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## A cycloparaphenylene nanoring with graphenic hexabenzocoronene sidewalls<sup>†</sup>

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Herein we report the synthesis of a novel hexabenzocoronene-containing cycloparaphenylene carbon nanoring, cyclo[12]-paraphenylene[2]-2,11hexabenzocoronenylene, by metal-mediated cross-coupling reactions. The nanoring was accomplished by rationally designed palladiumcatalyzed coupling of diborylhexabenzocoronene and L-shaped cyclohexane units, followed by nickel-mediated C–Br/C–Br coupling and the aromatization of cyclohexane moieties. The structure was confirmed by NMR and HR-MS. Especially, the cycloparaphenylene structure is firstly observed by STM. The photophysical properties were studied using UV-Vis spectroscopy, photoluminescence (PL) spectroscopy, and theoretical calculations.

As the shortest conjugated fragment of armchair carbon nanotubes (CNTs), cycloparaphenylenes (CPPs) have recently attracted increasing attention from scientists.<sup>1</sup> CPPs have simple hoopshaped structures consisting of aromatic rings with *para*-linkage, structures which were hypothesized half a century ago,<sup>2</sup> but which were synthesized only in the last decade.<sup>3</sup> Moreover, these molecular entities have size-dependent, tunable optoelectronic properties due to their cyclic and curved conjugating structures.<sup>3,4</sup> In addition, CPPs exhibit strong host–guest interactions<sup>4b,5</sup> and they can be exploited for supramolecular assemblies or as components of novel carbon materials. Concise synthesis of CNTs through a stepwise growth process from carbon nanorings is a fantastic strategy to provide structurally uniform CNTs with high purity. Therefore, there is great expectation that CPPs might function as an ideal precursor or seed for bottom-up synthesis of CNTs with a fixed diameter.  $^{1a,6}$ 

The main challenge of chemical synthesis of CPPs lies in the high strain energy because of the bending of the planar phenyl rings. After the synthesis of [10]cyclophenacene via chemical modification of [60]fullerene for the first time by Nakamura and coworkers,<sup>7</sup> the synthesis of [9]-, [12]-, and [18]CPPs was reported by Jasti and Bertozzi in 2008.<sup>3</sup> A bent cyclohexadiene can be converted to an aromatic benzene unit by reductive aromatization and this approach has been applied in the synthesis of CPPs with different benzene rings.4c,5a,8 Itami and coworkers applied an L-shaped building block based on cyclohexane for selective synthesis of CPPs.9 Yamago and coworkers developed a strategy based on square-shaped tetranuclear platinum complexes for the synthesis of CPPs.<sup>10</sup> Several other  $\pi$ -extended CPP carbon nanorings have also been successfully synthesized, such as [9]cyclo-1,4-naphthylene ([9]CN)<sup>11</sup> and tetraphenyl-substituted [12]CPP.<sup>12</sup> Very recently, the Müllen group synthesized dodecaaryl [9]CPP and three dimensional  $\pi$ -extended polyphenylene cylinders to achieve hexabenzocoronenecontaining cyclic molecules through a final cyclodehydrogenation reaction.13

In the present study, we report a novel strategy for the synthesis of a hexabenzocoronene (HBC)-containing cycloparaphenylene carbon nanoring, cyclo[12]-paraphenylene[2]-2,11-hexabenzocoronenylene, by Pd- and Ni-mediated cross-coupling reactions. To avoid possible structural change or incomplete cyclodehydrogenation in the final step,<sup>13a,b</sup> the HBC moiety was initially introduced into the molecular scaffold. HBC, which is a fundamental structure of polycyclic aromatic hydrocarbons (PAHs) and an important segment of two-dimensional graphene, has received much attention due to its self-assembling behavior at the molecular level and rich optoelectronic properties.<sup>14</sup> CPP carbon nanorings bearing HBCs are thought to be good precursors for the growth of carbon nanotubes (Fig. 1). Therefore, it is highly interesting to achieve such molecules. The product was characterized by high resolution mass spectrometry (HR-MS), nuclear magnetic resonance (NMR) spectroscopy, steady-state spectroscopy, and theoretical calculations. In addition, the

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Fig. 1 Carbon nanoring with graphenic sidewalls as the precursor for the growth of CNTs.

scanning tunneling microscopy (STM) imaging technique was successfully applied to view this molecule.

The main challenge of synthesizing cyclo[12]-paraphenylene[2]-2,11-hexabenzocoronenylene lies in the high strain energy that results from ring closure in the cyclization step. Inspired by previous studies,<sup>9b,c,15</sup> we chose the L-shaped unit, *cis*-cyclohexane-1,4-diyl, as the building block of cyclo[12]-paraphenylene[2]-2,11hexabenzocoronenvlene to provide the curvature for subsequent cyclization. As shown in Fig. 2, we hypothesized that 2,11-diboryl hexabenzocoronenvlene can function as a linear unit to construct the U-shaped dibromide building block by Pd-catalyzed crosscoupling with the L-shaped unit via a sequence of oxidative addition-transmetalation-reductive elimination processes.<sup>16</sup> Then, Ni-mediated C-Br/C-Br coupling can connect two U-shaped dibromide building blocks into a macrocycle, followed by the final aromatization step to achieve the target molecule. It is noteworthy to mention that it is very difficult to achieve the CPP product when the cyclodehydrogenation reaction is conducted after cyclization as in previous studies.<sup>13</sup> The cyclodehydrogenation step might be quite difficult in the presence of high ring strain resulting from macrocyclization and the resulting complicated mixtures would make the subsequent separation and purification very difficult. Therefore, it is better to conduct cyclodehydrogenation reaction prior to the macrocyclization reaction.

The synthesis details of the cyclo[12]-paraphenylene[2]-2,11hexabenzocoronenylene 5 are provided in Fig. 3. The L-shaped building block 1 was prepared by adding 4-bromophenyllithium to cyclohexane-1,4-dione, followed by protecting the hydroxyl groups with the methoxymethyl (MOM) group.<sup>9b</sup> The linear unit 2 bearing an HBC structure was prepared from commercially available reagents and the synthesis details can be found in the ESI.<sup>†</sup> We also attempted to use tetra-*tert*-butyl HBC as the graphenic unit. However, its poor solubility in most organic solvents made the subsequent reactions very difficult. With more trials using other functional groups, we finally found that



Fig. 2 Synthesis strategy for target molecule 5.



Fig. 3 Synthesis procedures of 5. Reaction conditions: (a)  $Pd(PPh_3)_4$ ,  $Na_2CO_3$ , n- $Bu_4NBr$ , THF,  $H_2O$ , 66 °C, 48 h, shielded from light; (b)  $Ni(cod)_2$ , 2,2'-bipyridyl, THF, 66 °C, 72 h, shielded from light; (c)  $NaHSO_4$ · $H_2O$ , DMSO, m-xylene, 150 °C, 72 h, in air, shielded from light.

the tetramesityl HBC is a suitable building block for the present work. This tetramesityl HBC unit can be achieved by Kumada coupling of tetrabromohexaphenylbenzene with mesitylmagnesium bromide in THF, followed by cyclodehydrogenation with FeCl<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>.<sup>17</sup> This highly soluble compound was then converted to diboryltetramesityl HBC **2** by the iridium-catalyzed borylation reaction with bis(pinacolato)diboron in a mesitylene/ *tert*-butyl methyl ether mixed solvent.

The next step was performed to construct the U-shaped HBC-containing building block **3**. It can be prepared in a yield of ~68% as a yellow solid by the Suzuki–Miyaura cross-coupling reaction of diboryltetramesityl HBC **2** (1 equiv.) with an excess amount of **1** (10.3 equiv.) in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> catalyst (8.4 mol%), Na<sub>2</sub>CO<sub>3</sub> (7.9 equiv.), and *n*-Bu<sub>4</sub>NBr (1.3 equiv.) in THF/H<sub>2</sub>O (v/v = 7 : 1). With the U-shaped building block **3** in hand, we next investigated the cyclization reaction to synthesize macrocycle **4**. The Ni(cod)<sub>2</sub>-mediated Yamamoto coupling reaction was applied for the synthesis of **4** in the presence of **3** (1 equiv.), Ni(cod)<sub>2</sub> (2.5 equiv.), and 2,2'-bipyridyl (2.7 equiv.) in dry THF.<sup>8c,11,13a,15</sup> The good planarity and high rigidity of the HBC fragment in the backbone of the building precursor seemed to have a deleterious effect on the conformation for cyclization, since the yield for this step was relatively low.

Subsequently, the crude product obtained *via* the macrocyclization step was directly subjected to aromatization without thorough purification. The cyclohexane-1,4-diyl moieties were converted to the corresponding benzene rings with NaHSO<sub>4</sub>·H<sub>2</sub>O in mixed solvents of DMSO and *m*-xylene at 150 °C for 2 days in air. After extensive purification initially by flash column chromatography and then by preparative thin layer chromatography, the target molecule 5 was obtained in ~2% yield over two steps as a yellow solid. This compound was characterized by NMR and HR-MS. Its isotopic pattern obtained in mass spectrometry was in good agreement with the simulated values (Fig. S1, ESI<sup>†</sup>).

The cyclic structure of 5 was further confirmed by the STM imaging technique at the submolecular level. A direct view of the molecular profile was obtained in real space with the molecular film deposited on an Au(111) surface by the drop casting method. Fig. 4 shows the STM images of the molecular film after annealing treatment. A large-scale STM image with singly dispersed carbon nanoring molecules is shown in Fig. 4a. These molecules were adsorbed onto the surface in an unordered fashion. In order to have a clearer view of the morphology of these molecules, a higher resolution image was also collected (Fig. 4b), from which the individual molecule can be recognized and the molecular structure was clearly identified. Two graphenic HBC fragments in each macrocyclic molecule can be clearly resolved with a flat-flying configuration on the surface, embraced by two curved poly-benzene linkers as two bead chains. Note that each benzene group corresponds to one bright spot, but not all the benzene rings can be resolved due to the twisted configuration. The result shows the nanoringlike structure lying on the substrate, which matches the molecular model of 5 very well, further confirming the carbon nanoring structure.

The photophysical properties of cyclo[12]-paraphenylene[2]-2,11-hexabenzocoronenylene 5 were studied using UV-Vis absorption spectroscopy and steady-state fluorescence spectroscopy (Fig. 5a). Tetramesityl HBC was used as a reference compound for comparison. The absorption bands of 5 are observed at 300– 420 nm and the strongest maximum absorption peak is located at  $\lambda_{max} = 371$  nm with the absorption coefficient  $\varepsilon = 1.0 \times 10^5$  cm<sup>-1</sup> M<sup>-1</sup>. Two moderate absorption peaks were also observed with maxima at  $\lambda_{max} = 354$  nm and 425 nm. It is noteworthy to mention that  $\lambda_{max}$  of the absorption bands have obvious redshift in comparison with the reference compound (tetramesityl HBC) and those of other CPPs.<sup>18</sup> This can be ascribed to a much larger  $\pi$  conjugation system of the graphenic HBC units in the structure. The fluorescence emission spectrum of 5 was studied at room temperature under an excitation at 370 nm. Multiple emission peaks were observed



**Fig. 4** STM images of the sample deposited on Au(111). The sample was prepared by the drop casting method and the images were obtained in UHV. (a) A STM image showing the singly dispersed carbon nanoring molecule **5** adsorbed on the Au(111) surface in an unordered fashion. (b) A smaller area STM image showing the existing morphology of the target molecules with the cyclic-shaped structure. The molecular configuration was illustrated by matching the molecular models on the STM image. Imaging conditions: U = 1.5 V, I = 1 nA.



Fig. 5 (a) UV-Vis absorption (solid lines) and fluorescence (dashed lines) spectra of 5 (green line) and tetramesityl HBC (blue line) in CH<sub>2</sub>Cl<sub>2</sub> with a concentration of 5 × 10<sup>-6</sup> M; (b) fluorescence of 5 in CH<sub>2</sub>Cl<sub>2</sub> (5 × 10<sup>-6</sup> M) under 365 nm irradiation using a hand-held UV lamp.

at 471 nm, 491 nm, and 534 nm, respectively. The fluorescence quantum yield was determined to be  $\Phi_{\rm F}$  = 7.5% using anthracene in ethanol as the reference ( $\Phi_{\rm F}$  = 30%). This value is lower than that of tetramesityl HBC ( $\Phi_{\rm F}$  = 14.8%), which might be due to the effect of cyclization. Compound 5 shows intense green-yellow photoluminescence in solution under UV irradiation (Fig. 5b).

Fluorescence decay measurements were performed using a nanosecond pulsed laser system in degassed  $CH_2Cl_2$  solution at room temperature. The lifetime ( $\tau_s$ ) of 5 was determined to be ~ 14.2 ns at 544 nm with single-exponential decay when excited at 390 nm (Fig. S2, ESI<sup>†</sup>). As for tetramesityl HBC, a similar single-exponential decay was observed with  $\tau_s = 18.0$  ns at 520 nm at the same excitation wavelength (Fig. S3, ESI<sup>†</sup>). Compared to CPPs ( $\tau_s = 10.6$  ns for [9]CPP and  $\tau_s = 2.2$  ns for [12]CPP<sup>18</sup>), the fluorescence lifetime of 5 is longer, which could be attributed to the contribution of the HBC units.

Finally, we performed a density functional theory (DFT) study at the B3LYP/6-31G level to reveal the electronic nature of the cyclo[12]-paraphenylene[2]-2,11-hexabenzocoronenylene 5. The optimized geometry and pictorial representations of frontier molecular orbitals (MOs) of 5 are shown in Fig. 6. The optimized geometry shows a  $C_{2h}$  symmetry with a highly twisted CPP core. The diameters were calculated to be around 19.5 Å and 26.6 Å from Cartesian coordinates (Table S1, ESI<sup>+</sup>). Two more side views of the optimized structure of 5 are shown in Fig. S4 (ESI<sup>+</sup>). The energy levels of the HOMO and the LUMO are -5.10 eV (HOMO) and -1.88 eV (LUMO), respectively. The energy diagrams of the frontier MOs of 5 are shown in Fig. S5 (ESI<sup>†</sup>). Based on the calculation results, the spatial distribution of the HOMO and the LUMO of 5 is mainly localized on two HBC moieties. The fact that frontier MOs of 5 are dominated by HBC structures is likely the main reason why the shapes of its UV-Vis absorption and fluorescence spectra show similarity with those of tetramesityl HBC. The strongest maximum absorption peak for 5 observed at  $\lambda_{max}$  = 371 nm can be assigned to the HOMO-4  $\rightarrow$  LUMO 3, HOMO-3  $\rightarrow$  LUMO 4, HOMO-1  $\rightarrow$ LUMO 5, and HOMO–5  $\rightarrow$  LUMO 1  $\pi$ - $\pi$ \* transitions at 379 nm and 378 nm with oscillator strengths f = 2.4562 and f = 2.3971, respectively (Table S2, ESI<sup>†</sup>).



Fig. 6 Optimized geometry and frontier MOs of **5**: (a) top view of the molecular structure, (b) side view of the molecular structure, (c) HOMO of **5**, (d) LUMO of **5**.

In conclusion, we synthesized an HBC-containing cycloparaphenylene, cyclo[12]-paraphenylene[2]-2,11-hexabenzocoronenylene. A palladium-catalyzed cross-coupling reaction was used to construct our building block 3 containing hexabenzocoronene and L-shaped cyclohexane units. The macrocyclization step was achieved by Ni-catalyzed Yamamoto coupling, followed by aromatization to transform cyclohexane moieties into phenyl units. This synthesis route provides a good strategy to overcome the problem of cyclodehydrogenation in the presence of high ring strain and successfully achieved the target molecule. This molecule was characterized by HR-MS, NMR, and STM techniques. The direct view of the molecular profile further confirmed its structure. Further challenges including designing and synthesizing carbon nanorings more similar to CNT segments, and producing sizedefined CNTs are subjects of research currently underway in our laboratory.

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