempted.⁹ Single crystal of **3** was obtained from 1,2-dichloroethane solution of **3** with vapor diffusion of pentane. The ORTEP drawing of **3** is shown in Figure 3. As clearly seen, **3** forms a rectangular structure. Four 1,2-dichloroethane molecules are incorporated into the cavity of **3**. The 4,4'-biphenylene moieties are located at the axial positions of four cyclohexane moieties whereas 1,4-phenylene moieties are at the equatorial positions.

Scheme 1. Synthetic routes to [10]CPP.

Figure 3. ORTEP drawing of $3 \cdot 4C_2H_4Cl_2$ with 50% probability. Half of the entire structure constitutes an asymmetric unit. All hydrogen atoms are omitted for clarity. Red: oxygen, green: chlorine.

In our previous report,^{3c} it was confirmed by using NMR study and DFT calculation that the cyclohexane moieties in the macrocyclic precursor of [12]CPP can be easily flipped in solution. To estimate the stable conformation of **3** in solution, theoretical calculation of the macrocyclic precursor **3** was studied by B3LYP/6-31G(d) level of theory. As shown in Scheme 3, the three conformational isomers **4a–c**, the simplified structure of **3**, were optimized. The structure **4a** represents the conformation of **3** observed by X-ray crystallography. The hypothetical homodesmotic reaction revealed that **4a** and **4b** are unstrained molecules and only **4c** has small strain energy ($2.9 \text{ kcal mol}^{-1}$), which implies that the compound **3** adopts conformation **4a** and **4b** in solution. Considering that the strain energy for previously reported [10]CPP precursor **B** is $5.9 \text{ kcal mol}^{-1}$, one possible reason why **3** can be obtained in high yield should be the low strain energy of **3**.

Scheme 3. Hypothetical homodesmotic reaction for estimating the strain energy (ΔH) of **4a–c**.

3. Conclusion

We have developed the first palladium/platinum-free synthesis of [10]CPP. The nickel-mediated macrocyclization reaction of the U-shaped unit **2** was unusually high yielding. X-ray crystallography as well as DFT calculation indicated that the macrocyclic precursor **3** is essentially strain-free, which should

be one of the reasons for the high yield observed in the nickel-mediated macrocyclization reaction.

4. Experimental section

General

Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF) and dichloromethane were purified by passing through a solvent purification system (Glass Contour). All reactions were performed using standard vacuum-line and Schlenk techniques. Work-up and purification procedures were carried out with reagent-grade solvents under air. Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm). Flash column chromatography was performed with E. Merck silica gel 60 (230–400 mesh). High-resolution mass spectra (HRMS) were obtained from a JEOL JMS-S3000 SpiralTOF (MALDI-TOF MS) with 9-nitroanthracene as matrix. Melting points were measured on a MPA100 Optimelt automated melting point system. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECA-600 (^1H 600 MHz, ^{13}C 150 MHz) spectrometer. Chemical shifts for ^1H NMR are expressed in parts per million (ppm) relative to CHCl_3 (δ 7.26 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to CDCl_3 (δ 77.0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, m = multiplet, br = broad signal), coupling constant (Hz), and integration.

Synthesis of 2

To a 500-mL three-necked flask equipped with dropping funnel were added 1,4-dibromobenzene (3.59 g, 15.2 mmol) and dry THF (80 mL). The solution was cooled to -78°C and *tert*-butyllithium (40 mL, 64 mmol) was then dropped into the solution. After the mixture was stirred for 1 h at -78°C , a THF (70 mL) solution of **1** (10.0 g, 32.0 mmol) was transferred to the mixture by cannula. The reaction mixture was allowed to warm up to room temperature and quenched by saturated NH_4Cl aqueous solution. The same reaction was carried out in another flask at the same time. Then these mixtures were combined and extracted by EtOAc. Combined organic phase was dried over Na_2SO_4 . After evaporation in vacuo, the resulting white solid was put into a 300-mL two-necked flask containing a magnetic stirring bar. Dry CH_2Cl_2 (130 mL) was added to the flask to dissolve the white solid. Diisopropylethylamine (21.0 mL, 122 mmol) and chloromethyl methyl ether (9.1 mL, 122 mmol) were added at 0°C . The mixture was allowed to warm up to room temperature and stirred for 18 h. After quenching with water, the reaction mixture was extracted by EtOAc. The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/EtOAc = 4:1 to 2:1) to afford **2** as a white solid (8.72 g, 36%). ^1H NMR (600 MHz, CDCl_3) δ 1.85–2.35 (br m, 16H), 3.38 (s, 12H), 4.38 (s, 4H), 4.40 (s, 4H), 7.31 (d, J = 8.2 Hz, 4H), 7.34 (s, 4H), 7.44 (d, J = 8.2 Hz, 4H); ^{13}C NMR (600 MHz, CDCl_3) δ 32.7 (CH_2), 32.9 (CH_2), 55.9 (CH_3), 56.0 (CH_3), 77.8 (4°), 92.1 (CH_2), 92.2 (CH_2), 121.7 (CH), 126.7 (CH), 128.7 (CH), 131.5 (4°), 141.6 (br, 4°); HRMS (MALDI) m/z calcd for $\text{C}_{38}\text{H}_{48}\text{NaBr}_2\text{O}_8$ [$\text{M}+\text{Na}$] $^+$: 815.1592, found 815.1557; mp: 170°C (decomp.)

Synthesis of 3

To a 100-mL round-bottom flask containing a magnetic stirring bar were added **2** (2.88 g, 3.78 mmol), 2,2'-bipyridyl (1.14 g, 7.27 mmol), and dry THF (640 mL) under argon atmosphere. After the mixture was stirred to be homogeneous solution, Ni(cod)₂ (2.00 g, 7.27 mmol) was added. The resultant mixture was stirred at reflux for 24 h. After the reaction mixture was cooled down to room temperature, the mixture was passed through a short pad of Celite[®], washed with EtOAc, and solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography (hexane/EtOAc = 1:1 to EtOAc) to afford **3** (1.93 g, 82%) as a white solid. ¹H NMR (600 MHz, CDCl₃, 50 °C) δ 2.04–2.20 (br m, 16H), 2.30–2.45 (br m, 16H), 3.35 (s, 12H), 3.39 (s, 12H), 4.38 (s, 8H), 4.42 (s, 8H), 7.40–7.50 (br m, 24H), ¹³C NMR (600 MHz, CDCl₃) δ 32.7 (CH₂), 33.0 (CH₂), 55.8 (CH₃), 56.0 (CH₃), 77.8 (4°), 77.9 (4°), 92.1 (CH₂), 92.2 (CH₂), 126.8 (CH₂), 127.0 (CH₂), 127.3 (CH₂), 139.7 (4°), 141.8 (br, 4°), HRMS (MALDI) *m/z* calcd for C₇₆H₉₆O₁₆Na⁺: 1287.6596, found 1287.6600; mp: 170–172 °C

X-ray Crystallography of **3**

Intensity data were collected at 103 K on a Rigaku Single Crystal CCD X-ray Diffractometer (PILATUS with MicroMax-007) with graphite-monochromated Mo-Kα radiation (λ = 0.71075 Å). Total 29198 reflections were corrected, of which 7354 were independent reflections (*R*_{int} = 0.0341). The structure was solved by direct methods (SIR-97¹⁰) and refined by the full-matrix least-squares techniques against *F*² (SHELXL-97¹¹). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: C₄₂H₅₆Cl₄O₈, *FW* = 830.67, crystal size 0.20 × 0.10 × 0.10 mm³, triclinic, space group *P*-1. *a* = 8.5951(19) Å, *b* = 14.595(3) Å, *c* = 17.589(4) Å, α = 105.495(4)°, β = 103.182(3)°, γ = 99.022(5)°, *V* = 2099.0(8) Å³, *Z* = 2, *D*_{calc} = 1.314 g/cm³. The refinement converged to *R*₁ = 0.0523, *wR*₂ = 0.1281 (*I* > 2σ(*I*)), *R*₁ = 0.0686, *wR*₂ = 0.1524 (for all data), *GOF* = 1.082.

Synthesis of [10]CPP

To each 20-mL test tube containing a magnetic stirring bar were added **3** (31.6 mg), NaHSO₄·H₂O (69.1 mg), *m*-xylene (5 mL) and dry DMSO (1.5 mL). Total of 16 test tubes were heated by aluminum blocks with stirring at 150 °C for 48 h under air. The 16 reaction mixtures were combined and cooled down to room temperature, the mixture was quenched with saturated NaHCO₃ aq. and passed through a short pad of Celite[®]. Then the mixture was extracted with EtOAc. The combined organic phase was dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/CHCl₃ = 2:1) to afford [10]CPP (81.0 mg, 26%) as a pale yellow solid. ¹H NMR (600 MHz, CDCl₃) δ 7.56 (s, 40H).

Computational study

The Gaussian 09 program¹² running on a SGI Altix4700 system was used for optimization (B3LYP/6-31G(d)).¹³

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