

Macrocycles Hot Paper

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Towards the Highly Efficient Synthesis and Selective Methylation of C(sp³)-Bridged [6]Cycloparaphenylenes from Fluoren[3]arenes

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Abstract: An approach to the highly efficient synthesis of C(sp3)-bridged [6]cycloparaphenylenes (C[6]CPPs) from fluoren[3]arenes (F[3]As) was developed. Consequently, *F*[3]As as a new kind of macrocyclic arenes were synthesized. Followed by the demethylation, triflation and intramolecular aryl-aryl coupling reactions, C[6]CPPs were then conveniently obtained. Interestingly, C[6]CPPs could be selectively methylated to produce their fully outer-methyl-substituted derivatives. The crystal structures showed the hydroxyl-substituted F[3]As had bowl-shaped conformations, and the C[6]CPPs exhibited rigid belt-shaped structures with deep cavities. Moreover, C[6]CPPs exhibited high HOMO energies and narrow energy gaps. An unclosed belt was further obtained, and it not only showed a similar narrow energy gap to those of the aromatic belts, but also displayed strong fluorescence property, which can play a vital role in the design and synthesis of new aromatic belts.

Introduction

Aromatic belts as sections of nanotubes,^[1] belonging to a unique class of macrocycles with radially oriented porbitals,^[2] have attracted an increasing interest in recent years owing to their aesthetic structures, specific physical properties, potential applications in supramolecular chemistry and materials science. More importantly, they were of the possibilities to act as seeds for rationally chemical synthesis of single walled carbon nanotubes.^[3-7] The chemical synthesis of aromatic belts has been a long sought-after target.^[8] Up to date, some successful examples for the synthetic segments of arm-chaired,^[9] chiral^[10,11] and zig-zag^[12-14] carbon nanotubes have been reported. Nonetheless, the design and construction of aromatic belts are still a hot topic and represent a challenging synthetic target.

Till now, much more attentions have been paid to developing the strategies of highly efficient fabrication of aromatic belts. Traditionally, the construction of an aromatic belt mainly experienced three steps: a macrocyclization step,

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a belt-forming step and strain-inducing step. It was commonly known that the macrocyclization was in fact the most predominant step in the synthesis of aromatic belts.^[15,16] Along with the development of macrocyclic chemistry, the strategy to synthesize the aromatic belts from the most common macrocycles opens the way to rational design and synthesis of such kinds of interesting structures. Recently, resorcin[4]arenes and their derivatives were explored to construct zig-zag hydrocarbon belts by Wang's group, representing a breakthrough in this area.^[17-21] Very recently, Itami et al.^[22] reported a fully alternant methylene-bridged [6]cycloparaphenylene (M[6]CPP), which was cleverly designed and synthesized in about 10% total yield starting from ethylsubstituted pillar[6]arene derivative. The M[6]CPP represents a new kind of aromatic belt as the belt segment of a haeckelite nanotube,^[23] and also endows itself promising applications in nanoelectronics and photonics.^[24] However, synthesis of M[6]CPP from the pillar[6]arene was still in a low efficiency because of up to 12 multiple of reactive sites during the intramolecular aryl-aryl coupling to form six new C-C bonds, inner-side vertical flip of the OTf groups to adapt their reactivities, and the originally poor separated yield of pillar-[6] arene itself. Although various macrocyclic arenes^[25-32] have hitherto been reported, the macrocycles that favor to the formation of aromatic belts are very limited. What is more, the synthesis of aromatic belts with conjugated structures from the macrocyclic arenes still remains a considerable challenge.

Herein, we first report a new kind of macrocyclic arenes, F[3]As, which could be conveniently synthesized in 48–67% yield by BF₃·OEt₂-catalyzed condensation between 2,7alkoxyl-substituted fluorenes and paraformaldehyde. By the demethylation and triflation of F[3]As, and then followed by the intramolecular aryl-aryl coupling reactions (Scheme 1), a new and powerful approach to the highly efficient synthesis of C[6]CPPs was developed. Interestingly, the treatment of C[6]CPPs with iodomethane in the presence of t-BuOK selectively produced the fully outer-methyl-substituted derivatives in almost quantitative yields. The crystal structures showed the fully hydroxyl-substituted F[3]As possessed bowl-



Scheme 1. Design for the synthesis of CIGICPPs from FI3IAS.

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shaped conformations, and the **C[6]CPPs** showed rigid beltshaped structures and deep cavities. The experimental results and theoretical calculations indicated that all of the **C[6]CPPs** exhibited high HOMO energies and narrow HOMO–LUMO gaps. Moreover, an unclosed belt **UB** was obtained, and it not only showed the similar narrow HOMO–LUMO energy gap to those of the aromatic belts, but also displayed a strong fluorescence property.

Results and Discussion

Synthesis and Structures of F[3]As

Synthesis of **F[3]As** was depicted in Scheme 2. Under the optimized conditions (Table S1), **F[3]A1** could be conveniently synthesized in 64% yield by one-pot condensation between 2,7-dimethoxy-9*H*-fluorene and paraformaldehyde in dichloromethane (DCM) at room temperature for 1.0 hour in the presence of BF₃·OEt₂. The ¹H NMR spectrum of **F[3]A1** showed two single peaks for the aromatic protons and three single peaks for the methyl, the methylene groups in the fluorene subunit and the bridged methylene groups, indicating its high symmetric structure and low inversion barrier in solution. The MALDI-TOF HRMS at 714.2973 further confirmed the chemical structure of **F[3]A1** (Figure S12).

According to the similar synthetic approach to that of F[3]A1, we could also easily obtain F[3]A2 and F[3]A3 in 67% and 54% yield starting from 2,7-dimethoxy-9,9-dimethylfluorene and 9,9-dipropyl-2,7-dimethoxylfluorene, respectively. If 2,7-dimethoxy-9-propyl-9H-fluorene was used as the precursor, F[3]A4 as a mixture of two isomers was obtained in 61% total yield. Compared to F[3]A1 with the poor solubility in common solvents including chloroform and dichloromethane, F[3]A2 showed a poor solubility as well, but F[3]A3 and F[3]A4 had very good solubilities in common solvents due to introducing the propyl groups. Under the same reaction conditions, the F[3]A5 was also obtained in 48% yield. As expected, F[3]A5 showed markedly increased solubility in chloroform compared with F[3]A1. The variable temperature ¹H NMR spectra of **F[3]A5** showed that a free rotation of the fluorene subunit in solution occurred due to the low inversion barrier (Figure S25).

We obtained the crystal structures of macrocycles **F[3]A3** and **F[3]A5**. As shown in Figure 1 a, it was found that two 9,9-





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Figure 1. Crystal structures of a) F[3]A3 and b) F[3]A5.[39]

dipropyl-2,7-dimethoxylfluorene subunits in **F[3]A3** positioned at one side, while the other fluorene subunit took the reversed conformation owing to the steric effect of the adjacent methoxyl groups and the propyl groups. For **F[3]A5**, it adopted the similar conformation to that **F[3]A3** in the solid state (Figure 1b). Moreover, there existed strong C–H…O hydrogen bonds of intermolecular **F[3]A5** with the distance at 2.655 Å, but no efficient π - π interaction was observed (Figure S77).

Synthesis and Structures of C[6]CPPs

The demethylation of **F[3]As** was then performed. As shown in Scheme 3, **2,7-OH-F[3]As** could be easily obtained in high yields by treating **F[3]As** with boron tribromide in dichloromethane at 0°C. For the demethylation of **F[3]A4**, two isomeric products as a mixture were obtained in high total yield as well, but they could not be separated by column chromatography. It was found that **2,7-OH-F[3]As** have good solubilities in acetone and DMSO. The ¹H NMR spectral analyses of **2,7-OH-F[3]As** indicated the fully hydroxylsubstituted macrocycles adopted an averaged C_{3h} symmetry in solution due to a fast conformational interconversion. By slow diffusion of CH₂Cl₂ into the acetone solution of **2,7-OH-F[3]A2**, we also obtained the single crystal of **2,7-OH-**



Scheme 3. Synthetic routes of C[6]CPPs.

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Figure 2. Crystal structures. a) Top view and b) side view of **2,7-OH-F[3]A2**; c) top view and d) side view of *i*,*i*,*i*-**2,7-OH-F[3]A4**; and e) top view and (f) side view of *o*,*o*,*i*-**2,7-OH-F[3]A4**. Blue lines represent the intramolecular hydrogen bonding interactions. Hydrogen atoms not involved in the non-covalent interactions were omitted for clarity.^[39]

F[3]A2. As shown in Figure 2 a, the crystal structure showed that three of the fluorene subunits in **2,7-OH-F[3]A2** positioned at the same side to form a bowl shaped structure, in which intramolecular hydrogen bonding interactions between the adjacent hydroxyl groups with an average distance of 1.97 Å played a vital role (Figure 2 a). The upper and lower rim of the bowl had an approximately diameter of 10.1 Å and 5.4 Å, and the cavity depth was measured about 4.5 Å. Moreover, it was also found that acetone and H₂O molecules existed in the crystal structure, and the intermolecular hydrogen bonds between **2,7-OH-F[3]A2** and the solvent molecules played an important role in formation of the stable bowl shaped structure as well (Figure S79).

By slow evaporation of 2,7-OH-F[3]A4 in CH₂Cl₂ and acetone mixed solution, we obtained two different crystal structures for the isomers. In one crystal structure, three propyl groups were all positioned inside of the cavity, named *i,i,i*-2,7-OH-F[3]A4 (Figure 2c and d). The other crystal structure showed that the two propyl groups positioned outside of the cavity while the other one was inside of the cavity, which was named as o.o.i-2,7-OH-F[3]A4 (Figure 2e and f). Similar to that of 2,7-OH-F[3]A2, both i,i,i-2,7-OH-F[3]A4 and o,o,i-2,7-OH-F[3]A4 adopted the bowl shaped structures in the solid state (Figure 2), in which the intramolecular hydrogen bonding interactions between the adjacent hydroxyl groups played a predominant role. These macrocycles with specific structures will be used as a new kind of promising synthetic hosts for wide applications in supramolecular chemistry.

As shown in Scheme 3, 2,7-fluoren[3]arene triflates (2,7-OTf-F[3]As) were easily prepared in almost quantitative yields by the treatment of 2,7-OH-F[3]As with trifluoroacetic anhydride in CH₂Cl₂ in the presence of 4-dimethylaminopyridine (DMAP). The ¹H NMR and ¹³C NMR spectra of 2,7-OTf-F[3]A1 (Figure S39,40) and 2,7-OTf-F[3]A2 (Figure S43,44) showed only one set of signals, which were similar to those of their precursors. However, for 2,7-OTf-F[3]A3 (Figure S47,48), its NMR spectra displayed more than one set of signals, which could be attributed to the increased steric hinderance of the triflate groups in 2,7-OTf-F[3]A3. The Xray crystal structure of 2,7-OTf-F[3]A2 showed that it adopted an unsymmetric conformation (Figure S82), in which the two fluorene subunits were positioned in one side while another one was at the other side. This case was very similar to that of F[3]A5.

With **2,7-OTf-F[3]As** in hand, we then performed the synthesis of the aromatic belts. Consequently, by the treatment of **2,7-OTf-F[3]A1** with 6.0 equiv of Ni(cod)₂/2,2'-bipyridyl (bpy) at 80 °C for 2 h, it was found that the arylaryl coupling reaction could efficiently occur to produce the aromatic belt **C[6]CPP1** in 90 % yield (Scheme 3), which was markedly higher than that from pillar[6]arene^[22] probably due to the preorganized structure of the macrocyclic precursor, the free outer rotation of the OTf groups, and the formation of only three new C–C bonds in our system.

Under the same conditions, C[6]CPP2 could also be separated as a red solid starting from 2,7-OTf-F[3]A2 (Table 1, entry 1), but the yield was only 24%. Meantime,

Table 1: The Optimization of aryl-aryl coupling reaction from 2,7-OTf-F[3]A2.

Entry	<i>T</i> [°C]	<i>t</i> [h]	Yield [%] of C[6]CPP2/UB
1	80	2	24/36
2	100	2	29/0
3	80	4	47/19
4	80	8	62/0
5	80	12	60/0

we obtained one intermediate containing two triflate groups, named an unclosed belt (UB), in 36% yield as well (Figure 5a). Interestingly, we found that UB could produce the aromatic belt C[6]CPP2 in 98% yield in the presence of Ni(cod)₂/bpy, which indicated that the yield of C[6]CPP2 could be improved by increasing the reaction temperature or prolonging the reaction time. Consequently, we optimized the aryl-aryl coupling reaction and the results were summarized in Table 1. It was found that if the temperature rose from 80°C to 100°C, C[6]CPP2 was only separated in 29% yield (Table 1, entry 2). So, we still carried out the reaction at 80 °C, but prolonged the reaction time up to 4 hours, the yield of C[6]CPP2 was markedly improved while the yield of UB was decreased (Table 1, entry 3). When the reaction time was prolonged 8 hours, we found that C[6]CPP2 could be obtained in 62% yield, while no UB was separated (Table 1, entry 4). If we continued to prolong the reaction time, no increase of the yield was observed (Table 1, entry 5). In the case of 2,7-OTf-F[3]A3, no aromatic belt C[6]CPP3 was obtained even we prolonged the reaction time for more than 24 hours, which was probably resulted from the prominent steric hindrance of the propyl groups. Both C[6]CPP1 and C[6]CPP2 showed good solubility in common solvents, such as chloroform and dichloromethane. The chemical structures of the aromatic belts were confirmed by their ¹H NMR, ¹³C NMR and HRMS spectra (see Supporting Information for details).

In the ¹H NMR spectrum of **C[6]CPP1** in CD_2Cl_2 , the methylene groups showed broad signals for the aliphatic protons which was hard to be distinguished. However, it was surprisingly found that if a mixture solvents of C_6D_6 and

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 CD_2Cl_2 (4:1, v/v) was used, a distinct split ¹H NMR spectrum of **C[6]CPP1** was observed (Figure S51), in which one singlet at 7.73 ppm belonged to the aromatic proton, while the inner and outer protons of the methylene groups showed two doublets at 4.15 and 3.83 ppm, respectively. This result also indicated its high D_{3d} symmetric structure. Moreover, the red crystal of **C[6]CPP1** could be obtained by slow diffusion of methanol into a CH₂Cl₂ solution of **C[6]CPP1** at room temperature. The crystal structure showed **C[6]CPP1** had a cylindrical shape-like structure with an average diameter and cavity depth 7.766 Å and 3.971 Å, respectively, and an average C–C single bond that connected the phenylene units was 1.475 Å, which were all consistent with those of the Itami's report.^[22]

Since **C[6]CPP2** showed good solubility in benzene, its ¹H NMR spectrum in C₆D₆ was then performed. As shown in Figure 3, with the aid of 2D NOESY NMR analysis, two singlets H¹ and H² at 7.71 ppm and 7.75 ppm were assigned to the aromatic protons close to $-C(CH_3)_2$ and $-CH_2$, respectively. The ¹H-¹³C HSQC spectrum further distinguished the inner and outer protons (H⁴ⁱ and H^{4o} respectively) of the methylene group (Figure 3 e). Moreover, it was also found that CH₂Cl₂ could be encapsulated in the cavity of **C[6]CPP2** with a highfield shift of the proton signal from 4.27 to 3.48 ppm, and the crossing signal between the proton of CH₂Cl₂ and H² implied it might position at the non-methylated side.

By slow diffusion of *n*-hexane into a CH_2Cl_2 solution of **C[6]CPP2** at room temperature, we also obtained the red single crystals of **C[6]CPP2**. As shown in Figure 3b. the crystal structure showed **C[6]CPP2** had a cylindrical shape-like structure as well with an average diameter of 7.772 Å and

an average C–C single bond that connected the phenylene units of 1.478 Å. Comparatively, both of the diameter and the average C–C single bond length were smaller than those of [6]CPP,^[33,34] demonstrating that the C(sp³)-bridged [6]CPP possessed a condensed belt structure. Moreover, **C[6]CPP2** with the inner substituted methyl groups showed both a deeper cavity (5.200 Å) than that of **C[6]CPP1** and a shrunken upper rim. These structural properties made the encapsulated *n*-hexane difficult to thread the cavity (Figure S85). This clear observation was in agreement with the result from 2D NOESY analysis, in which CH_2Cl_2 positioned at the nonmethylated side.

The optimized structure of UB was first calculated by using B3LYP/6-31G(d) level of theory, which showed its fishlike and symmetrical structure (Figure 4b). As shown in Figure 4c, UB exhibited a comparatively complex ¹H NMR spectrum in CD₂Cl₂. According to the 2D NOESY spectrum (Figure 4d), the NOE signals between aromatic protons and the inner protons of the methylene and methyl groups enabled us to give a full assignment of the six singlets for the aromatic protons. With the aid of ¹H-¹³C HSQC spectrum (Figure 4e), H7/H8 and H9/H10 could be easily distinguished to the outer and inner protons of the two methylene groups, respectively. Moreover, two singlets H13 and H14 at 1.82 ppm and 1.18 ppm were assigned to the methyl protons of one $C(CH_3)_2$, while two singlets H11 and H12 at 1.38 ppm and 1.14 ppm was assigned to the methyl protons of another $C(CH_3)_2$. Interestingly, it was further found that **UB** showed



Figure 3. a) Chemical structure of **C[6]CPP2**. b) Crystal structure of **C[6]CPP2** from top view and side view. c) ¹H NMR spectrum (400 MHz, 298 K) of **C[6]CPP2** in C₆D₆. d) Partial 2D NOESY spectrum, and e) partial ¹H-¹³C HSQC spectrum of **C[6]CPP2** in C₆D₆.^[39]



Figure 4. a) Chemical structure of **UB**. b) DFT optimized structure of **UB**. c) ¹H NMR spectrum (500 MHz, CD₂Cl₂, 298 K) of **UB**. d) Partial 2D NOESY spectrum of **UB**. e) Partial ¹H-¹³C HSQC spectrum of **UB**.^[39]

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strong fluorescence under 365 nm UV lamp probably due to the two strong electron-deficient triflate groups, which was obviously different from those of the aromatic belts **C-[6]CPPs** with fully carbon conjugated structures. Molecule **UB** could not only be very helpful for us to understand the formation process of the aromatic belt, but also be of great meaningfulness to further design new systems with specific structure and property.

Selective Methylation of C[6]CPPs

Post modification of aromatic belts is vital for their further functionalization and application researches. Because of the activation of conjugated rigid structure, the methylene groups of **C[6]CPP1** possessed higher reactivity than the monomer 2,7-dimethoxy-9*H*-fluorene. Consequently, we tried the methylation of **C[6]CPP1** with CH₃I at 0°C in the presence of excess *t*-BuOK. As shown in Scheme 4, it was interestingly



Scheme 4. Selective post-methylation of C[6]CPP1-2.

found that **C[6]CPP4** in which the six methyl groups were all positioned outside was obtained in 98% yield as the only product. No reactions occurred in the presence of *t*-BuONa or NaH. Similarly, the treatment of **C[6]CPP2** with CH₃I in the presence of excess *t*-BuOK also selectively produced **C**-**[6]CPP5** in 96% yield, in which the three methyl substituents were all positioned outside. The selective methylation of **C[6]CPPs** might be attributed to the big steric hindrance effect that impeded the inner protons to take place the methylation. The fully outer-methyl-substituted **C[6]CPPs** could also make them as a new kind of useful synthetic hosts for wide potential applications in supramolecular chemistry and materials science.

The ¹H NMR spectrum of **C[6]CPP4** in C₆D₆:CD₂Cl₂ (4:1, v/v) showed one singlet at 7.64 ppm for the aromatic protons, one quartet at 4.04 ppm for the inner protons of $C(sp^3)$ -bridge and one doublet at 1.55 ppm for the outside methyl groups (Figure 5 a), which indicated its high D_{3d} symmetry. In the case of **C[6]CPP5**, its ¹H NMR spectrum in C₆D₆ (Figure 5 b) exhibited two singlets at 7.66 ppm and 7.72 ppm for the aromatic protons H1 and H2, respectively. Moreover, one quartet at 4.17 ppm for the inner hydrogen H3, one doublet at 1.68 ppm for the newly formed methyl groups, and two singlets at 1.80 ppm and around 1.67 ppm for the outer and inner -CH₃, respectively, were observed, which was consistent with its D_{3h} symmetric structure.





Figure 5. a) Chemical structure and the ¹H NMR spectrum (500 MHz, $C_6D_6:CD_2Cl_2=4:1, 298$ K) of **C[6]CPP4**. b) Chemical structure and the ¹H NMR spectrum (500 MHz, C_6D_6 , 298 K) of **C[6]CPP5**. c) Top view and side view of crystal structure of **C[6]CPP4**. d) Top view and side view of crystal structure of **C[6]CPP5**. Hydrogen atoms are omitted for clarity.^[39]

The red crystals of C[6]CPP4 were obtained by slow diffusion of methanol into a mixed solution of C[6]CPP4 at room temperature (Figure S87). The crystal structure of C[6]CPP4 showed an obvious elliptic deformation and cylindrical-like cavity with the average diameter and cavity depth of 7.769 Å and 5.166 Å, respectively (Figure 5c). The six methyl groups were all positioned outside of the cavity. The average C-C single bond that connected the phenylene units was 1.491 Å. Moreover, aromatic belt C[6]CPP4 could pack into nanotube structures with CH₂Cl₂ and H₂O molecules inside its cavity. Interestingly, six adjacent molecules of C[6]CPP4 could also self-assemble into a six membered ringlike structure by virtue of the intermolecular $C(sp^2)$ -H··· π interaction with an average distance of 2.878 Å, which further packed into tube-like architectures with benzene and CHCl₃ molecules encapsulated inside the cavity (Figure S88). Besides, $C(sp^3)$ -H···Cl hydrogen bonding between C[6]CPP4 and CHCl₃ with the distance of 2.876 Å, and the strong C- $H \cdots \pi$ interaction between benzene and $CHCl_3$ with the distance of 2.865 Å also played significant roles in formation of the architectures in the solid state.

Similarly, it was found that **C[6]CPP5** (Figure 5d) showed a cylindrical shape structure in the solid state as well, in which an average diameter and cavity depth of 7.764 Å and 5.828 Å, respectively, were observed. Moreover, the average C–C single bond that connected the phenylene units was 1.480 Å. The main interactions in the packing mode of **C[6]CPP5** were

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found to be the intermolecular $C(sp^3)$ -H··· π interactions between the adjacent molecules of **C[6]CPP5** with the distances of 2.829 Å and 2.880 Å, and the intermolecular $C(sp^2)$ -H··· π interaction with an average distance of 2.834 Å (Figure S90).

Photophysical and Electrochemical Properties of C[6]CPPs and UB

The photophysical properties of C[6]CPPs were measured in CH_2Cl_2 . Compared to C[6]CPP1 (Figure 6a, solid red line) with two major absorption bands at 347 nm and 370 nm and a very weak broad absorption band at 400–600 nm, C[6]CPP2, C[6]CPP4 and C[6]CPP5 showed bath-ochromic shifts with increasing numbers of methyl group at $C(sp^3)$ atoms. As a result, the major absorption bands of C[6]CPP2 and C[6]CPP4 containing six methyl groups at 353 nm and 354 nm were observed, respectively, and C-[6]CPP5 with nine methyl groups showed the maximum absorption band at 357 nm.

In the case of **UB**, major absorption bands at 335, 358, 423, 453 and 482 nm, respectively, were found. Interestingly, **UB** also showed strong fluorescence property with the maximum emission at 522 nm (Figure 6c), and the fluorescence quantum yield was determined to be 0.21. This result was obviously different from those of **C[6]CPPs**, in which there was no detectable fluorescence. Energy gap of **UB** was approximately calculated to be 2.48 eV,^[35] which suggested the **UB** possessed a similar energy gap (E_g) to that of **C[6]CPP1** (2.67 eV).



Figure 6. a) UV–Vis absorption spectra of **C[6]CPP1** (solid red line), **C[6]CPP2** (solid blue line), **C[6]CPP4** (dash red line) and **C[6]CPP5** (dash blue line); [**C[6]CPP3**] = 4.0×10^{-5} M. b) Normalized cyclic voltammetry of **C[6]CPP2**, the measurement was carried out in 0.1 M TBAP/CH₂Cl₂ at room temperature at a scan rate of 100 mVs⁻¹, potentials were recorded versus Fc/Fc⁺. c) UV–Vis absorption and fluorescence spectra of **UB**, [**UB**] = 1.0×10^{-5} M. d) Normalized cyclic voltammetry of **UB**, the measurement was carried out in 0.1 M TBAP/CH₂Cl₂ at room temperature at a scan rate of 100 mVs⁻¹, potentials were recorded versus Fc/Fc⁺.

The electrochemical properties of the aromatic belts were carried out by cyclic voltammetry in CH_2Cl_2 . Consequently, it was found aromatic belts **C[6]CPP1**, **C[6]CPP2** (Figure 6b), **C[6]CPP4** and **C[6]CPP5** showed quite similar oxidation potential, in which two reversible oxidation processes were observed. However, the curve of the ferrocene/ferrocenium couple (Fc/Fc⁺) was overlapped with that of **C[6]CPPs**, as shown in Figure S95-98. The half-wave potentials of **C-**[6]CPP2 could not be given accurately. In the case of **UB**, cyclic voltammetry in CH_2Cl_2 exhibited two reversible oxidation processes with half-wave potentials of 0.15 V and 0.29 V vs. the Fc/Fc⁺, as shown in Figure 6d. The HOMO energy of **UB** was calculated to be -4.27 eV. As a result, the LUMO energy of **UB** was approximately -1.79 eV.

Theoretical Calculations

To further understand the differences observed in the absorption spectra of C[6]CPPs, the time-dependent density functional theory (TD-DFT) calculations were carried out by the B3LYP/6-31G(d) level of theory. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of C[6]CPPs showed that the frontier molecular orbitals were all delocalized over the phenylene backbone (Figure 7, Figure S100-103). The HO-MO-1 and HOMO-2, LUMO+2 and LUMO+3 were degenerate owing to the high symmetry of C[6]CPPs. Major electronic transitions for C[6]CPPs were summarized in Table S12-15, in which the observed absorption bands at around 347 nm and 370 nm for C[6]CPPs could be assigned to electronic transitions from the HOMO-1 and HOMO-2 to LUMO, and from the HOMO to LUMO + 2 and LUMO + 3. And the weak broad absorption band at 400-600 nm was attributed to the symmetry forbidden HOMO-LUMO transitions. Moreover, the calculated maximum absorptions of C[6]CPP1, C[6]CPP2, C[6]CPP4 and C[6]CPP5 were at 432, 347, 346 and 350 nm, respectively. These trends were in line with the experimental results. The HOMO-LUMO energy gaps of C[6]CPPs were calculated to be 2.61-2.67 eV, which were in agreement with the experimental values as well.



Figure 7. The comparison of the calculated frontier molecular orbitals of CI6ICPPs.

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These narrow HOMO–LUMO energy gaps were close to that of C_{60} ,^[36] implying a promising application of these **C[6]CPPs** in optoelectronic materials.

For a clear description of aforementioned properties of **UB**, TD-DFT calculations were also taken into account. Firstly, the calculated energies of the HOMO and LUMO and the corresponding major electronic transitions for UB were displayed in Figure 8. Similar to those of C[6]CPPs, the HOMO and LUMO of UB were mainly delocalized over the phenylene backbone, and the UB possessed degenerate HOMO-1 and HOMO-2, and degenerate LUMO+2 and LUMO + 3 as well. It was found that the HOMO energy of UB was -4.36 eV, which was consistent with the result from cyclic voltammetry. The HOMO-LUMO energy gap of UB is 2.62 eV, which is the same level as those of C[6]CPPs and close to the experimental result from absorption spectrum. The absorption spectrum of UB was simulated according to the analysis of major electronic transitions (Figure S105),^[37–38] which matched well with the experimentally observed Figure 6c. The major electronic transitions of the main absorption bands for UB were analyzed (Figure S106). Thus, the observed maximum absorption band at 482 nm for UB could be assigned to electronic transitions from the S_0 to S_1 , among



Figure 8. Calculated frontier molecular orbital profiles, energy diagram, and major electronic transitions of **UB**.

which the oscillator strength (*f*) was 0.1282. And the observed strongest absorption band at 358 nm could be assigned to electronic transitions from the S₀ to S₅, where the *f* value was 1.0408. Secondly, the strong fluorescence of **UB** was theoretically analyzed (Figure S107), and the *f* value at 603 nm was 0.1441 (single electron calculation in vacuum), confirming an efficient S₁ \rightarrow S₀ transition.

Conclusion

In summary, we have designed and synthesized a new kind of macrocyclic arenes, F[3]As in up to 67% yield by the BF₃·OEt₂ catalyzed one-pot condensation between 2,7-alkoxyl-substituted fluorenes and paraformaldehyde. Starting from F[3]As, an approach to highly efficient synthesis of C[6]CPPs was developed. Thus, the C[6]CPP1 was easily obtained in 90% yield, which was markedly higher than that from pillar[6]arene probably due to the preorganized structure of the macrocycle, the free outer rotations of the OTf groups, and the formation of only three new C-C bonds in our system. Similarly, C[6]CPP2 could also be synthesized in good yields from F[3]A2. For F[3]A3, no corresponding aromatic belt was obtained due to the steric effect of the inner *n*-propyl groups to impede the ring-closing reactions. Interestingly, we also found the selective methylation of C[6]CPP1 and C[6]CPP2 gave their fully outer-methyl-substituted derivatives in more than 96 % yields. The X-ray crystal structures of the fully hydroxyl-substituted 2,7-OH-F[3]As showed bowlshaped structures, and the methyl-substituted C[6]CPPs exhibited cylindrical shaped structures with deep cavities. The experimental results and theoretical calculations indicated C[6]CPPs all exhibited high HOMO energies and narrow HOMO-LUMO gaps. Moreover, a precursor of C[6]CPP2, the unclosed belt UB, was also obtained, and it not only showed the similar narrow HOMO-LUMO energy gap to those of the aromatic belts, but also displayed strong fluorescence property. We believe that these easily available aromatic belts and their precursors with specific cavity structures and properties could be promising candidates as new kinds of macrocyclic hosts and find wide applications in supramolecular chemistry and materials science.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: [6]cycloparaphenylene \cdot aromatic belt \cdot fluoren[3]arene \cdot intramolecular aryl–aryl coupling \cdot macrocycles

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Macrocycles

X.-S. Du, D.-W. Zhang, Y. Guo, J. Li, Y. Han, C.-F. Chen* _____

Towards the Highly Efficient Synthesis and Selective Methylation of C(sp³)-Bridged [6]Cycloparaphenylenes from Fluoren[3]arenes



Starting from fluoren[3]arenes, a new kind of easily available macrocyclic arenes, a powerful approach to the highly efficient synthesis of $C(sp^3)$ -bridged [6]cycloparaphenylenes (**C[6]CPPs**) with aesthetic conjugated belt structures was developed. Moreover, the bridged methylene of **C[6]CPPs** could be selectively methylated to produce their fully outermethyl-substituted derivatives in \geq 96% yields.