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A strained π-extended [10]cycloparaphenylene carbon nanoring

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ABSTRACT

Herein, we report the facile synthesis of a highly strained hexabenzocoronene-containing carbon nanoring, cyclo[4]-paraphenylene[2]-2,11-hexabenzocoronenylene (**[4,2]CPHBC**), as the segment of a [10,10] single-walled carbon nanotube ([10,10]SWNT). **[4,2]CPHBC** was synthesized based on the platinum-mediated assembly of diborylbiphenyl and diborylhexabenzocoronene, forming a tetranuclear platinum complex, followed by reductive elimination. This nanoring molecule was confirmed by NMR and HR-MS, and its photophysical properties were studied using steady-state and time-resolved spectroscopies. Moreover, the selective supramolecular host-guest interaction between **[4,2]CPHBC** and C_{60} was also investigated.

Cyclic conjugated molecules have attracted extensive attention because of their unique optoelectronic properties, esthetic appeal and synthetic challenges [1–4]. Among these types of compounds, [*n*]cycloparaphenylenes ([*n*]CPPs), the simplest structural unit of armchair carbon nanotubes (CNTs), were hypothesized half a century ago [5], which were synthesized in 2008 for the first time by Jasti and Bertozzi [6]. Since then, [*n*]CPPs with different diameters and various CPP derivatives have been synthesized using different synthetic methods [7–12]. Among the family of [*n*]CPPs, [10]CPP is a very interesting member due to its highest binding affinity to fullerene C_{60}. The supramolecular interaction between [10]CPP and C_{60} has been recently studied. The Yamago group and Jasti group have confirmed that [10]CPP forms a supramolecular complex with C_{60} by NMR and crystal structure, respectively [13,14]. In 2015, Itami reported the CPP-based ionic donor–acceptor supramolecule $Li^{+}@C_{60}$[10]CPP and confirmed the existence of a strong charge-transfer interaction between [10]CPP and $Li^{+}@C_{60}$ [15]. Moreover, modular porphyrin-[10]CPP-fullerene complexes and a rotaxane based on C_{60} and [10]CPP were developed by Delius and coworkers [16,17]. All these reports demonstrated that [10]CPP is a useful host scaffold for supramolecular chemistry.

Recently, much effort has been focused on fabricating π-extended carbon nanorings because they more closely resemble a CNT segment and display many unexpected properties. Synthesis of π-extended carbon nanorings can be achieved by post- and preconstruction [18]. In 2019, our group reported the synthesis of TBP-[10]CPP and HBC-[10]CPP by a preconstruction method, which showed enhanced binding constants compared to [10]CPP and generated photocurrents under visible light [19]. More recently, Araceli and coworkers used a similar strategy to synthesize hept–HBC-[10]CPP, which also displayed increased binding affinity with C_{60} and versatile photochemical responses in this host-guest complex [20]. Using a postconstruction strategy, we reported a fixed two-bond approach to synthesize a nanographene-embedded [10]CPP carbon nanoring by the Scholl reaction, which can be used as the electron transport material [21]. Despite all of the above progress, a highly strained π-extended carbon nanoring containing two HBC units incorporated into a [10]CPP framework has not been achieved, and the study of its behavior as a supramolecular host is still unexplored.

Herein, we report the synthesis of a hexabenzocoronene (HBC)-containing cycloparaphenylene carbon nanoring, cyclo[4]-paraphenylene[2]–2,11-hexabenzocoronenylene (**[4,2]CPHBC**) (Fig. 1), which represents the sidewall segment of [10,10]SWNT, using the platinum-mediated assembly route. **[4,2]CPHBC** was fully characterized by high-resolution mass spectrometry (HR-MS), nuclear magnetic resonance (NMR) spectroscopy, and steady-state and time-resolved spectroscopies. Moreover, the selective supramolecular host-guest interaction between **[4,2]CPHBC** and C_{60} was also investigated.

To obtain a highly strained π-extended [10]CPP carbon nanoring containing two HBC units, it is important to rationally select

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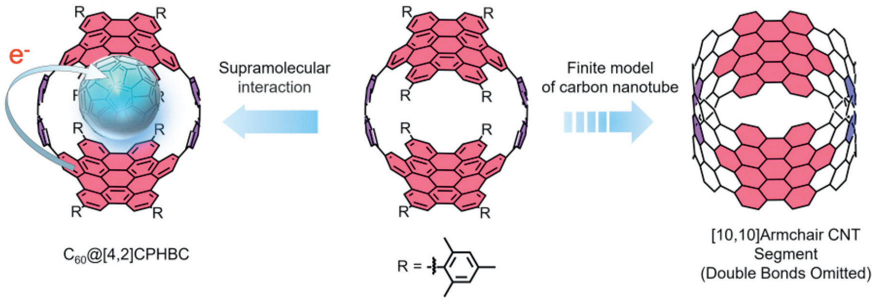

Fig. 1. A carbon nanoring with double graphenic sidewalls, proposed as the conjugated segment of armchair [10,10]CNTs.

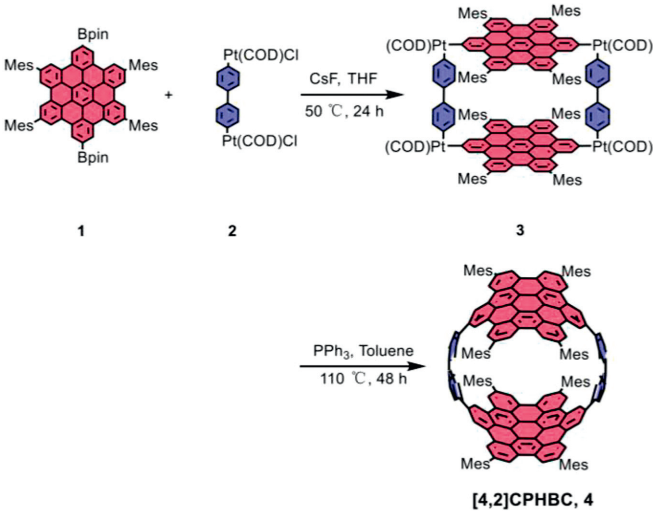

Fig. 2. Synthesis procedure of **[4,2]CPHBC**.

the synthesis methodology. Previous studies reported the synthesis of conjugated macrocycles with two different aromatic subunits in an -A-B-A-B- pattern *via* the platinum-mediated assembly route [22,23]. Inspired by these reports, **[4,2]CPHBC** was synthesized by the assembly of two different building units to form a tetranuclear metal complex with a square shape, followed by reductive elimination.

The synthesis procedure for **[4,2]CPHBC** is shown in Fig. 2. Precursor **1** was prepared according to previously reported study [24]. Transmetalation of diborylbiphenyl with dichloro(1,5-cyclooctadiene)platinum(II) provides precursor **2**. Compound **1** was heated with an equimolar amount of **2** in THF containing CsF as the base, giving square-shaped platinum complex **3**. Then, **3** was directly subjected to reductive elimination of platinum by heating in the presence of excess triphenylphosphine in toluene for 48 h under nitrogen. Purified by flash column chromatography and preparative thin-layer chromatography, the final product (**[4,2]CPHBC**) was obtained in 12% yield over two steps as a yellow solid.

The successful synthesis of the target compound **[4,2]CPHBC** can be confirmed by HR-MS and NMR spectroscopies (Figs. 3a and b). The molecular weight of **[4,2]CPHBC** was confirmed by MALDI-TOF MS spectrometry. A main peak at *m/z* 2290.0016 was observed (calcd. for $C_{180}H_{128}$ $[m/z]^+$: 2290.0050), indicating the successful synthesis of the target molecule (Fig. 3a). The ^1H NMR spectrum of **[4,2]CPHBC** exhibited six sets of peaks in the aromatic region, indicating its highly symmetric structure (Fig. 3b). According to the ^1H NMR spectra of tetramesityl-substituted HBC reported in the literature [25], the singlets at δ 8.84, 8.77, and 8.73 ppm in ^1H NMR can be assigned to the protons a, b_1, and b_2 of the HBC units, respectively. The two doublets at δ 7.69 and 7.38 ppm are from protons d and e in the *para*-linked biphenyl. The aromatic protons c on the mesityl groups were observed at δ 7.13 and 7.08 ppm as two singlet signals. Thus, the observed signals in ^1H NMR for **[4,2]CPHBC** can be well assigned.

UV–vis absorption spectroscopy, steady-state fluorescence spectroscopy, and time-resolved fluorescence decay were used to investigate the photophysical properties of **[4,2]CPHBC**. For comparison, [10]CPP was used as a reference compound, and the absorption spectra were measured at room temperature (Fig. 3c). The absorption bands of **[4,2]CPHBC** were observed between 300 nm and 490 nm, and the maximum absorption peak (λ_{max}) was located at 373 nm with an absorption coefficient (ε) of approximately 5.4×10^4 L mol^{-1} cm^{-1}. The absorption spectrum of **[4,2]CPHBC** has a broad shoulder in the visible region between 410 and 490 nm. Compared with the absorption of [10]CPP, this absorption feature in the visible region could be ascribed to the contribution of the embedded large conjugated HBC units. The fluorescence emission spectrum of **[4,2]CPHBC** was recorded at room temperature at an excitation wavelength of 350 nm (Fig. 3c). Multiple emission peaks were observed at 482 nm and 515 nm. The fluorescence quantum yield was determined to be $\Phi_F = 1.8\%$ using anthracene in ethanol as the reference ($\Phi_F = 30\%$), which is much lower than that of [10]CPP ($\Phi_F = 65\%$), probably due to the high proportion of no nradiative decay in the low-energy emission. Interestingly, the emission colors of [10]CPP and **[4,2]CPHBC** are blue and green, respectively, under a hand-held UV lamp (365 nm) (Fig. 3c, inset). Fluorescence decay measurements were performed through a nanosecond pulsed laser system in degassed CH_2Cl_2 solution at room temperature (Fig. 3d). Upon excitation at 390 nm, the decay of **[4,2]CPHBC** follows first-order kinetics with a lifetime (τ_s) of 12.53 ns at 482 nm.

The cyclic structures of [*n*]CPPs and their analogs are suitable for supramolecular assembly. [10]CPP has an ideal diameter to encapsulate C_{60}, showing a binding constant K_a of 2.79×10^6 L/mol [13]. Moreover, π-extended carbon nanorings based on [10]CPP display a highly enhanced binding affinity for C_{60} [19]. All these studies indicate that it is possible for **[4,2]CPHBC** to form a host-guest supramolecular complex with fullerene C_{60} (Fig. 4a). The supramolecular interaction can be confirmed by HR-MS spectrometry. A new mass peak appeared at *m/z* 3011.0028 (calcd. for $C_{240}H_{128}$ [C_{60}@**[4,2]CPHBC**]$^+$: 3011.0083), suggesting the formation of a C_{60}@**[4,2]CPHBC** complex (Fig. S6 in Supporting information). Moreover, we performed fluorescence quenching titration with C_{60} solution in toluene to confirm the existence of supramolecular interactions between **[4,2]CPHBC** and C_{60} (Fig. 4b). When C_{60} was added into a **[4,2]CPHBC** solution, the fluorescence of **[4,2]CPHBC** was significantly quenched under a hand-held UV lamp excited at 365 nm (Fig. 4b, inset). Based on the observed fluorescence quenching and fitting of the corresponding data (Fig. 4c), the binding constant K_a between **[4,2]CPHBC** and C_{60} was calculated to be $\sim 2.77 \times 10^7$ L/mol. Compared with the K_a of C_{60}@[10]CPP ($2.79 \times$

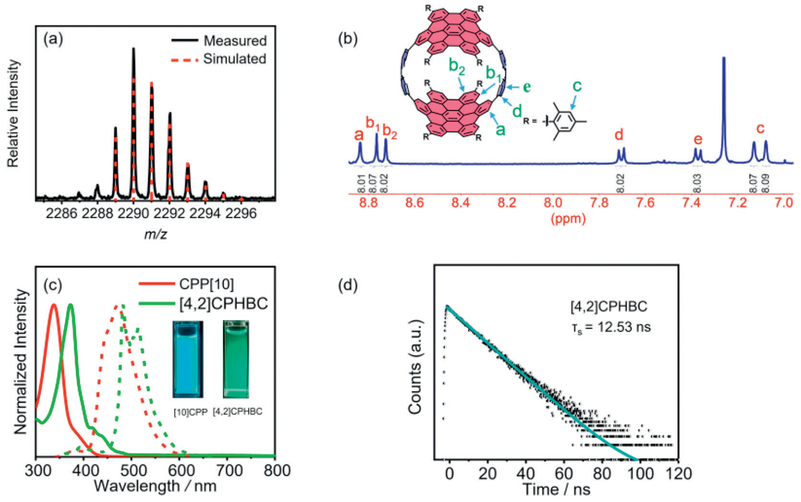

Fig. 3. (a) The MALDI-TOF spectrometry and simulated data for **[4,2]CPHBC**. (b) ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the aromatic regions for **[4,2]CPHBC**. (c) UV–vis absorption (solid line) and fluorescence (dashed line) spectra of [10]CPP (red) and **[4,2]CPHBC** (green) in CH_2Cl_2. Inset: photographs of the fluorescence of [10]CPP and **[4,2]CPHBC** under 365 nm irradiation. (d) Emission lifetime for **[4,2]CPHBC** in CH_2Cl_2 measured at 390 nm.

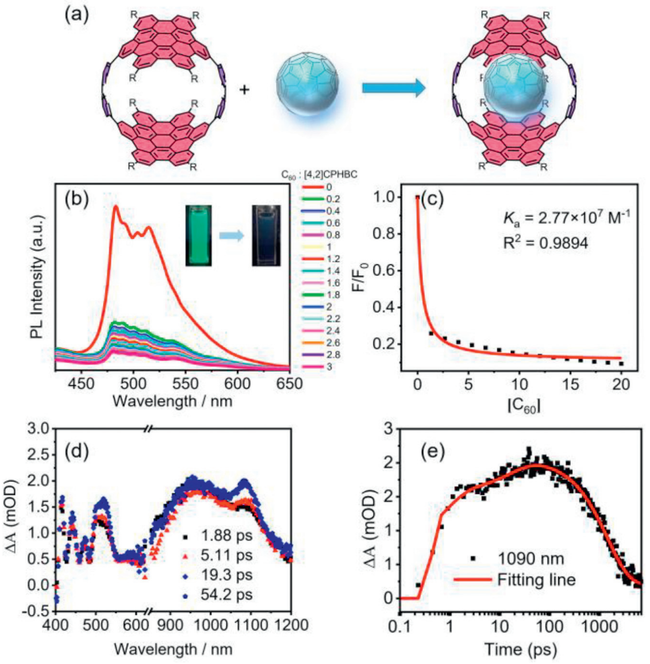

Fig. 4. (a) Supramolecular interaction between **[4,2]CPHBC** and C_{60}. (b) Fluorescence spectra of **[4,2]CPHBC** (0.67×10^{-6} mol/L) titrated with C_{60} in toluene at room temperature. Inset: Photographs of the emission of **[4,2]CPHBC** before and after the addition of C_{60}. The concentrations of C_{60} range from 0 to 2.0×10^{-6} mol/L from top to bottom. (c) Correlation of $[C_{60}]$ on the fluorescence intensity of **[4,2]CPHBC** in toluene for calculating K_a. R^2 represents the standard deviation. (d) Differential absorption spectra at 1.88, 5.11, 19.3 and 54.2 ps obtained upon fs-TA experiments ($\lambda_{ex} = 350$ nm) of the C_{60}@**[4,2]CPHBC** complex in toluene at room temperature. (e) Kinetics and corresponding fitting line of the ESA peak of the C_{60} radical anion at 1090 nm.

10^6 L/mol), the increased binding constant between **[4,2]CPHBC** and C_{60} can be ascribed to the stronger π-π interactions with large π-extended hexabenzocoronene units.

To understand the quenching mechanism between the photoexcited **[4,2]CPHBC** host and C_{60} guest, femtosecond transient absorption (fs-TA) measurements were performed. For both **[4,2]CPHBC** and the C_{60}@**[4,2]CPHBC** complex, the excitation wavelength was 350 nm. Upon excitation of **[4,2]CPHBC**, the excited state absorption (ESA) spectrum showed a singlet excited state with maximum peaks at 410, 433, 448, and 1030 nm (Fig. S5 in Supporting information). For C_{60}@**[4,2]CPHBC**, distinct maximum ESA peaks evolved at 415, 442, and 525 nm in the visible region as well as at 1090 nm in the near-infrared region (Fig. 4d). The ESA peak maximized at approximately 1090 nm is well known as the radical anion absorption feature of C_{60}, which is related to the one-electron reduction process of C_{60} [16]. These time-resolved absorption changes presumably involve one-electron oxidation of **[4,2]CPHBC** to form **[4,2]CPHBC**$^{+\cdot}$ species. By fitting the formation and decay kinetics of the radical anion probed at 1090 nm (Fig. 4e), the rate constants for charge separation and recombination can be determined as 5.7×10^{10} and 6.7×10^8 s^{-1}, respectively. Therefore, the intermolecular fluorescence quenching process between the **[4,2]CPHBC** host and C_{60} guest can be confirmed by the electron transfer process.

In summary, we have successfully synthesized a highly strained HBC-containing cycloparaphenylene carbon nanoring, **[4,2]CPHBC**, as the sidewall segment of [10,10]SWNT by a platinum-mediated reductive-elimination reaction. The target product was confirmed by NMR and HR-MS results. In addition, steady-state spectroscopy revealed its unique photophysical properties. Furthermore, the supramolecular host-guest interaction between **[4,2]CPHBC** and C_{60} was investigated, and their binding constant was up to approximately 2.77×10^7 L/mol in toluene. The value is approximately 10 times larger than that obtained for C_{60}@[10]CPP. Transient absorption measurements demonstrated an efficient electron transfer process from **[4,2]CPHBC** (donor) to C_{60} (acceptor). This highly strained carbon nanoring could provide insights for the development of the controllable synthesis of CNTs and potential applications in supramolecular chemistry. Further challenges, including the design and synthesis of fully conjugated carbon nanobelts and the production of size-specific short CNTs are subjects of research currently in progress in our laboratory.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2023.109055.

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