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Selective synthesis and physical properties of a bismacrocycle: Cycloparaphenylene-pillar[5]arene

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ABSTRACT

Macrocyclic materials have attracted much attention due to their particular chemical and physical properties. Herein we report the precise synthesis and characterization of a new bismacrocycle structure base on cycloparaphenylene (CPP) and pillar[5]arene, named cycloparaphenylene-pillar[5]arenes (**CPPn[5]**). The bismacrocycle was fully characterized by NMR and HR-MS. The photophysical properties of **CPPn[5]** were investigated by UV–vis, and the maximum absorption peak was located at 331 nm, which was consistent with density functional theory (DFT) calculations. The fluorescence spectrum was further studied and the emission peak was maximized at 458 nm. The computational results indicate the strain energy of **CPPn[5]** is 27.80 kcal/mol and the HOMO-LUMO gap is 3.39 eV Notably, **CPPn[5]** showed interesting supramolecular properties.

The synthesis of different conjugated macrocyclic structures has attracted increasing attention in the past decade because of their unique structures and excellent properties [1,2]. π-Extended macrocycles with different functional groups have been used as photoactive materials [3–6], metal coordination ligands for molecular catalysis [7], and host molecules for supramolecular interactions [8–11]. Among them, pillararenes are emerging novel macrocycles, which are constructed from the derivatives of hydroquinone and connected by methylene bridges at the 2,5 positions of benzene rings. In 2008, the synthesis of pillararenes (Scheme 1a) was reported by the Ogoshi group [12]. Subsequently, the unique supramolecular properties and other physical properties of pillararenes started to be explored [13–21].

Meanwhile, hoop-shaped cycloparaphenylenes (CPPs, Scheme 1b) consisting of *para*-linked benzene units were reported in 2008 [22], which represent the smallest segments of armchair carbon nanotubes (CNTs). Compared to pillararenes, CPPs only comprise benzene rings and are fully conjugated with delocalized π orbitals over the whole carbon nanoring [23]. In the literature, very few bismacrocycles were reported because of their challenging syntheses [24]. In 2013–2014, two pillar[5]arene-crown ethers were synthesized as typical bismacrocycles [25,26]. In 2018, Gaeta's team synthesized a novel bismacrocycle named calix[4]arene-cycloparaphenylene [27]. Recently, our group reported the synthesis of a new class of bismacrocycles with two identical CPP rings [28]. Further studies were subsequently reported to functionalize CPP frameworks. For example, a three-segment CPP-peropyrene-CPP structure was reported [29], which demonstrated that the radially π-conjugated CPP framework is a unique structural platform to control spin distribution and its reactivity. Recently, a few other pillararene-based bismacrocycle structures have also been synthesized [30–32]. Although CPP and pillararene structures have been reported and studied for more than one decade, bismacrocycles containing complete CPP and pillararene reported in the literature are still very rare.

In this present work, we report the synthesis and physical properties of a new bismacrocycle structure **CPPn[5]** (cycloparaphenylene-pillar[5]arene). **CPPn[5]** contained two asymmetrical macrocycles: one is pillar[5]arene, and the other is [10]CPP (Scheme 1c). This bicyclic structure stands out for its completely different types of macrocycles (π-conjugated macrocycles [10]CPP and nonconjugated macrocycle pillare[5]arene). The compound was fully characterized by high-resolution mass spectrometry (HR-MS), ^{1}H, ^{13}C and 2D NMR spectroscopy, steady-state spectroscopies, time-resolved photoluminescence decay and theoretical calculations. Theoretical calculations indicate that the strain energy of **CPPn[5]** is as high as 27.80 kcal/mol. In addition, its physical and supramolecular properties were studied.

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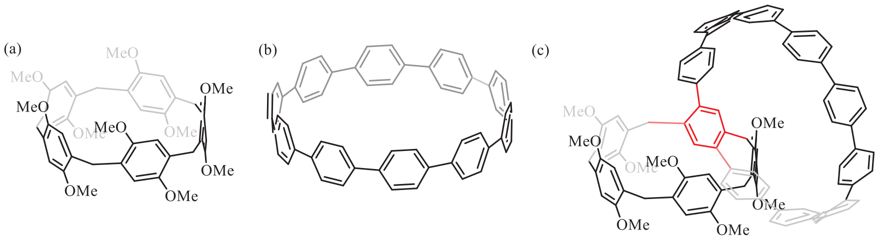
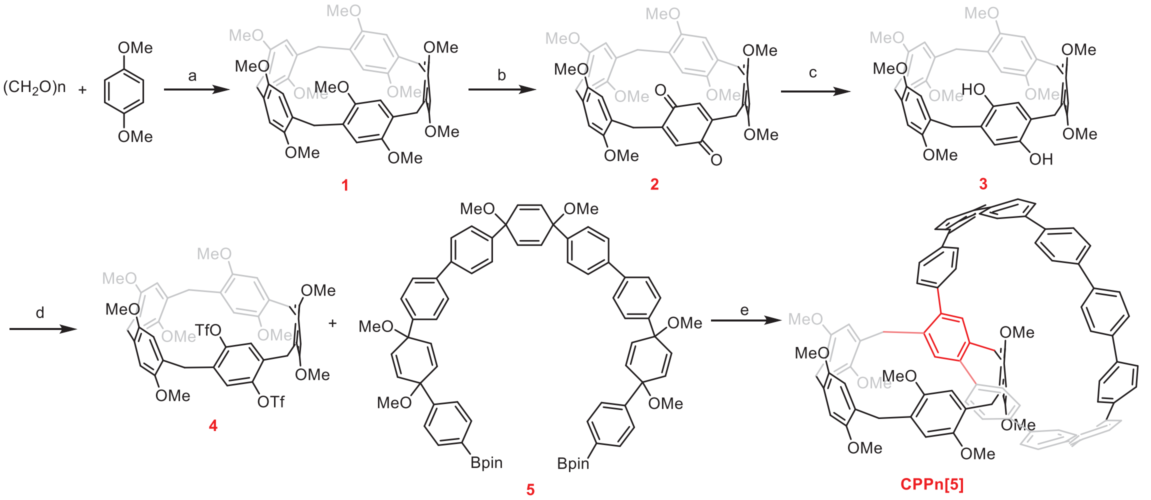


Scheme 1. Molecular structures of (a) pillar[5]arene, (b) [10]CPP and (c) **CPPn[5]**.



Scheme 2. Synthesis route for **CPPn[5]**. Reaction conditions: (a) $BF_3 \cdot O(C_2H_5)_2$, CH_2Cl_2 (DCM), 0 °C, 30 min, 50%; (b) CAN, DCM/H_2O, r.t., 40 min, 60%; (c) $Na_2S_2O_4$, DCM/H_2O, r.t., Ar, 12 h, 98%; (d) Tf_2O, pyridine, DCM, 0 °C, Ar, 12 h, 90%; (e) (1) $Pd(PPh_3)_4$, K_2CO_3, THF/H_2O, Ar, 75 °C, 72 h; (2) sodium naphthalide, THF, −78 °C, 1 h, 24% (two steps from compound **4**).

The synthesis of the bismacrocycle structure **CPPn[5]** is provided in Scheme 2. To synthesize this compound, we designed a strategy by reacting the ditriflate functionalized pillar[5]arene derivatives with a suitable curved molecule **5**. Curved molecule **5** [33] has a specific angle for the formation of the macrocyclic system. In addition, these cyclohexadienyl structures can alleviate strain energy during the macrocyclization step, which is a good linker to react with the ditriflate functionalized pillar[5]arene derivatives. Ditriflate functionalized pillar[5]arene was obtained from DMpillar[5]arene with a high yield (>40%) in three steps [34]. Then, compound **1** reacted with ditriflate pillar[5]arene through a Pd-catalyzed Suzuki-Miyaura reaction to afford the curved intermediate molecule. The target product was obtained from the intermediate molecule through a reductive aromatization reaction with sodium naphthalide in 24% yield over two steps.

The successful synthesis of the target molecule was confirmed by HR-MS and NMR spectroscopies. The exact mass spectrometry showed the main peak at *m/z* 1373.6187, which matched well with the calculated mass at *m/z* 1373.6175. The ^1H NMR spectrum of **CPPn[5]** in $CDCl_3$ is shown in Fig. 1. The aromatic protons include multiplets at 7.51–7.62 ppm, two doublets at 7.41 ppm and 7.21 ppm, and singlets at 6.96, 6.82, 6.61, 6.56 and 6.39 ppm. To fully assign these aromatic proton signals in **CPPn[5]** (Fig. 1b), 2D ^1H-^1H COSY NMR measurements were carried out (Fig. 1d). Based on these results, the multiplets at 7.51–7.62 ppm ($\mathbf{H_1}$, blue) can be confirmed from the protons in the paraphenylene fragment according to the number of integral protons and chemical shifts. Due to the inner and outer shielding effects, the protons at 7.41 ppm and 7.21 ppm can be assigned to $\mathbf{H_2}$ (purple) and $\mathbf{H_3}$ (pink), respectively. In particular, $\mathbf{H_2}$ showed an obvious interaction with $\mathbf{H_3}$ in the 2D COSY NMR spectrum, and this result can fully assign the protons of **CPPn[5]**. The protons on pillararene can be assigned to five single peaks at 6.39–7.18 ppm ($\mathbf{H_{4}}$–$\mathbf{H_8}$, red) because of their singlet peak patterns and absence of interaction with other peaks. These peaks were consistent with a previously reported study [34]. The remaining signals are assigned to the protons in the methoxy and methylene groups. Further characterization data including ^{13}C NMR and full spectrum COSY NMR are provided in the supporting information. All these characterizations verified the successful synthesis of this new bismacrocycle.

The photophysical properties of **CPPn[5]** were further studied by UV–vis absorption spectroscopy, steady-state fluorescence spectroscopy, and time-resolved fluorescence decay. The diluted solution of **CPPn[5]** in DCM ($c = 1.0 \times 10^{-6}$ mol/L) displayed an obvious absorption band in the range of 250–450 nm, maximized at 331 nm in DCM solution with a molecular absorption coefficient of 1.63×10^4 L mol^{-1} cm^{-1} (Fig. 2a, black line). Compared with the absorption feature of macrocycle [10]CPP ($\lambda_{max} = 338.5$ nm, red line), the blueshift and extended absorption of **CPPn[5]** could be ascribed to the pillararene part which contains a nonconjugated structure of the methylene moiety, and the result matched well with the HOMO-LUMO gaps based on the theoretical density functional theory (DFT) calculations (3.38782 eV for **CPPn[5]**, 3.34183 eV for [10]CPP). Moreover, the UV computational results (Table S3 in Supporting information) obtained by using the TDDFT method show that the maximum absorption peaks appear at 356.67 nm and 347.98 nm, consistent with the experimental values.

The fluorescence emission spectrum of [10]CPP showed one obvious emission band maximized at 471 nm upon excitation at 350 nm (Fig. 2, red plot). Interestingly, the emission spectrum of **CPPn[5]** exhibited a slight blueshift with one maximum emission peak at 458 nm (black plot). Compared to the Stokes shift of [10]CPP, **CPPn[5]** had a smaller Stokes shift of 13 nm, probably due to the influence of the pillararene macrocycle decreasing the whole molecular conjugate structure. Using anthracene as the reference ($\Phi_f = 30\%$ in ethanol), the photoluminescence quantum

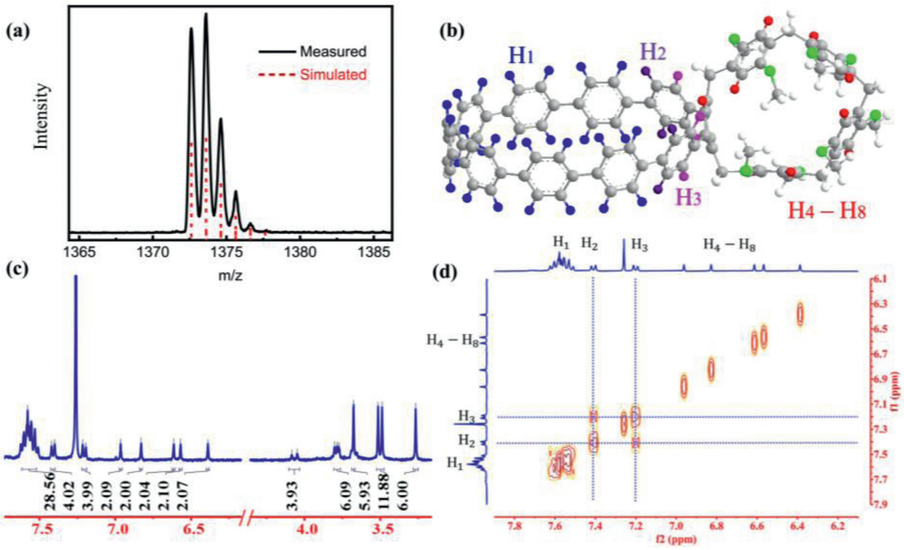


Fig. 1. Characterization spectra for **CPPn[5]**. (a) Partial HR-MS (MALDI-TOF) data. (b) Classification of protons in **CPPn[5]**. (c) Partial ^{1}H NMR spectrum of **CPPn[5]** in $CDCl_3$. (d) Expanded 2D ^{1}H-^{1}H COSY NMR spectrum (400 MHz, $CDCl_3$) of **CPPn[5]**.

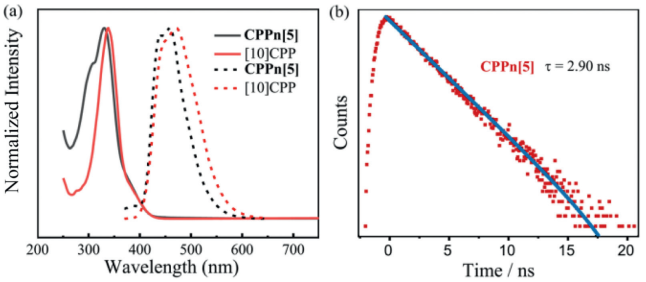


Fig. 2. (a) UV–vis absorption (solid lines) and fluorescence spectra (dotted lines) of **CPPn[5]** (black) and [10]CPP (red) in CH_2Cl_2. (b) Emission lifetime measured at λ = 458 nm for **CPPn[5]** in CH_2Cl_2 solution.

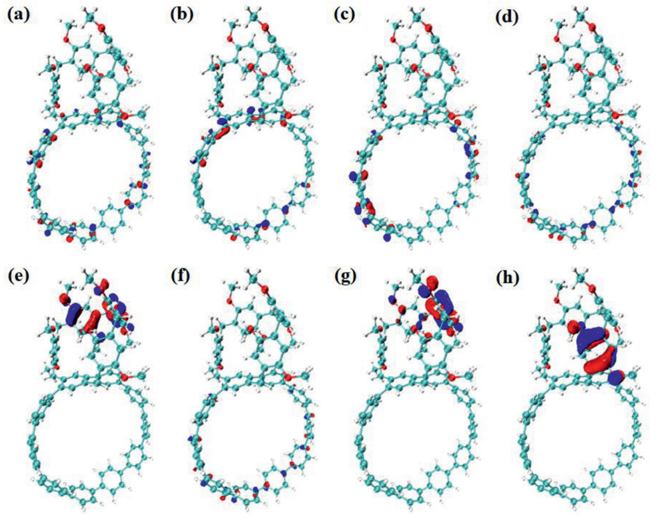


Fig. 3. Frontier molecular orbitals of **CPPn[5]:** (a) LUMO+3, (b) LUMO+2, (c) LUMO+1, (d) LUMO, (e) HOMO, (f) HOMO-1, (g) HOMO-2 and (h) HOMO-3.

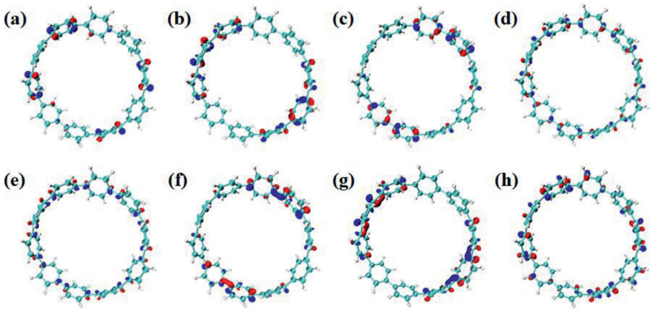


Fig. 4. Frontier molecular orbitals of [10]CPP: (a) LUMO+3, (b) LUMO+2, (c) LUMO+1, (d) LUMO, (e) HOMO, (f) HOMO-1, (g) HOMO-2 and (h) HOMO-3.

yield of **CPPn[5]** was determined to be $\Phi_f = 40\%$, which is lower than that of [10]CPP ($\Phi_f = 65\%$) probably resulting from a high proportion of nonradiative decay in the low-energy emission.

The fluorescence lifetime (τ_s) of **CPPn[5]** was measured by time-resolved fluorescence decay using the time-resolved photoluminescence (TRPL) technique. The emission lifetime was observed to be approximately 2.90 ns at 458 nm by monoexponential decay fitting excited at 390 nm.

To investigate the properties of **CPPn[5]**, density functional theory calculations were performed at the theoretical level of D3BJ-B3LYP/6–31G(d, p) utilizing the Gaussian 16 program [38]. Geometrical optimization results reveal that the larger average torsion angles (41.95°) of **CPPn[5]** than that (28.13°) for [10]CPP results in more strain energy (27.80 kcal/mol) of **CPPn[5]** than that of [10]CPP (26.88 kcal/mol) [39]. Frontier molecular orbital analysis results (Figs. 3 and 4, Table S2 in Supporting information) demonstrated that the energy level of unoccupied molecular orbitals moves downward due to the combination of [10]CPP and pillar[5]arene, while those of occupied molecular orbitals move upward, leading to a decline in the **CPPn[5]** HOMO-LUMO gap.

In addition, **CPPn[5]** should have interesting supramolecular properties because of its two different macrocyclic structures. To confirm this assumption, we chose two guests including ionic liquid guest G_1 (1–butyl–3-methyl imidazolium tetrafluoroborate) [35] and C_{60} guest for further study [10,36,37]. The supramolecular properties were investigated by ^{1}H NMR. According to the literature, the pillar[5]arene was allowed to form a complex, pillar[5]arene@G_1, with the ionic liquid guest G_1 [25]. From that result, we suppose that **CPPn[5]** has similar supramolecular properties because of its analogous pillararene ring. Adding excess ionic liquid G_1 into a solution of **CPPn[5]** in $CDCl_3$, the aromatic protons on CPP (**H_1** and **H_2**) have no significant shifts, but the aro-

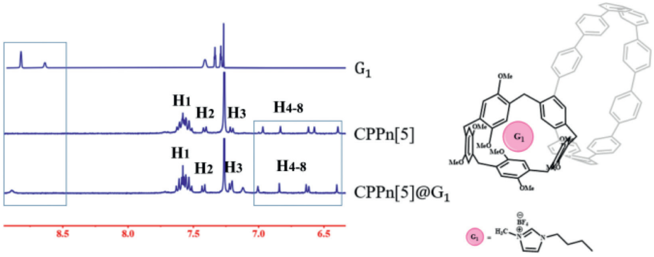


Fig. 5. Partial ^{1}H NMR spectrum of **CPPn[5]**@G_1 in $CDCl_3$.

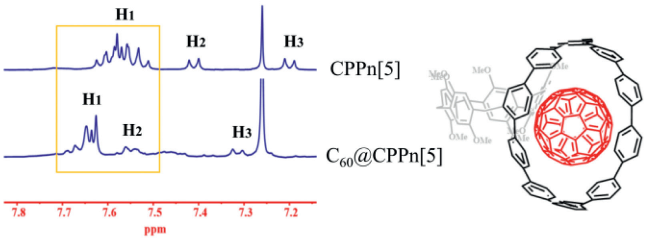


Fig. 6. Partial ^{1}H NMR spectrum of C_{60}@**CPPn[5]** in $CDCl_3$.

matic protons on pillar[5]arene (**H_4–H_8**) exhibited obvious changes in peak shapes and positions (Fig. 5). The addition of G_1 resulted in obvious upfield shifts for the proton signals on the pillararene of **CPPn[5]** ($\Delta\delta = -0.04$, -0.01, -0.02, -0.04, and -0.06 ppm for **H_{4-8}**, respectively). These changes can be defined as the host-guest interaction of aromatic protons pillar[5]arene (**H_4–H_8**) with G_1, and the result is consistent with the published results [25]. Obvious broadening effects and position changes for protons on G_1 can be observed (Fig. S9 in Supporting information). The protons from methoxy have no significant change, and this phenomenon can be described as the large average torsion angles of **CPPn[5]**, which made the host-guest interaction weaker than that of normal pillar[5]arene. We performed the NMR titrations experiments in $CDCl_3$ with G_1 and **CPPn[5]**, and the association constant (K_a) of **CPPn[5]@**G_1 was calculated to be 2.73×10^2 L/mol. All the evidence confirmed that the pillar[5]arene structure in **CPPn[5]** could act as a supramolecular host for G_1 to obtain **CPPn[5]@**G_1.

The supramolecular interaction between **CPPn[5]** and C_{60} was further observed by ^{1}H NMR spectroscopy. According to the literature, [10]CPP was allowed to form a complex, C_{60}@[10]CPP and this host-guest interaction caused ^{1}H NMR signal movement [36]. When excess C_{60} was added into **CPPn[5]** solution in $CDCl_3$ (Fig. 6), the peaks at 7.51–7.62 ppm for **H_1** shifted downfield to 7.60–7.70 ppm. The protons for **H_2** and **H_3** (7.41 ppm and 7.21 ppm) shifted to 7.55 ppm and 7.31 ppm, respectively. In addition, the protons for **H_4–H_8** merged into four single peaks. These results confirmed that **CPPn[5]** can act as a supramolecular host for C_{60} to obtain C_{60}@**CPPn[5]**. Moreover, We performed UV–vis titrations experiments in toluene with C_{60} and **CPPn[5]**, and K_a of C_{60}@**CPPn[5]** was calculated to be 1.67×10^5 L/mol. All the results indicate that the two macrocycles in **CPPn[5]** have independent supramolecular properties and revealed that **CPPn[5]** could be a potential supramolecular material.

In summary, we have successfully synthesized the bismacrocycle structure **CPPn[5]** by Pd-catalyzed Suzuki-Miyanra coupling of a nine-ring segment and ditriflate pillar[5]arene. This bismacrocycle had a π-conjugated carbon nanoring [10]CPP and a non-conjugated macrocycle pillar[5]arene centered on a benzene ring. Two cyclic frameworks in the structure had slight interactions with their physical properties. The supermolecular properties of **CPPn[5]** showed that the two macrocycles still have independent chemical properties. The computational result indicates that its strain energy is 27.80 kcal/mol and the HOMO-LUMO gap is 3.39 eV Further research should focus on functional macrocycles and explore their unique chemical and physical properties.

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.

Acknowledgments

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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.2023.108593.

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