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Synthesis, Photophysical and Supramolecular Properties of a π -Conjugated Molecular Crown Containing a Pentagonal Unit: A Model Compound for Fullerene C₂₄₀

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Abstract The total synthesis of carbon onions is a significant challenge in the fields of materials science and organic chemistry. To date, the synthesis of even a fragment of fullerene C_{240} and its smallest carbon onion $C_{60}@C_{240}$ remains poorly explored. Herein, we demonstrate a bottom-up strategy to produce a novel π -extended molecular crownshaped molecule (MC3) containing curved pentagonal and hexagonal units. This molecular crown represents a curved model compound for fullerene C_{240} and is fully characterized by NMR, mass spectrometry, UV-vis absorption, and from its emission spectra. Its supramolecular host–guest interaction with fullerene C_{60} is also investigated. MC3 and $C_{60}@MC3$ can potentially be employed as seeds or templates for the bottom-up synthesis of fullerene C_{240} and the carbon onion $C_{60}@C_{240}$, respectively.

Key words carbon onion, fullerenes, macrocycles, bottom-up synthesis, supramolecular chemistry

Fluoranthene-based polycyclic aromatic hydrocarbons (FPAHs) are a class of organic compounds that are related to buckminsterfullerenes and are used for constructing fused hexagonal and pentagonal arrays of carbon atoms.¹ FPAHs have attracted significant interest due to their potential applications in fluorescent chemosensors, supramolecular assemblies, and nanovehicles.² In the past few decades, FPAHs (such as corannulene and sumanene) have been intensively investigated as subunits of C_{60} .³ The pioneering work by Scott and co-workers produced the first rational synthesis of C_{60} using small FPAH molecules.⁴

The curvature provided by the pentagonal unit is usually required to synthesize fullerenes, hence many previous studies on fullerene chemistry focused on the positive curvature from the pentagon unit as segments of fullerene C_{60} and C_{70} .⁵ Based on their geometrical features, there are two kinds of $I_{\rm h}$ fullerenes:⁶ One is 20k² and the other is 60k², where k = 1, 2, 3, etc. Fullerenes of the latter type, such as C_{60} , C_{240} , C_{540} , C_{960} , and C_{1500} , can be constructed geometrically by combining 12 pentagonal faces and varying the number of hexagonal faces in their molecular structures. Based on these fullerene structures, it has been proposed that the central part, the [n]cyclo-para-phenylene $([n]CPP)^7$ unit, can be first obtained by n hexagonal faces bonding through the *para*-position, and then other carbon atoms filling into the framework to form the corresponding fullerene structure.⁶ Therefore, the structures of the pentagonal faces and [5]cyclo-para-phenylene curved framework can be considered as vital parts of C₆₀. Similarly, the pentagonal faces and [10]cyclo-para-phenylene curved framework are representative structures in C₂₄₀.

Carbon onions, firstly discovered by Ugarte in 1992,⁸ are obtained by intense electron irradiation of carbon soot. These structures are spherical particles based on multiple carbon layers surrounding a buckyball core, with their name being derived from their concentric structure, which is similar to an onion. The structural formula of the ideal carbon onion can be expressed as $C_{60}@C_{240}@C_{540}@$ the ellipsis between C_{960} and C_{60n}^2 (where n represents the number of layers). Subsequently, $C_{60}@C_{240}$ was first constructed in 2000 by heating at high temperature.⁹ In recent years, curved molecular carbon structures have attracted much

В

 MC3 Fullerene C_{sub} segment
 Image: Comparison of the smallest carbon onion

 MC1
 MC1

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Figure 1 Top: The design of the molecular crown **MC3** as a finite model of fullerene C_{240} . The supramolecular complex between **MC3** and fullerene C_{60} can form the conjugated segment of the smallest stable carbon onion ($C_{60}@C_{240}$). Bottom: Two curved molecular crowns containing only hexagonal units (**MC1** and **MC2**)

attention and have been used to construct many interesting structures such as carbon nanotubes, fullerene segments, and molecular peapods.^{7i,10}

Herein, we report the synthesis of a novel π -extended molecular crown-shaped molecule (**MC3**) bearing both pentagonal and hexagonal units. Previously, we reported two curved molecular crowns containing only hexagonal units (named as **MC1** and **MC2**).¹¹ In addition, small fullerene C₆₀ is incorporated into the framework to produce the corresponding supramolecular complex. The complex can be regarded as a carbon onion fragment of C₆₀@C₂₄₀ (Figure 1). Analysis of the UV-vis absorption and emission spectra revealed its interesting photophysical properties, and the supramolecular host–guest interaction between **MC3** and C₆₀ was also investigated.

To construct the segment of C_{240} with both pentagon and curved hexagons, our synthetic strategy was to link two parts, one a curved component and the other an FPAH pentagonal component, into a crown-shaped molecule via a Pd-catalyzed Suzuki coupling reaction. The C-shaped synthon 10 (see Scheme 2), which can be considered as the curved hexagon component precursor, was prepared according to previous studies.^{11,12} The FPAH pentagonal component was constructed and then embedded into the cyclic structure. Scheme 1 summarizes the synthesis of the FPAH component. Initially, compound 1 was used to synthesize diphenyl ketone 2 using dicyclohexylcarbodiimide (DCC) and N,N-dimethylaminopyridine (DMAP).¹³ Next, a Knoevenagel condensation between compounds 2 and 3 was conducted in ethanol/toluene under reflux to yield cyclopentadienone precursor 4 in a yield of >85%. Compound 4 was then transformed into dibrominated fluoranthene 5 by a Diels-Alder reaction with 2,5-norbornadiene in toluene under a nitrogen atmosphere. Diborylfluoranthene 6 was subsequently obtained from compound 5 via a Mivaura borylation reaction in the presence of Pd(dppf)Cl₂, bis(pinacolato)diboron, and KOAc in dioxane.

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With the FPAH pentagonal component **6** in hand, the next step was to embed it into the curved hexagon component **10** to fabricate the molecular crown **MC3** (Scheme 2). The C-shaped compound **10** was synthesized according to our previously reported method¹¹ starting from commercially available compound **7**. The pinacol boronic ester **6** was reacted with compound **10** under standard Pd-catalyzed Suzuki–Miyaura cross-coupling conditions to give the macrocyclic intermediate **11**, the formation of which was confirmed by MALDI-TOF mass spectrometry (see Figure S1, Supporting Information). Subsequent reductive aromatization with sodium naphthalide in anhydrous THF produced the target product **MC3** as a yellow solid (20% yield over two steps).

The target compound **MC3** was fully characterized by ¹H NMR, ¹³C NMR, 2D ¹H-¹H COSY NMR, 2D ¹H-¹³C HSQC NMR, 2D ¹H-¹³C HMBC NMR spectroscopy and by MALDI-TOF mass spectrometry. The ¹H NMR data shows the typical proton shifts of the FPAHs and the cyclic phenyl rings (see Figure S2, Supporting Information). The characteristic singlets at 8.20, 7.86, and 6.82 ppm can be assigned to hydro-



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gen atoms in the FPAH unit on the basis of anisotropy effects. Figure S3 shows the ¹³C NMR spectrum of MC3. To fully assign the signals in the ¹H NMR and ¹³C NMR spectra of MC3, we recorded its 2D ¹H-¹H COSY NMR, 2D ¹H-¹³C HSQC NMR and 2D ¹H-¹³C HMBC NMR spectra (see Figures S4-S6). In the 2D ¹H-¹H COSY NMR spectrum (Figure S4), the singlet at 6.82 ppm belongs to the *e* site and the doublet at 7.78 ppm belongs to the *d* site. Moreover, the signals at 8.20 ppm and 7.86 ppm correlated with the proton signal at 7.60 ppm, suggesting that the signal at 7.60 ppm can be assigned to the *b* site. To further assign the signals in the 1 H NMR spectrum for all the aromatic proton sites, we recorded the 2D ¹H-¹³C HSQC NMR spectrum (Figure S5). The *e* site proton correlates with the carbon signal at 132.40 ppm, suggesting that the latter can be ascribed to the *e* site. By similar analysis, the signals at 128.74 ppm in the ¹³C NMR spectrum can be assigned to the d site. Figure S6 shows the expanded 2D ¹H-¹³C HMBC NMR spectrum of **MC3**. We observed that the proton signal at 8.20 ppm is correlated with the carbon signals at the *e* site and the quaternary carbon at 132.68 ppm, suggesting that the proton signal at 8.20 ppm can be assigned to the c site. Similarly, the signal at 7.86 ppm in the ¹H NMR spectrum can be assigned to the *a* site. The exact mass of **MC3** was confirmed by MALDI-TOF-MS. as shown in Figure 2 (a) and Figure S7. The main peak at m/z

884.3441 for **MC3** matches well with its calculated data (884.3443 for **MC3**). All these data suggest the successful synthesis of the target molecule **MC3**.

The photophysical properties of **MC3** were studied by UV-vis absorption spectroscopy and steady-state fluorescence spectroscopy. The absorption and steady-state fluorescence spectra of a dilute **MC3** solution were measured at room temperature (Figure 2, b and c). For comparison, the UV-vis spectrum of [10]cyclo-*para*-phenylene was also recorded under the same conditions. **MC3** showed obvious absorption bands between 260 nm and 478 nm, maximized at 340 nm, and the absorption coefficient (ε) was ~3.41 × 10⁴ cm⁻¹ mol⁻¹. Interestingly, a broad absorption shoulder exists in the visible region on the low-energy side between 380 nm and 460 nm (Figure 2, b). Compared to [10]cyclo*para*-phenylene, this shoulder feature of **MC3** can be ascribed to the contribution from the fluoranthene moiety.

The steady-state fluorescence emission spectrum of **MC3** was further measured at room temperature (Figure 2, c). An intense emission band was observed under excitation at 340 nm. The maximum emission peak (λ_{max}) was observed at 488 nm, and the fluorescence quantum yield (Φ_F) was determined to be 49% using anthracene in ethanol as the reference (Φ_F = 30%). The **MC3** solution in CH₂Cl₂



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Figure 2 (a) The MALDI-TOF spectrum and simulated data for compound **MC3**. (b) UV-vis absorption spectra of **MC3** (red) and [10]CPP (blue). (c) Fluorescence spectra for **MC3** (red) and [10]CPP (blue). Inset: photographs of the fluorescence of **MC3** and [10]CPP under 365 nm irradiation. (d) Emission lifetime decay measured at 488 nm for **MC3**. All data were measured using CH_2Cl_2 solutions with a concentration of 1.0×10^{-5} M.

showed strong green photoluminescence under a handheld UV lamp (Figure 2, c, inset). Fluorescence decay measurements were conducted using a nanosecond pulsed laser system in degassed CH_2Cl_2 solution at room temperature (Figure 2, d). The fluorescence decay profile follows first-order kinetics with a lifetime (τ_s) of 4.7 ns at 488 nm with single-exponential decay when excited at ~390 nm.

Considering the hydrophobic, electron-rich cavity and the perfect diameter of MC3 as a good supramolecular host, we next assembled the segment of carbon onion $C_{60}@C_{240}$ and systematically investigated the supramolecular properties between MC3 and the guest molecule C₆₀. To determine the complexation ratio between the host and the guest, we observed a mass peak at m/z 1605.3356 (calcd 1605.3477 for C₆₀@MC3) (Figure 3, a, inset), which confirms the formation of a 1:1 complex. Also, a UV-vis titration experiment was performed in toluene at room temperature (Figure 3, a). The maximum absorption change, according to the Job plot (Figure 3, b), was observed when the molar ratio of the host molecule and C_{60} reached 1:1. We also measured the Stern–Völmer constant and the binding constant (K_a) between C₆₀ and MC3 by fluorescence quenching experiments (Figure 3, c). Based on the quenching results, the binding constant (K_a) of C₆₀@MC3 was estimated to be approximately 1.44×10^6 M⁻¹ (Figure 3, d). The Stern–Völmer constant (K_{SV}) of C₆₀@**MC3** was determined to be 2.6 × 10⁶ M⁻¹ in toluene (see Figure S8, Supporting Information).



Figure 3 (a) UV-vis absorption spectra of **MC3** and C_{60} at different ratios in toluene for Job plot analysis. Inset: MALDI-TOF-MS (red) and simulated data (black) for the supramolecular complex C_{60} @**MC3**. (b) The Job plot of **MC3** and C_{60} . (c) Fluorescence spectra of **MC3** (1.0×10^{-5} M) in the presence of C_{60} in toluene. The concentrations of C_{60} range from 0 to 2.80 × 10⁻⁵ M. (d) Plot of the absorption changes at 488 nm versus [C_{60}] in toluene for calculating the binding constant (K_a)

To compare the binding properties between MC3 and other molecules, a larger fullerene C_{70} was used as the supramolecular guest. Mass spectrometry showed that C₇₀ can also form a supramolecular complex with MC3 and the mass peak occurred at *m*/*z* 1725.3466 (calcd 1725.3477 for C₇₀@MC3) (see Figure S9, Supporting Information). The results of the UV-vis titration experiments and the Job plot analysis indicated the formation of a 1:1 complex. The binding constant (K_a) between C_{70} and **MC3** was calculated to be 5.9×10^4 M⁻¹, which is 24 times lower than that of C_{60} @MC3, suggesting good selectivity for C_{60} over C_{70} . Compared with the K_a values of C_{60} @MC1 (3.34 × 10⁶ M⁻¹), C_{60} @MC2 (2.33 × 10⁷ M⁻¹), C_{60} @[10]CPP (2.79 × 10⁶ M⁻¹), and C_{60} @MC3, we found that the binding constants follow the order: $C_{60}@MC2 > C_{60}@MC1 > C_{60}@[10]CPP > C_{60}@MC3 >$ C₇₀@MC3.

In summary, we have successfully synthesized novel conjugated molecular crown **MC3**, bearing a pentagonal unit and curved hexagonal components, as a fragment of fullerene C₂₄₀. A study of the photophysical properties of **MC3** revealed obvious red shifts in both the absorption and emission due to conjugated π -extension. In addition, the supramolecular host–guest interaction between **MC3** and C₆₀@**MC3** can be potentially employed as a seed or template for the bottom-up synthesis of fullerene C₂₄₀ and the smallest stable carbon onion (C₆₀@C₂₄₀), respectively.

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All solvents used for syntheses were dried by distillation under nitrogen prior to use. THF and 1,4-dioxane were distilled under nitrogen after reflux over sodium. Other chemicals were obtained from commercial suppliers (Innochem or Acros). Air-sensitive reactions were carried out under argon or nitrogen atmospheres. C_{60} (99.9%) and C_{70} (99.9%) fullerenes were purchased from Suzhou Dade Carbon Nanotechnology Co., Ltd. 7,10-bis[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]fluoranthene (6)¹⁴ and compound 10¹¹ were synthesized according to the reported procedures. IR spectra were recorded using a spectrophotometer. NMR spectra were recorded on a Bruker BioSpin (1H, 400 MHz; 13C, 100 MHz) spectrometer. Chemical shifts (δ) are reported in ppm relative to CDCl₃ (7.26 ppm for ¹H NMR and 77.0 ppm for ¹³C NMR). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (Hz), integration. High-resolution mass spectrometry (HRMS) was carried out on spectrometer using MALDI-TOF-MS techniques. UV-vis absorption spectra were obtained using a UNIC-3802 spectrophotometer.

Compound 11

To a mixture of 7,10-bis[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)phenyl]fluoranthene (**6**) (113 mg, 0.186 mmol), compound **10**¹¹ (163.32 mg, 0.186 mmol) and potassium hydroxide (134 mg, 2.388 mmol) in a round-bottomed flask (500 mL) were added THF (250 mL), H₂O (10 mL), and Pd(PPh₃)₄ (30.06 mg, 0.026 mmol) under an argon atmosphere. Thereafter, the solution was heated at 80 °C for 48 h. After cooling to room temperature, the solvent was removed under vacuum and the remaining aqueous fraction was extracted with CH₂Cl₂. The combined organic layer was dried and concentrated under reduced pressure to afford crude product **11** as a gray solid that was used in the next step without further purification.

HRMS (MALDI-TOF): m/z [M]⁺ calcd for C₇₆H₆₂O₆: 1070.4546; found: 1070.4538.

Molecular Crown MC3

To a round-bottomed flask (50 mL) (vessel A) containing a magnetic stir bar were added sodium metal (274 mg, 11.9 mmol), anhydrous THF (12 mL) and naphthalene (1.00 g, 7.82 mmol), and the resulting mixture was stirred at room temperature for 1 d. To another round-bottomed flask (200 mL) (vessel B) containing a magnetic stir bar were added the crude product **11** and dry THF (80 mL). A solution of sodium naphthalide (2 mL, 2 mmol, 1.0 M in THF) from vessel A was then added at -78 °C. After stirring the mixture at -78 °C for 2 h, a 1 M solution of I₂ in THF (1.5 mL) was added. After warming to room temperature, the mixture was quenched with aqueous saturated so-dium thiosulfate, extracted with CH₂Cl₂, dried over Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane/CH₂Cl₂, 4:1) to afford **MC3** (33 mg, 20% yield over two steps) as a yellow solid. Mp: >250 °C dec.

IR (KBr): 2960, 2923, 2852, 1741, 1667, 1593, 1482, 1459, 1375, 1263, 1185, 1158, 1102, 1039, 854, 812, 778, 741 $\rm cm^{-1}.$

¹H NMR (400 MHz, CDCl₃): δ = 8.20 (d, *J* = 6.8 Hz, 2 H), 7.85 (d, *J* = 8.4 Hz, 2 H), 7.77 (d, *J* = 8.4 Hz, 4 H), 7.60–7.53 (m, 34 H), 6.81 (s, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 123.08, 126.91, 127.36, 127.70, 128.74, 132.40, 135.93, 136.15, 136.44, 138.11, 138.18, 139.35, 139.61.

HRMS (MALDI-TOF): m/z [M]⁺ calcd for C₇₀H₄₄: 844.3443; found: 844.3341.

Job Plot Analysis

A solution of the C_{60} or C_{70} guest in toluene and a solution of **MC3** in toluene were mixed in different ratios to prepare 11 samples ([guest] + [**MC3**] = 6.67 × 10⁻⁶ M). The UV-vis absorption spectra were recorded for each sample, and the absorption changes at 340 nm were monitored for the Job plot analysis.

Fluorescence Quenching Experiments

Fluorescence quenching was studied by the addition of one fullerene guest to **MC3**. To a solution of **MC3** (1×10^{-5} M) in toluene was added a solution of the guest in toluene (1×10^{-3} M) at 25 °C. The changes in the fluorescence intensity of **MC3** were measured at 488 nm. The Stern–Völmer constant (K_{SV}) was determined by using equation 1:

 $F_0/F = 1 + K_{SV}[guest](eq 1)$

the binding constant (K_a) was determined by using equation 2:

 $F/F_0 = (1 + (k_f/k_s)K_a[guest])/(1 + K_a[guest]) (eq 2)$

where *F* is the fluorescence intensity, F_0 is the fluorescence of **MC3** before the addition of one fullerene guest, k_f is the proportionality constant of the complex, and k_s is the proportionality constant of the host.

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Supporting Information

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