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Synthesis and properties of cycloparaphenylene-2,7-pyrenylene: a pyrene-containing carbon nanoring†

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The first synthesis of a pyrene-containing carbon nanoring, cyclo[12]-paraphenylene[2]-2,7-pyrenylene ([12,2]CPPyr), is described. Through a sequence of stepwise macrocyclization using Pd and Ni catalysts followed by aromatization of L-shaped cyclohexane units afforded a [12,2]CPPyr in five steps from commercially available compounds. The UV-vis absorption and fluorescence spectra as well as TD-DFT calculations clarified the unique photophysical and electronic properties of the [12,2]CPPyr.

In recent years, considerable attention has been devoted to the chemistry of carbon nanorings that are macrocyclic aromatic hydrocarbons representing segments of carbon nanotubes (CNTs).[1] A carbon nanoring could not only serve as a template for a structurally well-defined CNT,[2] but is also an interesting π-conjugated molecule in its own right. Among various possible carbon nanorings, cycloparaphenylene (CPP) is the simplest carbon nanoring consisting solely of benzene rings. After many years of efforts by several groups including ours, the chemical synthesis of CPP has become possible in the last five years.[3] Since then, several sizes of CPPs,[4–6] CPP derivatives,[7,8] and related carbon nanorings[9,10] have been synthesized and their interesting properties have come to light.[11]

We next focused on the synthesis of benzannulated, π-extended CPPs that are similar to the structure of armchair CNTs. Considering the unique structural and photophysical properties of CPPs, modification of electronic properties of CPPs by benzannulation would provide novel macrocyclic aromatic systems. Although there have been three examples of simple aryl-substituted CPPs such as tetraaryl[12]CPP,[7a] phenylene- or naphthylene-bridged [8]CPP dimers,[7b] and dodecaaryl[9]CPP,[8] further benzannulation of these CPP derivatives has not been successful so far. In 2012, we reported the synthesis of [9]cyclo-1,4-naphthylene ([9]CN), which can be considered as a benzannulated [9]CPP at its ''K region''.[9b] A number of interesting properties derived from benzannulation (high ring strain, chiral conformation, and small Stokes shift compared to [9]CPP) have been observed in [9]CN. As shown in Fig. 1, the other position on CPP for benzannulation is its ''bay region'' to convert a biphenyl unit into a pyrene unit. Herein we report the synthesis of cycloparaphenylene-2,7-pyrenylene (CPPyr), the first pyrene-containing carbon nanoring. Structural and physical properties of CPPyr would also be of interest since it is well known that pyrene and its derivatives show characteristic photophysical properties such as long fluorescence lifetime[12] and excimer emission.[13]

We applied our general and modular synthetic strategy using a benzene-convertible L-shaped cyclohexane unit **1** to the synthesis of CPPyr.[3b] In our previous syntheses of CPP derivatives, coupling of the L-shaped unit and 1,4-diborylbenzene, 4,4′-diborylbiphenyl, 2,6-diborylnaphthalene, or 5,5′-dibromo-2,2′-bipyridyl furnished macrocyclic intermediates for CPPs,[4a,d] cycloparaphenylene-2,6-naphthylene,[9a] or cycloparaphenylene-2,5-pyridylidene,[9c] respectively. We envisioned that a [12,2]CPPyr **5**, which consists of twelve benzenes and two pyrenes, can be synthesized by a stepwise

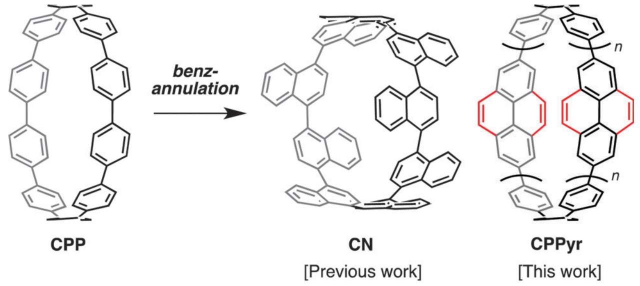

Fig. 1 CPP and two benzannulated, π-extended CPPs: CN and CPPyr.

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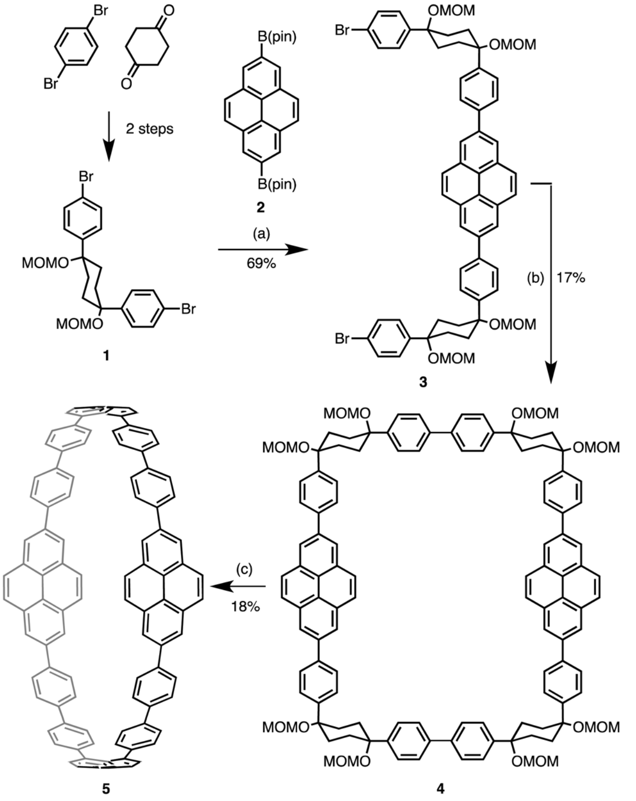

Scheme 1 Synthesis of **5**. Reaction conditions: (a) $Pd(PPh_3)_4$, Ag_2O, THF, reflux. (b) $Ni(cod)_2$, 2,2′-bipyridyl, 1,4-dioxane, 90 °C. (c) $NaHSO_4{\cdot}H_2O$, 1,2,4-trichlorobenzene, 150 °C. MOM = CH_2OCH_3, B(pin) = 4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl, THF = tetrahydrofuran.

coupling of the L-shaped unit **1** and 2,7-diborylpyrene **2**, followed by the aromatization of cyclohexane moieties. The ring size of the optimized structure of **5** (*ca.* 20 Å) is almost identical to that of [16]CPP.[4a] From a hypothetical homodesmotic reaction, the strain energy of **5** was estimated to be 37.9 kcal mol^{-1}, which is also similar to that of [16]CPP (35.6 kcal mol^{-1}).[11a]

Our synthesis of **5** is shown in Scheme 1. The L-shaped unit **1** and 2,7-diborylpyrene **2** were synthesized from commercially available reagents according to reported methods.[3b,14] The Suzuki–Miyaura cross-coupling of **2** (1.0 equiv.) with an excess amount of **1** (5 equiv.) produced a pyrene-containing U-shaped unit **3** in 69% yield. The $Ni(cod)_2$/2,2′-bipyridyl-promoted homocoupling of **3** afforded the corresponding box-shaped macrocycle **4** in 17% yield. In order to inhibit oligomerization of **3**, the reaction was performed under dilute conditions (1 mM). Finally, **4** was subjected to aromatization with $NaHSO_4$ (20 equiv.) in 1,2,4-trichlorobenzene at 150 °C and a [12,2]CPPyr **5** was obtained in 18% yield as a pale yellow solid. The high-temperature reaction in 1,2,4-trichlorobenzene was needed to accomplish the aromatization step. The solid of **5** was soluble in chlorinated solvents such as dichloromethane and chloroform, whereas it had poor solubility in other solvents such as ethyl acetate, methanol, and hexane. In the ^1H NMR spectrum of **5**, the two singlets that would be expected for a 2,7-disubstituted pyrene were observed: δ = 8.06 and 8.37 ppm in $CDCl_3$.[15] A broadened singlet signal belonging to the paraphenylene moieties was observed in a similar chemical shift (7.68 ppm) to that of [16]CPP (7.69 ppm).[4a]

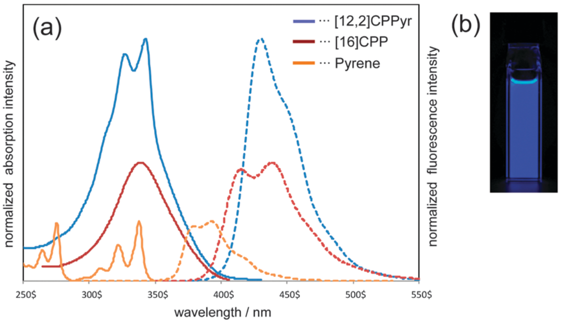

Fig. 2 (a) UV-vis absorption (solid lines) and fluorescence (broken lines) spectra of dichloromethane solution of **5** (blue line), chloroform solution of [16]CPP (red line) and chloroform solution of pyrene (orange line). (b) Fluorescence of **5**.

The UV-vis absorption and fluorescence spectra of the [12,2]CPPyr **5** were investigated to elucidate the effect of pyrene on the electronic properties of [12,2]CPPyr structures. The spectra of **5** taken as a dichloromethane solution are depicted in Fig. 2. Absorption peaks were observed at 328 nm and 343 nm with a shoulder on the long-wavelength side. The most intense absorption maximum (λ_{abs}) was observed at 343 nm and the molecular absorption coefficient (ε) was 6.1 × 10^5 cm^{-1} M^{-1}. Similar to [12]–[18]CPPs, **5** showed intense blue photoluminescence. Emission maxima (λ_{em}) were observed at 430 nm under excitation at 343 nm. Excimer emission was not observed even at the concentration of 10^{-3} M. The absolute fluorescence quantum yield (Φ_F) of **5** determined by a calibrated integrating sphere system was 0.21 ± 0.03. This value is lower than those of CPPs ([9]–[16]CPP, Φ_F = 0.73–0.90).[11a] On the other hand, the fluorescence lifetime of **5** was long (τ_s = 25.6 ns) in comparison with CPPs ([9]CPP and [12]CPP, τ_s = 10.6, 2.2 ns, respectively). Taking the long fluorescence lifetime of pyrenes[12] into consideration, inserted pyrenes would contribute to the long fluorescence lifetime of **5**. The radiative and nonradiative decay rate constants ($k_r = 8.4 \times 10^6\ s^{-1}$, $k_{nr} = 3.1 \times 10^7\ s^{-1}$) were determined from the observed quantum yield and fluorescence lifetime as well as the following equations: $\Phi_F = k_r \times \tau_s$ and $k_r + k_{nr} = \tau_s^{-1}$. The k_r values are one- or two orders of magnitude lower than those of CPPs ($k_r = 6.9 \times 10^7\ s^{-1}$ and $k_r = 4.0 \times 10^8\ s^{-1}$ for [9]CPP and [12]CPP, respectively), whereas the k_{nr} values are comparable to each other ($\sim 10^7\ s^{-1}$). The spectra of pyrene and [16]CPP are also shown in Fig. 2. The UV-vis spectrum of **5** seems to be a combination of two independent spectra of pyrene and [16]CPP. The fluorescence spectrum of **5** is red-shifted from those of pyrene and [16]CPP.

To understand the electronic nature of the [12,2]CPPyr **5**, a TD-DFT (time-dependent density functional theory) study was performed at the B3LYP/6-31G(d) level. Fig. 3 shows the energy diagrams and pictorial representations of six frontier molecular orbitals (MOs) of **5**. The orbitals of HOMO − 1 and HOMO − 2 as well as those of LUMO + 1 and LUMO + 2 are degenerate. In comparison with [16]CPP, the shapes and energy levels of HOMO

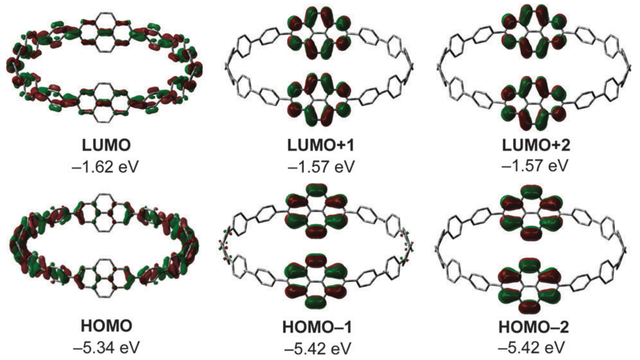

Fig. 3 Frontier MOs of **5** calculated at the B3LYP/6-31G(d) level.

and LUMO of **5** are very similar to those of [16]CPP: −5.32 eV (HOMO) and −1.61 eV (LUMO). However, HOMO − 1, HOMO − 2, LUMO + 1 and LUMO + 2 of **5** are localized on two pyrene moieties. Additionally, the shapes of these MOs of **5** are consistent with the HOMO and LUMO of pyrene and 2,7-diphenylpyrene.[15] The fact that frontier MOs of pyrene still remain even in **5** is the main reason why the shape of the absorption spectrum of **5** shows additivity in the spectra of pyrene and [16]CPP. In contrast, frontier MOs of pyrene are no longer HOMO and LUMO of **5** so that the emission wavelengths are mostly dependent on the cyclic paraphenylene structure.

In summary, the first synthesis of a pyrene-containing carbon nanoring has been achieved. Pd-catalyzed and Ni-mediated stepwise coupling reactions of a cyclohexane-based L-shaped unit and 2,7-diborylpyrene, followed by $NaHSO_4$-mediated aromatization successfully afforded a cyclo[12]paraphenylene[2]-2,7-pyrenylene **5**. The [12,2]CPPyr **5** has higher molecular absorption coefficient, lower fluorescence quantum yield and longer fluorescence lifetime (τ_s = 25.6 ns) than those of CPPs. The fact that the absorption of **5** shows a simple combination of CPP and pyrene reflects the poor conjugation of paraphenylene and 2,7-pyrenylene.

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