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Facile Three-Step Synthesis and Photophysical Properties of [8]-, [9]-, and [12]Cyclo-1,4-naphthalene Nanorings via Platinum-Mediated Reductive Elimination

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Herein we report the facile three-step synthesis of [8]-, [9]-, and [12]cyclo-1,4-naphthalenes nanorings as the conjugated segments of carbon nanotubes. The nanorings were created by platinum-mediated assembly of 1,4-naphthalene-based units and subsequent reductive elimination in the presence of triphenylphosphine. This present platinum-mediated approach is attractive because of its simple three-step process to produce the targeted nanorings in a high overall yield. In addition, their photophysical properties were studied using UV-Vis spectroscopy and photoluminescence (PL) spectroscopy, which further revealed their unique size-dependent properties.

Cyclic π-conjugated organic materials have attracted much attention in recent years. Cycloparaphenylenes (CPPs, Figure 1a) are hoop-shaped aromatic hydrocarbons consisting of *para*-linked phenylene rings, which have been received significant interest in the last few years due to their highly symmetric topological structures as the shortest structural segment of armchair carbon nanotubes (CNTs, Figure 1b).[1, 2] Moreover, CPPs have demonstrated many potential applications in material science and supramolecular chemistry.[3-6] It has been proposed the CPPs can be serve as seed compounds for diameter-controlled growth of CNTs.[7, 8] The bottom-up chemical synthesis of CPPs was proposed a few decades ago[1, 9, 10] but despite the simple structure, this synthesis was only recently achieved, with Bertozzi and Jasti reporting the first synthesis of [9]-, [12]-, and [18]CPPs in 2008.[11] After long-term exploration and unremitting efforts, CPPs with different diameters ([5]-[16], [18]CPPs) have been achieved by different research groups.[11-18]

Based on these fundamental studies, further π-extended CPP structures can be considered as closer precursors of CNTs and have attracted great attention. In the literature, different derivatives of CPPs have been synthesized using polycyclic aromatic hydrocarbons (PAHs) as the building blocks, such as chrysene,[19] anthracene,[1, 10] and pyrene.[20] Our group reported the use of a larger PAH, hexa-*peri*-hexabenzocoronene (HBC), as the building unit to synthesize highly conjugated giant nanorings.[6, 21] The first synthesis of a π-extended naphthalene-based nanoring, [9]cyclo-1,4-naphthalene ([9]CN), has been achieved from a L-shaped building unit by Itami and coworkers in 2012.[22] More recently, they have also synthesized a few even-numbered carbon nanorings, [*n*]CNs (*n* = 8, 10, 12, and 16), using a similar strategy.[23] Unfortunately, despite the successful synthesis, these studies displayed very poor yields for the final products (0.1% for [8]CN, 1.2% for [9]CN, and 1.5% for [12]CN), which has seriously hampered the further physical studies of naphthalene-based CPPs and their utilization in bottom-up synthesis of uniform CNTs. Therefore, the development of a new facile synthesis route is highly desired.

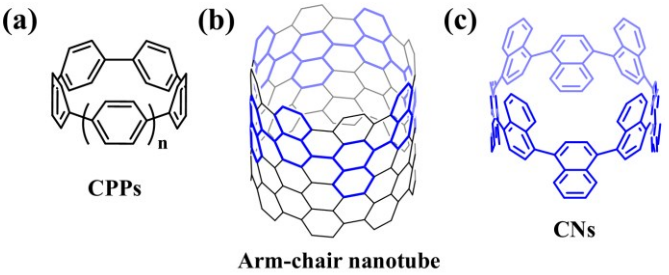

Figure 1. (a) Structure of [n + 4]CPP. (b) Structure of (8,8)armchair carbon nanotubes (CNTs). The constituent [8]CN unit is shown in blue. (c) Molecular structure of [8]CN.

In 2010, Yamago and coworkers developed a platinum-mediated assembly strategy to synthesize [8]CPP.[17] After that, more CPPs with difference sizes were also successfully synthesized by the same group.[12-14] Similar to the synthesis of CPPs, the major bottleneck for achieving CNs also lies in the increased strain energy resulting from the curved structure. Inspired by the platinum-mediated assembly strategy for the synthesis of CPPs,[6, 17] we envision that CNs could also be synthesized by the platinum-mediated

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assembly of naphthalene-based units and subsequent reductive elimination of platinum to form our target molecules, although the para position in the naphthalene unit is more bulky which probably causes more hindrance than that in the phenylene unit. Herein we report the synthesis of [8]-, [9]-, and [12]CNs with higher yields based on this platinum-mediated strategy. In addition, the CNs' photophysical properties using both steady-state and time-resolved spectroscopies in THF are experimentally investigated.

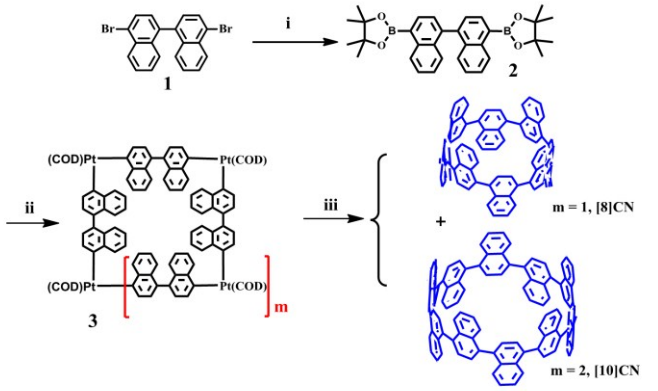

Figure 2. Synthesis procedures for [8]CN and [10]CN. Reagents and conditions: (i) **1** (1.0 equiv.), Bpin-bpin (3.0 equiv.), Pd(dppf)Cl_2 (5 mol%), KOAc (5.0 equiv.), 1,4-dioxane, 100 °C, 36 h; (ii) **2** (1.0 equiv.), Pt(COD)Cl_2 (1.0 equiv.), CsF (4.0 equiv.), THF, 40 °C, 24 h; (iii) PPh_3 (10.0 equiv.), toluene, 110 °C, 36 h.

To accomplish the above-mentioned goal, the naphthalene-based units should be functionalized with boronate esters or trialkyltin groups, which can be readily reacted with the platinum complex to form macrocycle precursors.[6, 17, 24-26] With these macrocycle precursors in hand, the final [*n*]CNs products can be obtained after reductive elimination of platinum. Initially, 4,4′-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-1,1′-binaphthalene (**2**) was synthesized from 4,4′-dibromo-1,1′-binaphthyl (**1**) via the Miyaura borylation reaction in the presence of Pd(dppf)Cl_2, bis(pinacolato)diboron, and KOAc. The synthesis details are provided in the supporting information (SI). The molecular structure of compound **3** was characterized by ^1H NMR (Figure S1), ^{13}C NMR (Figure S2) and ESI mass spectrometry (Figure S3). Next, compound **2** was treated with one equivalent of Pt(COD)Cl_2 (COD = 1,5-cyclooctadiene) in the presence of four equivalents of cesium fluoride in THF for 24 hours under argon. The resulting platinum-mediated complex **2** was obtained in a 40% yield as a white precipitate, which was subsequently subjected to reductive elimination by treating with ten equivalents of triphenylphosphine as a coordination ligand under refluxing anhydrous toluene for 36 hours. After purification through preparative thin-layer chromatography, the target product, [8]CN (2.6%) was obtained. These results indicate that the assembly of compound **2** with Pt(COD)Cl_2 can successfully provide a tetra-nuclear platinum macrocycle precursor. Interestingly, [10]CN was also detected by mass spectroscopy (Figure S10), but pure [10]CN was very difficult to isolate because of its much lower yield. The synthesis procedure of [8]CN is summarized and shown in Figure 2.

Encouraged by these results, we turned our attention to synthesizing larger [*n*]CNs using this approach. The starting material was functionalized with one more naphthalene unit to get 4,4′′-dibromo-1,1′:4′,1′′-ternaphthalene (**4**). After a similar Miyaura borylation reaction, compound **4** was readily transformed into 4,4′′-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-1,1′:4′,1′′-ternaphthalene (**5**), which is another key precursor for the synthesis of [*n*]CNs. Compound **5** was well characterized by ^1H (Figure S4) and ^{13}C NMR (Figure S5), as well as ESI mass spectrometry (Figure S6). The synthesis details can be found in the SI. Following a similar procedure to that of [8]CN, compound **5** was reacted with Pt(COD)Cl_2 to form the intermediate **6**. Finally, two types of carbon nanorings [9]CN (3.0%) and [12]CN (3.5%) were obtained after reductive elimination of the intermediate **6**. This result suggests that the assembly of compound **5** with Pt(COD)Cl_2 mainly afforded a mixture of tri- and tetra-nuclear platinum macrocycle precursors. The synthesis procedure for [9]CN and [12]CN is shown in Figure 3.

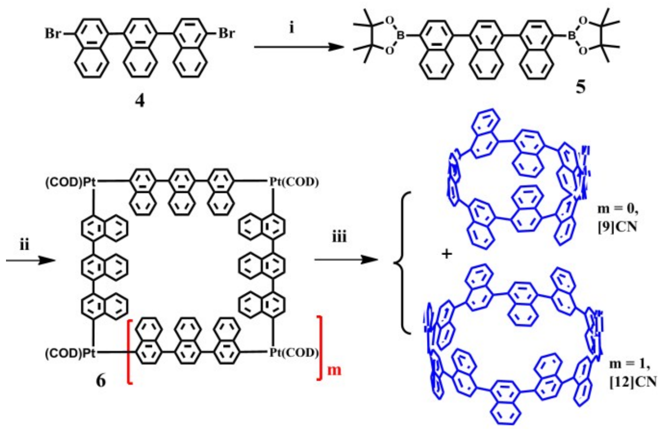

Figure 3. Synthesis procedures for [9]CN and [12]CN. Reagents and conditions: (i) **4** (1.0 equiv.), Bpin-bpin (3.0 equiv.), Pd(dppf)Cl_2 (5 mol%), KOAc (5.0 equiv.), DMF, 120 °C, 36 h; (ii) **5** (1.0 equiv.), Pt(COD)Cl_2 (1.0 equiv.), CsF (4.0 equiv.), THF, 40 °C, 24 h; (iii) PPh_3 (10.0 equiv.), toluene, 110 °C, 36 h.

The subsequent increase of the naphthalene unit to make larger nanorings was hampered by the poor solubility. As a result, using the platinum-mediated assembly and reductive elimination approach, [8]-, [9]-, [10]-, and [12]CNs were synthesized and pure [8]-, [9]-, and [12]CNs were obtained by careful separation. The structures of these three nanorings were confirmed by MALDI-TOF-MS spectrometry (Figures S7-S9). Moreover, the ^1H NMR data (Figures S11-S13) are consistent with the data reported by Itami and coworkers.[23] Compared with the yields of the reported method using a curved naphthalene-based precursor (0.1% for [8]CN, 1.2% for [9]CN, and 1.5% for [12]CN),[23] our present approach has much higher yields (2.6% for [8]CN, 3.0% for [9]CN, and 3.5% for [12]CN). Therefore, platinum-mediated assembly strategy is another interesting pathway for synthesis of [*n*]CNs from easily prepared starting materials **1** and **4**.

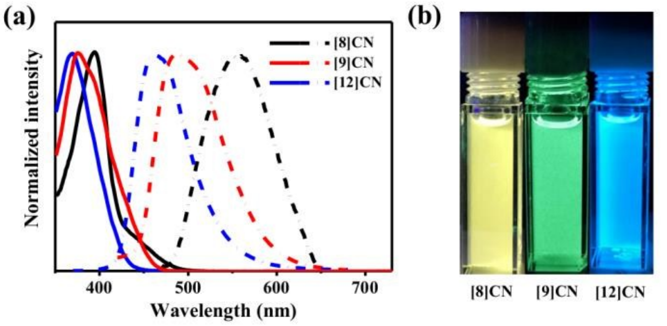

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Figure 4. (a) UV-vis absorption (solid line) and fluorescence (dash line) spectra of [8]CN (black), [9]CN (red), and [12]CN (blue). (b) Luminescent photographs of [8]CN (yellow), [9]CN (green), and [12]CN (blue) in THF under UV irradiation at λ = 365 nm.

Table 1. Absorption and emission data for [*n*]CNs[a]

Compounds	$\lambda_{abs}{}^{b}$ (nm) (ε, L mol^{-1} cm^{-1})	$\lambda_{em}{}^{c}$ (nm) (τ^{d}, ns)	$\Phi_F{}^{e}$
[8]CN	394 (1804)	556 (5.3)	0.22
[9]CN	376 (4312)	486 (1.7)	0.34
[12]CN	369 (32901)	463 (1.0)	0.42

[a] Data obtained at room temperature in THF. [b] Maximum absorption. [c] Maximum emission upon excitation at 350 nm. [d] Lifetime. [e] Fluorescence quantum yields.

The photophysical properties of the [8]-, [9]-, and [12]CNs in THF were further investigated using UV-vis absorption spectroscopy, steady-state fluorescence spectroscopy, and time-resolved fluorescence decay. The absorption and emission spectra are shown in Figure 4 and the data are summarized in Table 1. Interestingly, unlike CPPs, which absorb UV-vis light at similar wavelength regardless of their different sizes,[12] the UV-vis absorption spectra of the [8]-, [9]-, and [12]CNs clearly exhibit size-dependent properties: The maximum absorption (λ_{abs}) were blue-shifted with an increase in the size of the [*n*]CNs nanorings. This behavior is consistent with reports by Itami and coworkers.[23] The fluorescence emission measurements were performed under an excitation at 350 nm, and all [*n*]CNs emitted strong fluorescence in a variety of colors (yellow for [8]CN, green for [9]CN, and blue for [12]CN) in THF solutions). The fluorescence spectra also exhibit size-dependent properties. With increasing size of [*n*]CNs, the maximum emission (λ_{em}) were significantly blue-shifted. The λ_{em} peaks are 556 nm, 486 nm, and 463 nm for [8]-, [9]-, and [12]CNs, respectively. The fluorescence quantum yields (Φ_F) of [*n*]CNs were determined by using anthracene in ethanol as the reference. The Φ_F values are provided in Table 1 and the highest Φ_F is 0.42 for [12]CN. Similarly, the Φ_F values of [*n*]CNs increased with increasing size.

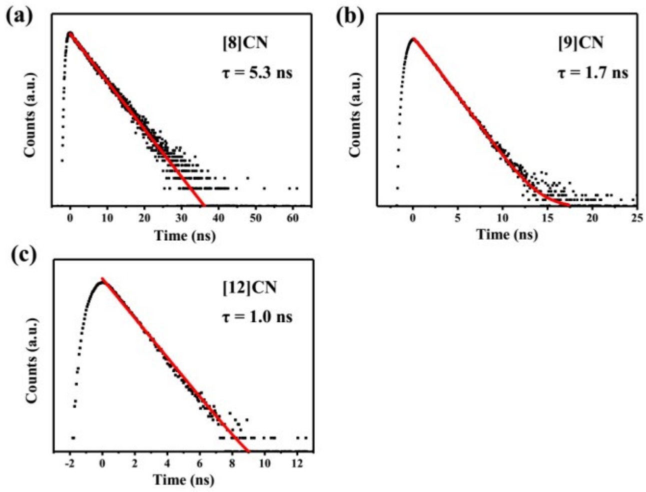

Figure 5. Luminescent decay profiles of (a) [8]CN, (b) [9]CN, and (c) [12]CN in THF at 298 K.

Fluorescence decay tests were conducted using a nanosecond pulsed laser system in degassed THF solution at room temperature. The fluorescence decay of [*n*]CNs followed first-order kinetics with a lifetime (τ) = 5.3 ns for [8]CN, 1.7 ns for [9]CN, and 1.0 ns for [12]CN, as measured by the single-photon counting method (Figure 5). According to the equation $k_r = \Phi_F/\tau$,[27] their radiation decay rate constant (k_r) could also be determined to be 4.2 × 10^7 s^{-1} for [8]CN, 2.0 × 10^8 s^{-1} for [9]CN, and 4.2 × 10^8 s^{-1} ns for [12]CN.

Conclusions

In conclusion, we developed a novel and efficient three-step synthesis approach to achieve [8]-, [9]-, and [12]CNs nanorings based on the platinum-mediated assembly of naphthalene units and subsequent reductive elimination. This synthesis route provides a good strategy to overcome the strain energy resulting from the curved structure and successfully achieved the target molecules with a relatively high yield. This method may open a new way for the synthesis of [*n*]CNs from easily prepared starting materials **2** and **5** and facilitate their further utilization in bottom-up synthesis of uniform CNTs. In addition, their photophysical properties in THF were experimentally investigated, revealing their unique size-dependent properties.

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TOC

Facile three-step synthesis of [8]-, [9]-, and [12]cyclo-1,4-naphthalenes nanorings were firstly accomplished by platinum-mediated assembly of 1,4-naphthalene-based units and subsequent reductive elimination reactions.