

Synthesis of Cycloparaphenylenes and Related Carbon Nanorings: A Step toward the Controlled Synthesis of Carbon Nanotubes

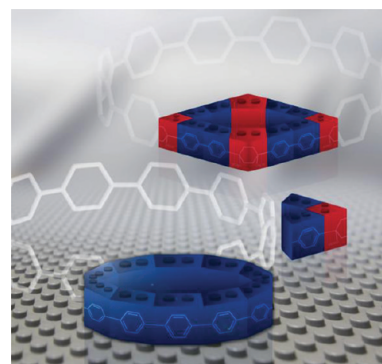
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RECEIVED ON FEBRUARY 20, 2012

CONSPECTUS

Since their discovery in 1991, carbon nanotubes (CNTs) have attracted significant attention because of their remarkable mechanical, electronic, and optical properties. Structural uniformity of the CNT is critically important because the sidewall structures (armchair, zigzag, and chiral) determine many of the significant properties of CNTs. Ideally researchers would synthesize CNTs with a defined target sidewall structure and diameter, but the current synthetic methods, such as arc discharge and chemical vapor deposition, only provide CNTs as the mixtures of various structures. Purification of these mixtures does not allow researchers to isolate a structurally uniform CNT, which is the bottleneck for fundamental studies and advanced applications of these materials. Therefore, the selective and predictable synthesis of structurally uniform CNTs would represent a critical advance in both nanocarbon science and synthetic chemistry.



This Account highlights our efforts toward the bottom-up synthesis of structurally uniform carbon nanotubes (CNTs). We envisioned a bottom-up synthesis of structurally uniform CNTs through a controlled growth process from a short carbon nanoring (template) that corresponds to the target structure of CNTs. Our simple retrosynthetic analysis led to the identification of cycloparaphenylenes (CPPs), acene-inserted CPPs, and cyclacenes as the shortest sidewall segments of armchair, chiral, and zigzag CNTs, respectively. With this overall picture in mind, we initiated our synthetic studies of aromatic rings/belts as an initial step toward structurally uniform CNTs in 2005. This research has led to (i) a general strategy for the synthesis of CPPs and related carbon nanorings using cyclohexane derivatives as a benzene-convertible L-shaped unit, (ii) a modular, size-selective, and scalable synthesis of $[n]$ CPPs (a shortest segment of armchair CNTs), (iii) the X-ray crystal structure analysis of CPPs, (iv) the design and synthesis of acene-inserted CPPs as the shortest segment of chiral CNTs, and (v) the first synthesis of cyclo-1,4-naphthylene, a π -extended CPP. We believe this work will serve as important initial steps toward a controlled synthesis of CNTs.

1. Introduction

Since the discovery by Iijima in 1991,¹ carbon nanotubes (CNTs) have attracted significant attention because of their remarkable mechanical, electronic, and optical properties.² A variety of applications such as fiber sheets,³ transparent conductive films,⁴ and biological sensors⁵ are greatly expected. Structural uniformity of CNT is critically important since many of the significant properties of CNTs are primarily determined by the sidewall structures (armchair, zigzag, and chiral). Depending on the way a graphene sheet is rolled up, the structures of CNTs are represented by a pair of chiral indices $[n,m]$ where $n \geq m \geq 0$, so-called "chirality".⁶

There are two extreme structures called armchair CNTs ($n = m$) and zigzag CNTs ($m = 0$). The structures other than these two are classified into chiral CNTs (Figure 1).^{2,6} As for the electronic properties of CNTs, the structures where $n - m = 3i$ (i is any integer) are metallic and the rest are known to possess semiconducting character.⁶ In particular, the armchair CNTs have complete metallic character, thereby showing remarkable electronic conductivity. Although the ideal situation is to synthesize a CNT with target sidewall structure and diameter, the current synthetic methods, as exemplified by arc discharge and chemical vapor deposition methods, only provide CNTs as mixtures of various

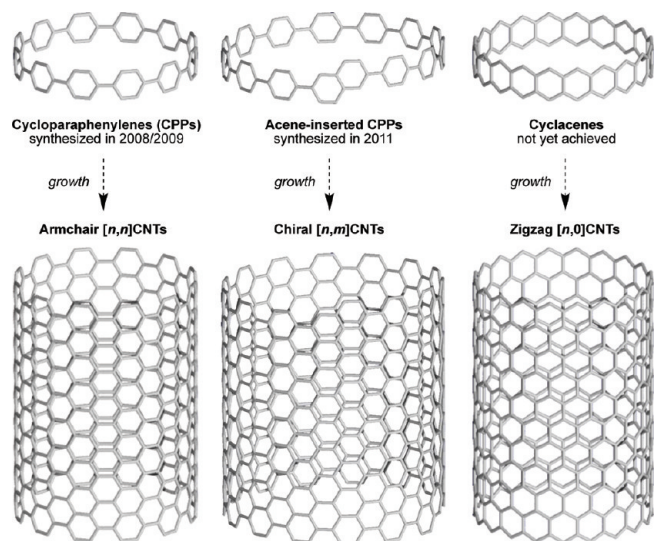


FIGURE 1. Structure of armchair, chiral, and zigzag CNTs and their shortest sidewall segments.

structures.² It is also not possible to purify such mixtures to isolate a structurally uniform CNT. Clearly, this is the bottleneck for fundamental studies and advanced applications of CNT. Thus, the selective and predictable synthesis of structurally uniform CNTs has been recognized as a Holy Grail both in nanocarbon science and synthetic chemistry.

We envisioned that the bottom-up synthesis of structurally uniform CNTs could be achieved through a controlled growth process from a short carbon nanoring (template) that corresponds to the target structure of CNTs.⁷ Such a simple retrosynthetic analysis led to the identification of cycloparaphenylenes (CPPs), acene-inserted CPPs, and cyclacenes⁸ as the shortest sidewall segments of armchair, chiral, and zigzag CNTs, respectively (Figure 1). Having such an overall picture in mind, we initiated our synthetic studies of these aromatic rings/belts ultimately aimed at contributing to a bottom-up organic synthesis of structurally uniform CNTs in 2005. For the first step toward selective synthesis of CNT, we accomplished the synthesis of CPPs,^{9–13} π -extended CPP (cyclo-1,4-naphthylene),¹⁴ and acene-inserted CPP.¹⁵ In addition, we revealed the structural features of these carbon nanorings from both theoretical and experimental aspects. In this Account, we describe our synthetic campaign of CPPs and related carbon nanorings.

In parallel to our work, the groups of Bertozzi (the first synthesis),¹⁶ Yamago,^{17,18} and Jasti.^{16,19,20} also reported the successful synthesis of CPPs. Currently, the modular,¹¹ size-selective,^{9,11,17,19,20} and scalable^{12,13} synthesis of $[n]$ CPPs is possible, and [12]CPP, prepared by the procedure developed in our group, has become commercially available.²¹ CPP is

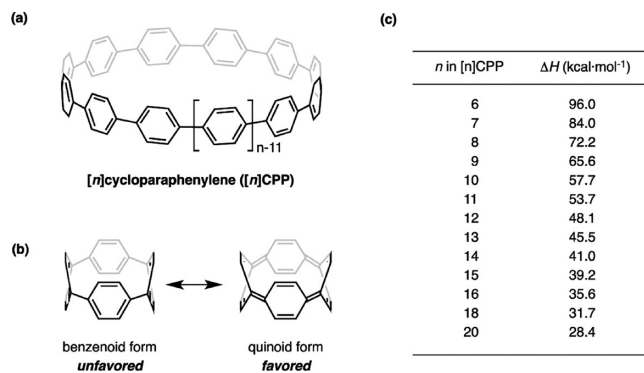


FIGURE 2. (a) Structure of $[n]$ CPP, (b) structural character of $[4]$ CPP, and (c) strain energies of $[n]$ CPPs.

an interesting and unique molecular entity not only because it represents the shortest sidewall segment of armchair CNT structures, but also because of its aesthetic appeal, unique cyclic and curved conjugation,¹⁰ photophysical properties,^{16,18,19} and guest-encapsulating properties.^{12,13,22} Very recently, Scott and co-workers synthesized the end cap of $[5,5]$ CNT using flash vacuum pyrolysis as a key reaction.²³ Related to our acene-inserted CPPs, Isobe et al. reported the synthesis of $[4]$ cyclo-2,8-chrysenylene as the second example of short segment of chiral CNTs.²⁴

2. Cycloparaphenylenes: Theoretical Study on Ring Structure

Cycloparaphenylene (CPP), a simple string of benzene, has attracted scientists because of their simple and beautiful structure and potential applications in materials science and supramolecular chemistry (Figure 2a).²⁵ Prior to achieving the chemical synthesis,²⁶ a number of theoretical studies predicted that CPP would exhibit unique properties owing to its cyclic π -conjugation and characteristic geometry of p-orbitals.^{25,27} For example, Tahara and Tobe reported the optimized geometries and bond lengths of small ring size CPPs by theoretical method.^{25b} They found that $[4]$ CPP prefers to have the quinoid structure rather than the benzenoid structure. In other words, double bonds are located at the linkage between six-membered rings (Figure 2b). As the ring size of CPP increases, the quinoid form would become unfavorable relative to the benzenoid form due to effective cyclic conjugation in the latter form. Thus, CPPs having more than five benzene rings can be considered as “true” CPPs. Indeed, several $[4]$ CPP analogues were found to exist in a quinoid form (Figure 2b).²⁸

The challenge for synthesizing CPPs lies in the strain energy caused by bending aromatic system. We systematically investigated the strain energy of CPP by the DFT calculation (B3LYP/6-31G(d)) using hypothetical homodesmotic reactions (Figure 2c).¹⁰

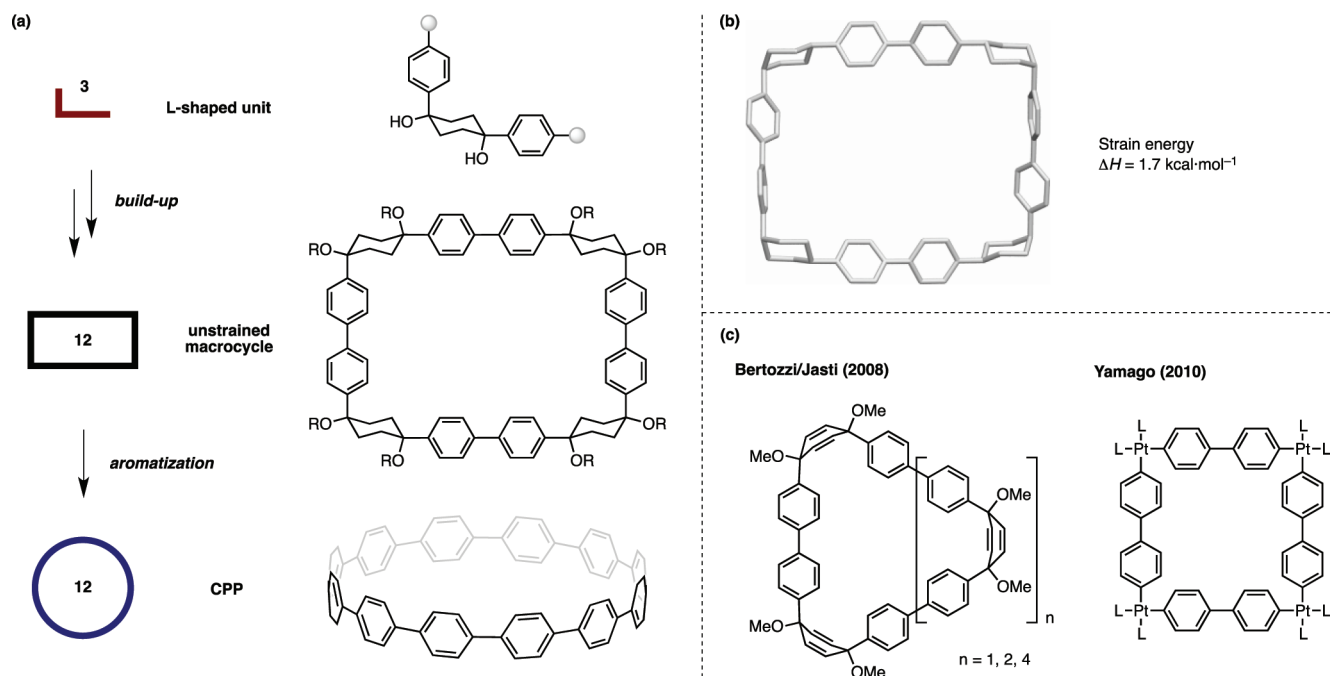


FIGURE 3. (a) Our strategy for the synthesis of CPP. (b) Strain energy of macrocyclic framework. (c) Key macrocycles in the synthesis of CPP by Bertozzi/Jasti and Yamago.

The strain energy (ΔH) of $[n]$ CPPs ($n = 6\text{--}20$) ranges from 96 to 28 $\text{kcal}\cdot\text{mol}^{-1}$, which gradually decreases as the number of benzene rings increases. However, it should be noted that [20]CPP still has relatively high strain energy (28 $\text{kcal}\cdot\text{mol}^{-1}$). We believe that these high strain energy values of CPPs speak well for the years (>75 years) required for chemists to achieve the bottom-up organic synthesis of CPPs.

3. Synthetic Strategy for Cycloparaphenylenes

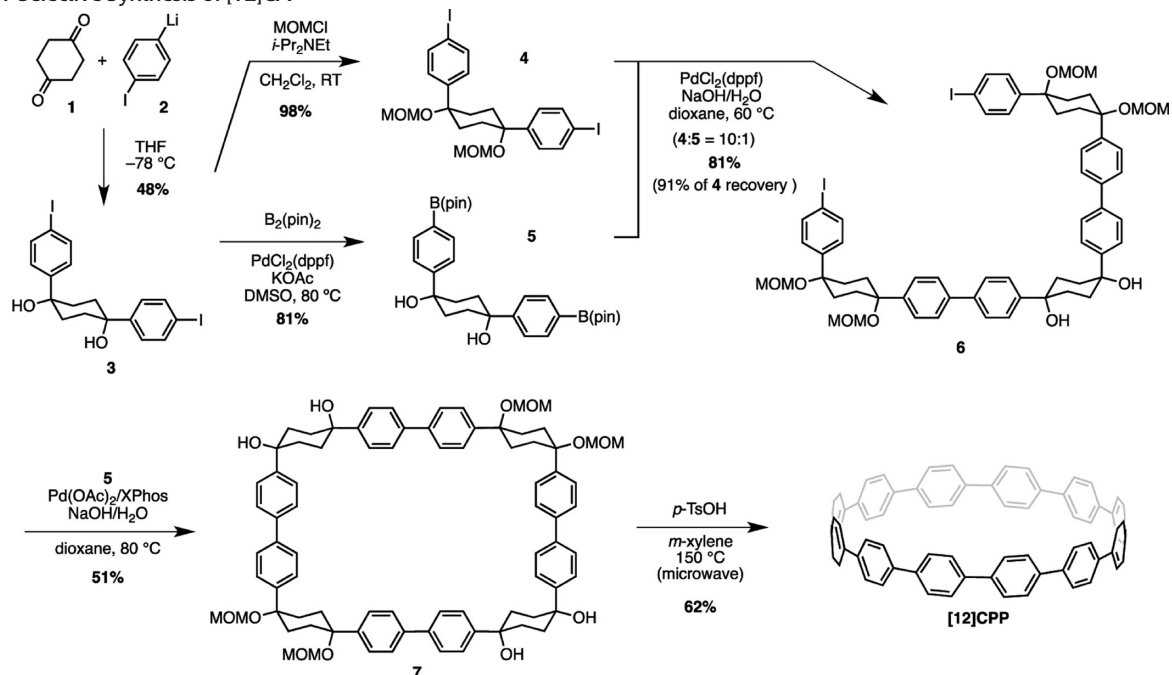
How to solve this ring strain problem is critically important for the synthesis of CPP. Inspired by the insightful works of Vögtle and co-workers,^{26b} we decided to introduce *cis*-1,4-diphenylcyclohexane monomers as a novel terphenyl-convertible L-shaped unit for realizing the chemical synthesis of highly strained CPP (Figure 3a). This L-shaped unit having nearly ideal “included” angles (ca. 80°), angles between connection points, would significantly attenuate the buildup of strain energy during the macrocyclization. For example, DFT calculations revealed that the strain energy of cyclic tetramer using L-shaped unit is only 1.7 $\text{kcal}\cdot\text{mol}^{-1}$ (Figure 3b). We expected that the formation of macrocyclic compounds through aryl–aryl bond formation connecting L-shaped units, followed by aromatization of cyclohexane moieties, would furnish CPP. As for the suitable cyclohexane moiety, we chose *cis*-1,4-dihydroxy-cyclohexane-1,4-diyl because the corresponding monomers can be readily made

by 2-fold carbonyl addition to commercially available cyclohexane-1,4-dione. We also expected the transformation of *cis*-1,4-dihydroxy-cyclohexane-1,4-diyl unit to benzene ring could be accomplished in the final step of synthesis by an acid-mediated 8-fold dehydration followed by auto-oxidation. In the synthesis by Bertozzi and Jasti, *cis*-1,4-dimethoxy-2,5-cyclohexadiene-1,4-diyl was utilized as a similar bent unit, where the aromatization step was accomplished under reductive conditions using lithium naphthalenide (Figure 3c).¹⁶ Yamago reported the synthesis of [8]CPP via tetranuclear Pt complex.¹⁷ In all cases including our own, attenuating the buildup of strain energy during the macrocyclization is the key for the successful synthesis of CPP.

4. Selective Synthesis of [12]CPP: First-Generation Synthesis

In 2009, we reported the first selective synthesis of [12]CPP (Scheme 1).⁹ This first-generation synthesis began with the preparation of L-shaped units. The 2-fold addition of 4-iodophenyllithium (**2**), prepared from 1,4-diiodobenzene and *n*-BuLi, to cyclohexane-1,4-dione (**1**) afforded the common 1,4-diphenylcyclohexane scaffold **3**, which was then converted into the methoxymethyl (MOM)-protected diiodide **4** (98%). The introduction of MOM groups significantly increases the solubility of intermediates en route to [12]CPP. By using a Miyaura borylation reaction, **3** was also converted to hydroxy-protected L-shaped diboronate **5** in 81% yield.²⁹

SCHEME 1. Selective Synthesis of [12]CPP



With suitable monomers in hand, the synthesis of cyclic tetramer **7** by the Suzuki–Miyaura coupling³⁰ was attempted. In early experiments, we identified that 1:1 coupling of **4** and **5** is not an easy task because of the difficulty to suppress the undesired linear oligomers. At this point, we changed our approach to the stepwise assembly of L-shaped units. After the screening of various Pd catalysts, we found that the use of PdCl₂(dppf) led to a very clean 2:1 cross-coupling reaction, when an excess of diiodide **4** was employed, providing trimer **6** in 81% yield. Notably, 91% of the unchanged starting material **4** (based on the consumption for trimer **6**) was recovered. The macrocyclization was accomplished by the inter/intramolecular cross-couplings of trimer **6** and monomer **5** by using the Buchwald XPhos ligand³¹ as the optimal ligand to furnish the cyclic tetramer **7** in 51% yield as the sole cyclic product. We anticipated that the treatment of **7** with acids would lead to a sequence of (i) deprotection of MOM group, (ii) 8-fold dehydration (conversion of dihydroxycyclohexane into cyclohexadiene), and (iii) oxidation (conversion of cyclohexadiene into benzene) to provide the target [12]CPP. Although we were aware of a number of unsuccessful examples of acid-mediated aromatization in the synthetic study of aromatic macrocycles, the treatment with a stoichiometric amount of *p*-toluenesulfonic acid (*p*-TsOH) in *m*-xylene at 150 °C under microwave irradiation afforded [12]CPP in 62% yield.

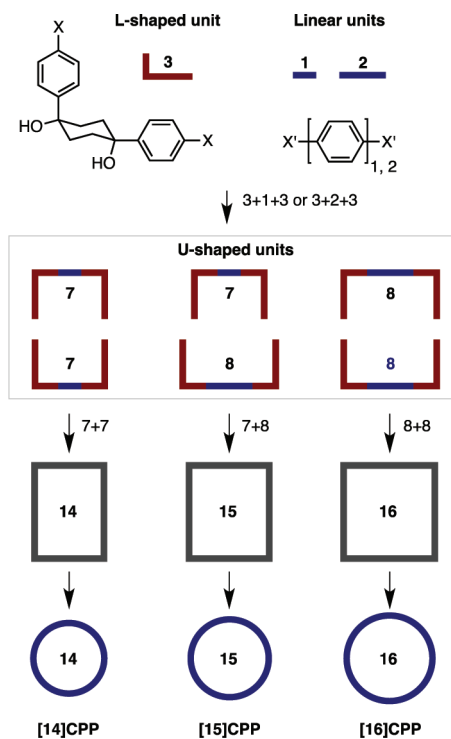
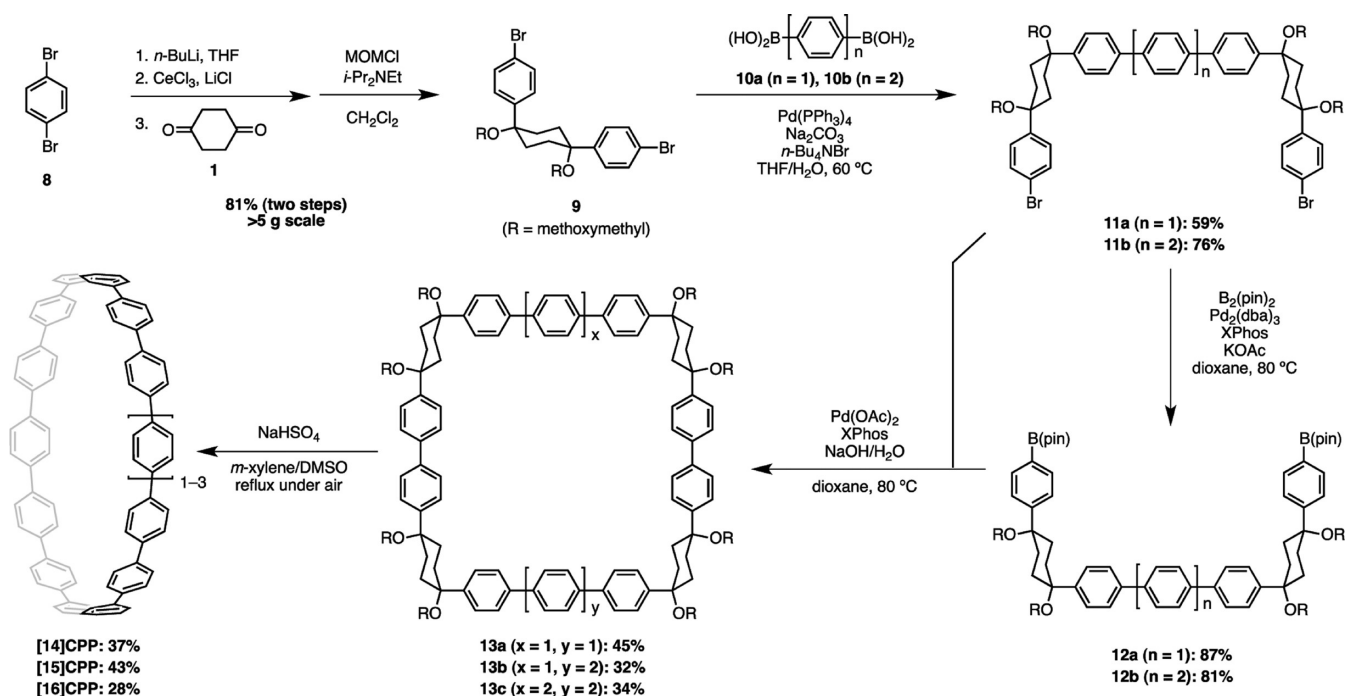


FIGURE 4. Concept of modular synthesis of [n]CPPs via U-shaped units.

5. Modular Synthesis of [n]CPP: Second-Generation CPP Synthesis

Our CPP synthesis is very flexible and modular, assembling bent and linear building blocks in a controlled manner. In essence, we synthesized [12]CPP in a 3+3+3+3 mode using

SCHEME 2. Modular synthesis of [14]-, [15]-, and [16]CPP



an L-shaped unit.⁹ By carefully selecting variable numbers of bent and linear units, a range of [n]CPPs can be accessed (Figure 4).¹¹ For example, U-shaped 7-benzene and 8-benzene units should be made by assembling an L-shaped unit and a linear benzene/biphenyl unit in a 3+1+3 or 3+2+3 mode, respectively. The cyclizative dimerization of these U-shaped units in a 7+7, 7+8, or 8+8 mode would ultimately lead to [14]-, [15]-, and [16]CPP. This new approach makes it possible to access these CPPs in a strategic way. In addition, as the number of benzene rings in the U-shaped units can be easily increased, this method can be a uniform synthetic strategy for all [n]CPPs ($n \geq 14$).

We first developed a high-yielding synthesis of L-shaped dibromide **9**: the 2-fold addition of 4-bromophenyllithium, which was prepared from 1,4-dibromobenzene (**8**) and *n*-BuLi, to cyclohexane-1,4-dione (**1**) in the presence of CeCl_3 and LiCl afforded diphenylcyclohexane-diol scaffold (Scheme 2).³² This Ce-based protocol provided the L-shaped unit with virtually complete *cis*-stereoselectivity. The unfavorable *trans* isomer and monoaddition product, which were observed in the previous Li-based method, were both suppressed. The thus obtained diol was then converted to the MOM-protected dibromide **9** in 81% overall yield from **8**.

The U-shaped units **11** were synthesized by the Suzuki–Miyaura coupling of benzene- or biphenyl-diboronic acids (**10a** or **10b**) with an excess amount of **9** under the catalytic influence of $\text{Pd(PPh}_3)_4$ in moderate yields

(**11a**: 59%, **11b**: 76%). The treatment of U-shaped dibromides **11** with $\text{B}_2(\text{pin})_2$ in the presence of $\text{Pd}_2(\text{dba})_3/\text{XPhos}$ catalyst and KOAc afforded the U-shaped diboronates **12** (**12a**: 87%, **12b**: 81%).³³ Then cyclizative Suzuki–Miyaura coupling of **11** and **12** under diluted conditions took place in the presence of $\text{Pd(OAc)}_2/\text{XPhos}$ catalyst. The 14-benzene box-shaped macrocycle **13a** was synthesized from 7-benzene U-shaped units **11a** and **12a** (45%). Similarly, the 16-benzene macrocycle **13c** was synthesized by the coupling of **11b** and **12b** (34%). Gratifyingly, the coupling of unsymmetrical U-shaped units **11b** and **12a** provided the odd-numbered 15-benzene macrocycle **13b** in 32% yield. Finally, these box-shaped macrocycles (**13a–13c**) were converted to [14]-, [15]-, and [16]CPP by treatment with NaHSO_4 in *m*-xylene/DMSO. It should be noted that this new protocol allowed us to conduct the aromatization step without using microwave irradiation.

The key for making odd-numbered [n]CPPs lies in the chair-flipping of the cyclohexane rings (Figure 5). From the conformations shown in Scheme 2, the “arch widths” of two U-shaped units (**11b** and **12a**) with different number of benzene rings are not matching for macrocyclization. However, when two cyclohexane rings in **12a** undergo chair-flipping, the “arch width” of the resulting new conformation nicely matches that of **11b** to produce **13b** (Figure 5, left). Thus, the arch-width change induced by two cyclohexane flips corresponds roughly to the width of one benzene ring. Calculated strain energies of 15-benzene box-shaped unit

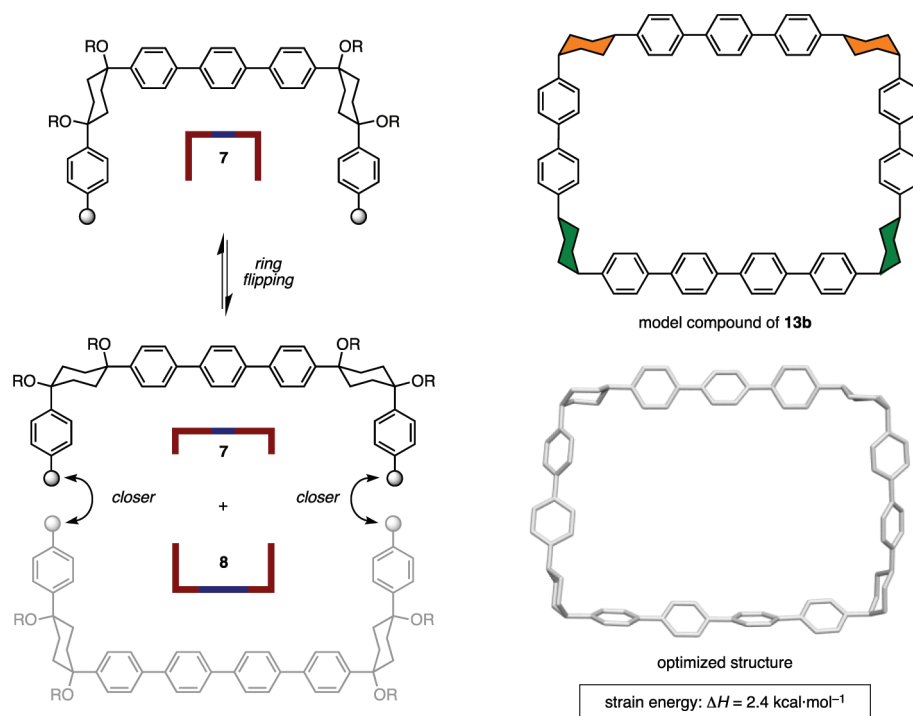
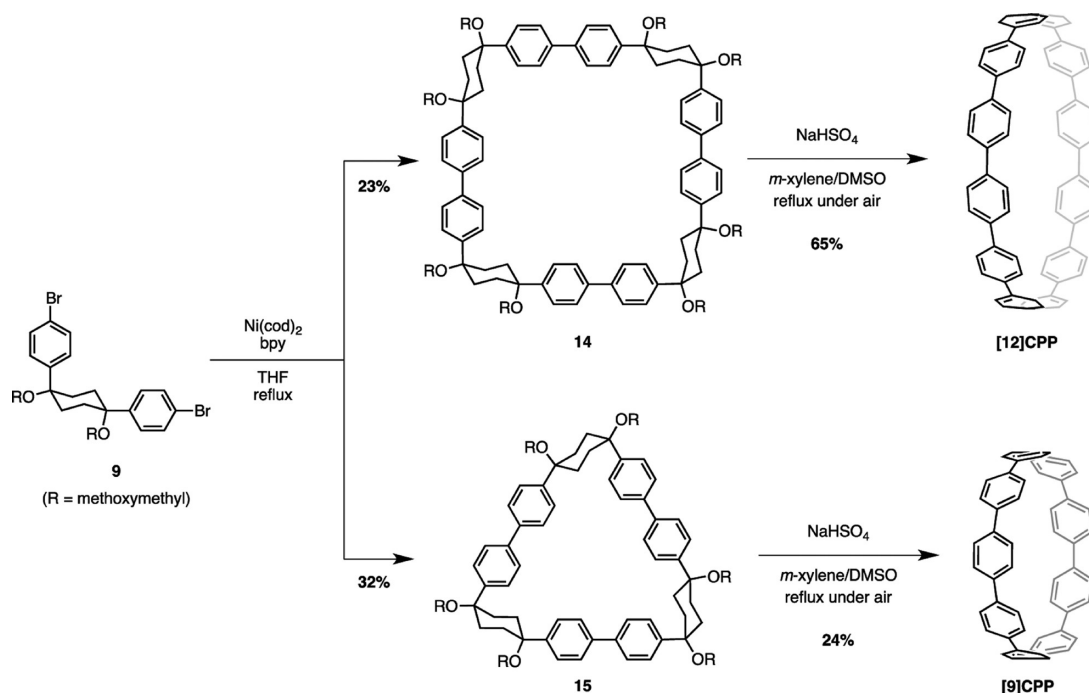


FIGURE 5. Flipping of cyclohexane rings in U-shaped units and strain energy of **13b** skeleton.

SCHEME 3. Ni-Mediated Concise Synthesis of [12]CPP and [9]CPP



with B3LYP/6-31G(d) level of theory also suggested the effective strain releasing by cyclohexane rings ($\Delta H = 2.4 \text{ kcal}\cdot\text{mol}^{-1}$). This conformational feature of cyclohexane ring is an advantage of the present strategy for accessing all possible $[n]$ CPPs including odd-numbered CPPs.

6. Scalable Synthesis of [12]CPP and [9]CPP: Third-Generation CPP Synthesis

Although previous protocols were effective for size-selective CPP synthesis, the requirement of multistep Pd-catalyzed coupling reactions using two monomers was problematic.

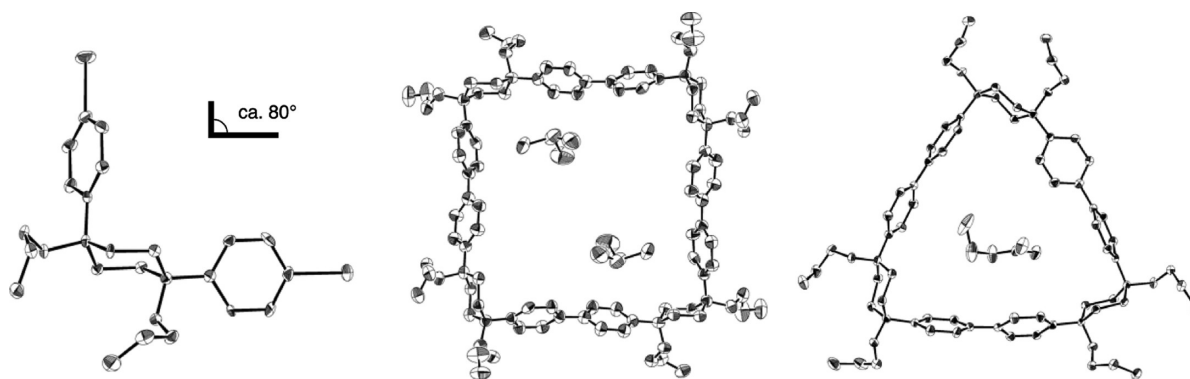


FIGURE 6. X-ray crystal structures of L-shaped unit **4**, **14**·2CHCl₃, and **15**·EtOAc.

These methods should be replaced by a more concise, cost-effective, and scalable route in order to provide CPPs in useful quantities. We postulated that a nickel-promoted “shotgun” macrocyclization of brominated L-shaped monomer (**9**)³⁴ might proceed to give cyclic tetramer **14** directly (Scheme 3). After extensive screening, we established that the combination of Ni(cod)₂/2,2′-bipyridyl is effective for such “shotgun” macrocyclization.¹² Quite surprisingly, unexpected cyclic trimer **15** was also generated (Scheme 3).¹³ It should be noted that more than half of a monomer was converted into CPP precursors **14** (23%) and **15** (32%) under optimized conditions. Both of the cyclic compounds **14** and **15** were subjected to aromatization to afford [12]CPP and [9]CPP, respectively, in reasonable yields by the treatment with NaHSO₄. This Ni-based synthetic method outperforms the previous routes using Pd-catalyzed reaction in terms of overall yield and cost.

The flexibility of the cyclohexane skeleton makes it possible to realize the formation of cyclic trimer **15**. All three cyclohexane moieties in the X-ray crystal structure of **15**·EtOAc adopt chair conformations with “included” angles of ca. 70° despite that the “included” angles of L-shaped monomer **4** and cyclic tetramer **14**·2CHCl₃ showed approximately right angle in the crystal state (Figure 6). Strain energy of the framework of **15** was estimated to be 8.0 kcal·mol⁻¹, which is 6.3 kcal·mol⁻¹ higher than that of **14**. Furthermore, we identified from VT-NMR study that cyclohexane rings can undergo rapid chair flipping even within macrocyclic structure.

7. X-ray Crystal Structures of CPP

Until our report in 2011,¹² all CPPs synthesized were characterized solely by NMR and MS spectra.^{9,11,16,17} The structure validation of the CPP molecules by X-ray crystal structure analysis had remained a great challenge because of their intrinsic properties, such as the high solubility in a

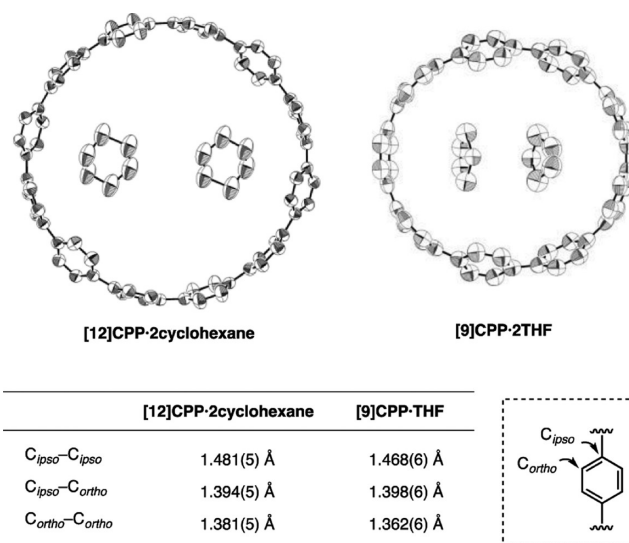


FIGURE 7. X-ray crystal structures and average bond lengths of [12]CPP·2cyclohexane and [9]CPP·2THF.

variety of solvents and the tendency to incorporate guest molecules within the ring. After extensive screening of conditions, we succeeded in the X-ray crystallographic analysis of [12]CPP and [9]CPP for the first time (Figure 7).^{12,13} Single crystals of [12]- and [9]CPP were obtained from chloroform/cyclohexane and THF/pentane, respectively. While [12]CPP has a highly symmetrical circular form, [9]CPP is slightly distorted to form an ellipsoid.

The average bond lengths of [12]CPP and [9]CPP in the crystalline state are also shown in Figure 7. While the C_{ippo}–C_{ortho} and C_{ortho}–C_{ortho} bond lengths of [12]CPP are almost identical within the range of experimental error (1.39 Å), the C_{ippo}–C_{ippo} bonds exhibit single-bond character (1.48 Å), suggesting no significant bond alternation in the benzene rings (Figure 7). Thus, the benzenoid character is reasonably preserved in [12]CPP. On the other hand, one can see that C_{ippo}–C_{ippo} and C_{ortho}–C_{ortho} bond lengths of [9]CPP are shorter than those of [12]CPP. This shows that [9]CPP still

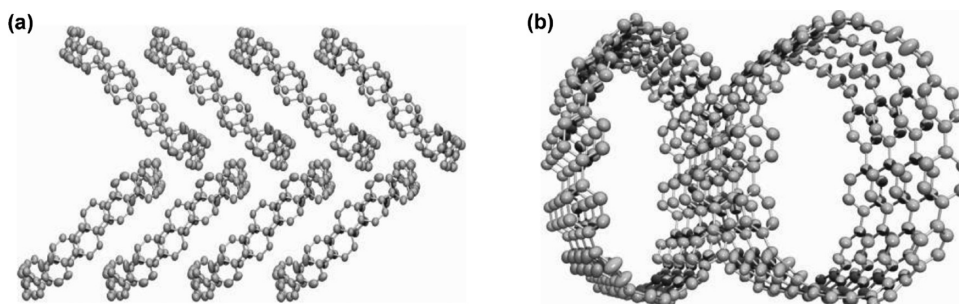


FIGURE 8. Herringbone packing (a) and tubular alignment (b) of [12]CPP in crystal.

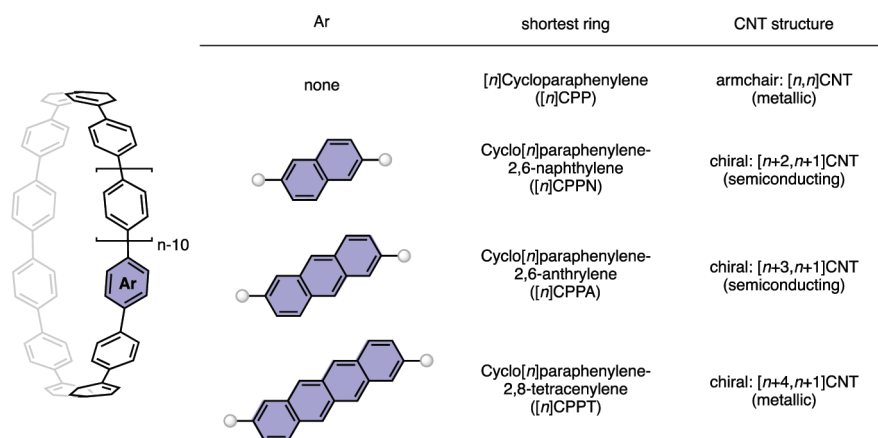


FIGURE 9. Shortest sidewall segments of armchair and chiral carbon nanotubes.

has mainly benzenoid character, but the contribution of the quinoidal property of CPP becomes larger as the ring size of CPP decreases.^{25b} In line with these structural features, the ¹H NMR chemical shift values of CPPs are upfield-shifted as the ring size decreases: $\delta = 7.68$ ([16]CPP), 7.67 ([15]CPP), 7.65 ([14]CPP), 7.61 ([12]CPP), 7.52 ppm ([9]CPP) in CDCl₃.

The packing mode of CPP molecules in the crystal is also interesting. As shown in Figure 8a, [12]CPP molecules align in a herringbone manner. More strikingly, in addition to the herringbone packing, the [12]CPP molecules align nicely to form a tubular structure (Figure 8b). The emergence of such a surprising channel structure obviously stimulates our imagination for various possibilities of CPP chemistry in the crystalline state.

8. Design, Synthesis, and Racemization Process of Chiral Carbon Nanorings

As already mentioned, the electronic properties of CNTs are primarily determined by the sidewall structures. With a bottom-up synthesis of chiral carbon nanotubes in mind, we designed and synthesized a shortest chiral CNT structure (chiral carbon nanoring).¹⁵ Our design of chiral carbon nanorings is quite simple, inserting acene unit into CPP

structures. For example, when inserting a naphthalene unit with a 2,6-linkage, the resulting cyclo[*n*]paraphenylene-2,6-naphthylene ([*n*]CPPN) will represent the shortest segment of [*n*+2,*n*+1]CNT (Figure 9). Similarly, the incorporation of anthrylene-2,6-diyl ([*n*]CPPA) and tetracenylenylene-2,8-diyl ([*n*]CPPT) will result in the shortest segments of [*n*+3,*n*+1]CNT and [*n*+4,*n*+1]CNT, respectively. By inserting these acenes with an appropriate linkage, all possible chiral structures of CNTs can be created.

We demonstrated the synthesis of [13]CPPN, which is the shortest segment of [15,14]CNT, as a proof-of-principle study (Scheme 4). Following our selective CPP synthesis, naphthalene-inserted U-shaped dibromide **17** was prepared by the 2:1 cross-coupling reaction of L-shaped dibromide **9** and 2,6-diborylated naphthalene **16** in the presence of Pd(PPh₃)₄ catalyst, Na₂CO₃, and *n*-Bu₄NBr in THF/H₂O (72% yield). The U-shaped unit **17** was then cross-coupled with **12a** in the presence of Pd₂(dba)₃/XPhos catalyst and K₃PO₄ in 1,4-dioxane/H₂O to furnish the macrocycle **18** in 35% yield. Finally, the treatment of **18** with NaHSO₄·H₂O in refluxing *m*-xylene/DMSO under air afforded [13]CPPN in 25% yield.

Chiral carbon nanorings such as [13]CPPN possess helical chirality (e.g., (**P**) and (**M**) in Figure 10a), corresponding to the

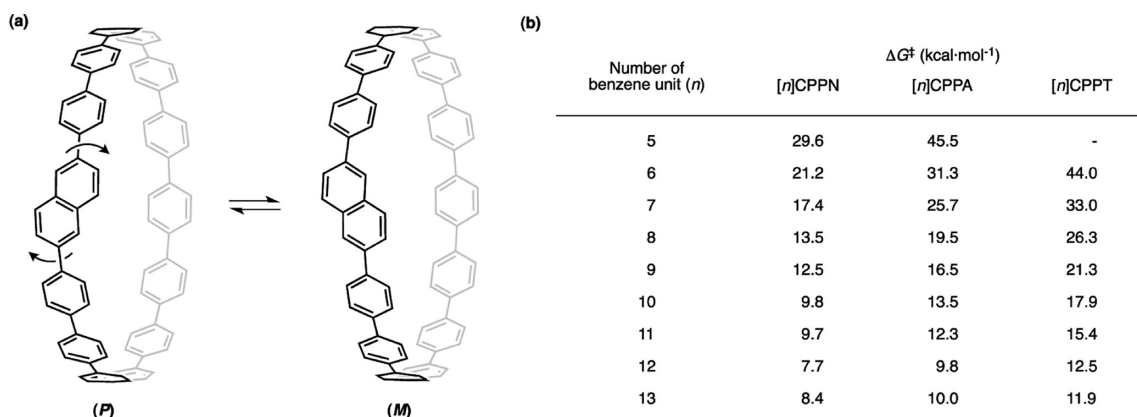
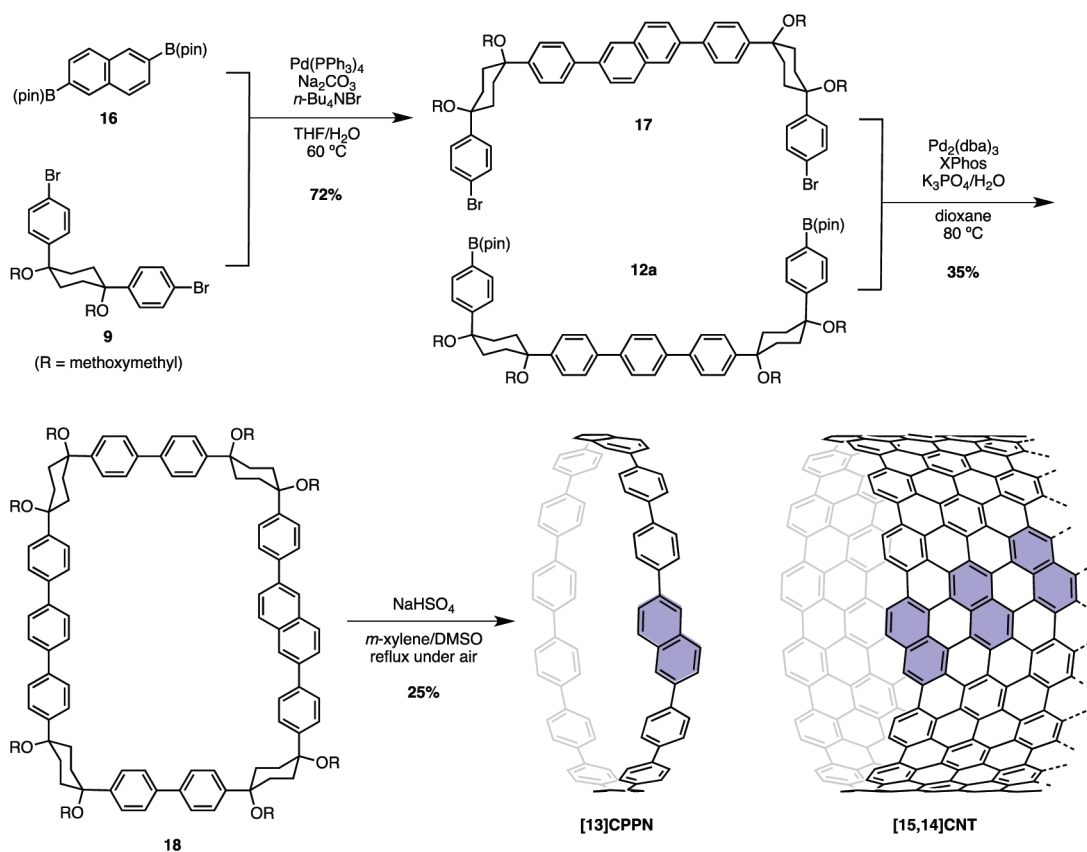


FIGURE 10. Racemization pathway (a) and B3LYP/6-31G(d) calculated barrier energies (b) of chiral carbon nanorings.

SCHEME 4. Synthesis of [13]CPPN



helical chirality of chiral CNTs. The racemization of chiral carbon nanorings occurs via the rotation of two C–C bonds between the inserted acene unit (naphthalene for [13]CPPN) and neighboring benzene units. We estimated the racemization barriers (ΔG^\ddagger) of chiral carbon nanorings, [*n*]CPPN, [*n*]CPPA, and [*n*]CPPT (*n* = 5–13), by the DFT calculation (B3LYP/6-31G(d)) in order to clarify the effect of ring size and acene unit of nanorings (Figure 10b). Although there are small upsets in the racemization

energies of [13]CPPN/[12]CPPN and [13]CPPA/[12]CPPA, the ΔG^\ddagger value generally increases (i) as the number of benzene units decreases (as the ring size decreases) or (ii) as the acene unit becomes larger. In addition to the racemization barriers, we also estimated the strain energies of these chiral carbon nanorings by DFT calculation (37.6–89.9 kcal·mol⁻¹). Based on these studies, we are now in a position to rationally design and synthesize a chiral carbon nanoring with target racemization aptitude.

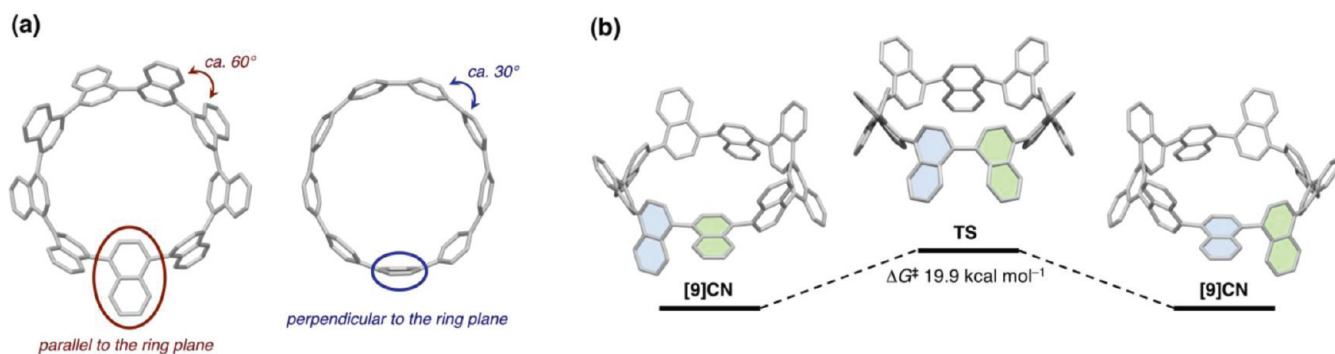
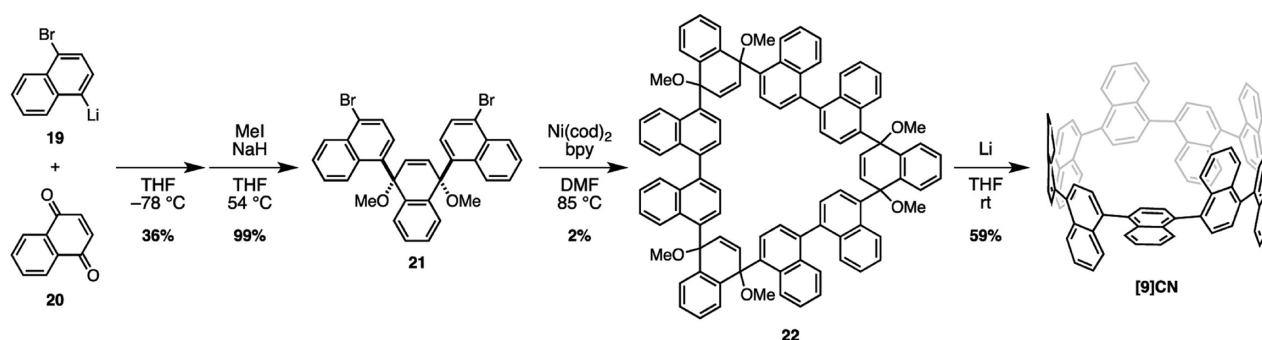


FIGURE 11. Comparison of the optimized structures of [9]CN and [9]CPP (a) and racemization pathway of [9]CN (b).

SCHEME 5. Synthesis of [9]CN



9. Synthesis and Properties of π -Extended Carbon Nanoring: [9]Cyclo-1,4-naphthylene

An important next step based on these fundamental studies of CPPs and acene-inserted CPPs is the synthesis of π -extended carbon nanorings that allows the elucidation of the structural and electronic effects present in the π -systems of carbon nanorings. In addition, we expect these π -extended carbon nanoring to be closer precursors of carbon nanobelts and tubes. The outcome of our extensive investigations is the first synthesis of [9]cyclo-1,4-naphthylene ([9]CN) shown in Scheme 5.¹⁴ Following our Ni-mediated “shotgun” method,^{12,13} the naphthalene-based L-shaped monomer **21**, which can be prepared from 1,4-dibromonaphthalene and 1,4-naphthoquinone, was treated with Ni(cod)₂ and 2,2'-bipyridyl in DMF at 85 °C to furnish the cyclic trimer **22** in 2% isolated yield after extensive purification. The final reductive aromatization³⁵ was achieved by the treatment of cyclic trimer **22** with granular lithium in THF at room temperature to afford [9]CN in 59% yield as a yellow powder (Scheme 5).

Careful structure analysis uncovered a number of unique structural features of [9]CN that are quite different from those of [9]CPP (Figure 11). Due to the sterically demanding naphthyl groups, the average dihedral angle between

neighboring naphthalene rings in [9]CN is considerably larger (ca. 60°) than that of [9]CPP (ca. 30°). It was also found that one naphthalene ring in [9]CN is parallel to the nanoring plane due to the larger dihedral angles (Figure 11a). This is quite different from the case of [9]CPP where one benzene ring aligns perpendicular to the plane of nanoring. Moreover, it was revealed that [9]CN is inherently a unique chiral molecule according to these structural features. Careful DFT calculations (B3LYP/6-31G(d)) uncovered the racemization pathway (arene rotation) as well as relatively low activation energies for arene rotation (19.9/21.4 kcal·mol⁻¹) in comparison with those of simple 1,1'-binaphthyl (34.3/25.4 kcal·mol⁻¹) (Figure 11b). These relatively lower barriers to arene rotation most likely stem from the ring strain of [9]CN. In the transition-state structures, the bending enforced by the ring structure alleviates C–H/C–H eclipsing interactions. Due in part to the π -extension of arene unit, [9]CN has an absorption maximum at a longer wavelength, and luminesces with smaller Stokes shift in comparison with [9]CPP.¹⁴

10. Conclusion and Future Perspective

In summary, we have accomplished the synthesis of CPPs, π -extended CPP (cyclo-1,4-naphthylene), and acene-inserted CPP using the L-shaped strategy. Our synthesis capitalizes on

the ability of cyclohexane-based L-shaped units to attenuate the buildup of strain energy during the macrocyclization, and exploits their benzene- or naphthalene-convertible nature. The stepwise Pd-catalyzed cross-coupling methods show great utilities for modular and size-selective synthesis of carbon nanorings. Flexibility of the cyclohexane moiety is an advantage of our strategy, which allows the deliberate construction of even/odd-numbered $[n]$ CPPs and acene-inserted CPP. This methodology would be applicable to a range of CPP-related carbon nanorings. A concise and cost-effective CPP synthesis via the Ni-mediated "shotgun" method was also developed. During these studies, we successfully validated the circular structures of CPPs by X-ray crystal structure analysis. The benzenoid characters of CPPs and the emergence of quinoid property in smaller CPPs were confirmed from their bond lengths. We also uncovered interesting tubular alignment of CPP molecules with herringbone packing in crystals. Additionally, some important energetic values, such as strain energies and racemization barriers (for acene-inserted CPPs and CN), have been systematically estimated for future molecular design of carbon nanorings. With these small templates in hand, we are currently trying to find a way to grow these templates (seeds) into the targeted CNT structures.

We thank all the co-workers for their significant contribution to the chemistry described in this paper. Ms. Miho Toyoshima is greatly appreciated for the help in artwork. This work was supported by the Funding Program for Next Generation World-Leading Researchers (JSPS), the Grants-in-Aid for Young Scientists (S) (JSPS), the PRESTO program (JST). The Nagoya University Global COE Program in Chemistry and the MEXT Joint Project of Chemical Synthesis Core Research Institutions are also acknowledged for support. H.O. thanks the JSPS for a predoctoral fellowship. Calculations were performed using the resources of the Research Center for Computational Science, Okazaki, Japan.

BIOGRAPHICAL INFORMATION

Haruka Omachi was born in Aichi, Japan (1985). He received his B.S. and M.S. degrees from Nagoya University (Japan) in 2008 and 2010, respectively, under the supervision of Professor Kenichiro Itami. He spent 3 months as a visiting student of Professor Graham Bodwell's group in Memorial University, Canada (2010). He is currently a Ph.D. student in the group of Professor Itami and also a recipient of a JSPS Predoctoral Fellowship.

Yasutomo Segawa was born in Chiba, Japan (1982). He received his B.S. degree from the University of Tokyo (Japan) under the guidance of Professor Takuzo Aida. He studied at the Graduate School of Engineering, the University of Tokyo under the supervision

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Kenichiro Itami was born in Pittsburgh, PA (1971) and raised in Tokyo. Educated in chemistry at Kyoto University (Japan) under the guidance of Professor Yoshihiko Ito, he received his Ph.D. in 1998. From 1997 to 1998, he was a predoctoral researcher in the group of Professor Jan-Erling Bäckvall at Uppsala University (Sweden). In the fall of 1998, he began his academic career at Kyoto University as an Assistant Professor (with Professor Jun-ichi Yoshida). He moved to Nagoya University to become an Associate Professor (with Professor Ryoji Noyori) in 2005, and was promoted to Full Professor in 2008. Representative awards include the Novartis-MIT Lecturer in Organic Chemistry (2012), the Nozoe Memorial Award for Young Organic Chemists (2011), Merck-Banyu Lectureship Award (2008), the Minister Award for Distinguished Young Scientists (2006), the Mitsui Chemicals Catalysis Science Award of Encouragement (2005), and the Chemical Society of Japan Award for Young Chemists (2005).

FOOTNOTES

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