

Synthesis, Characterization, and Properties of [4]Cyclo-2,7-pyrenylene: Effects of Cyclic Structure on the Electronic Properties of Pyrene Oligomers**

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Abstract: A cyclic tetramer of pyrene, [4]cyclo-2,7-pyrenylene ([4]CPY), was synthesized from pyrene in six steps and 18 % overall yield by the platinum-mediated assembly of pyrene units and subsequent reductive elimination of platinum. The structures of the two key intermediates were unambiguously determined by X-ray crystallographic analysis. DFT calculations showed that the topology of the frontier orbitals in [4]CPY was essentially the same as those in [8]cycloparaphenylene ([8]CPP), and that all the pyrene units were fully conjugated. The electrochemical analyses proved the electronic properties of [4]CPY to be similar to those of [8]CPP. The results are in sharp contrast to those obtained for the corresponding linear oligomers of pyrene in which each pyrene unit was electronically isolated. The results clearly show a novel effect of the cyclic structure on cyclic π -conjugated molecules.

Cycloparaphenylenes (CPPs, Figure 1a) and structurally related hoop-shaped, π -conjugated molecules have attracted significant attention from various perspectives.^[1] This attention is not only because of their aesthetic structure but also because of their physical properties and reactivities resulting from the distorted π orbitals, for example, CPP is the simplest structural unit of armchair carbon nanotubes (CNTs; Figure 1b). In particular, the chemistry of CPPs has progressed^[2]

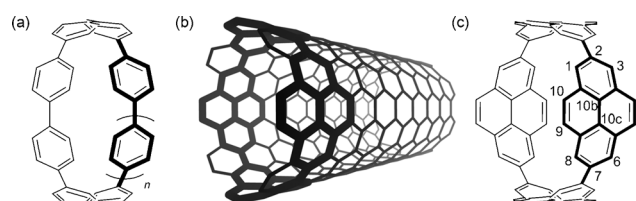


Figure 1. Structures of a) $[n + 7]$ cycloparaphenylene (CPP), b) (8,8) armchair carbon nanotube (CNT), and c) [4]cyclo-2,7-pyrenylene (CPY). The [4]CPY unit in CNT is shown in bold.

since the discovery of synthetic methods by Jasti, Bertozzi et al.,^[3] Itami et al.,^[4] and Yamago et al.^[5] For example, their applications in electronic materials^[5b,6] and as the building blocks for the preparation of π -expanded^[7] and π -layered materials^[8] have been investigated. The synthetic methods developed by Jasti, Bertozzi et al. and the group of Itami have been applied to the synthesis of several CPP derivatives by the research groups of Jasti, Itami, and Müllen,^[7a,9] and the method developed by the group of Yamago has been used for the synthesis of the structural units of chiral CNTs as reported by Isobe and co-workers.^[10]

Among the various properties of CPPs, electronic properties, as exemplified by the redox properties and orbital modulation, are among the most intriguing properties associated with the potential applications of CPPs in nanoelectronic materials.^[11] Theoretical studies by Yamago and co-workers indicated that,^[5b] in sharp contrast to linear oligoparaphenylenes, the HOMO–LUMO energy gap of CPPs becomes narrower as the number of phenylene rings decreases, because of the increase and decrease in the HOMO and LUMO energies, respectively (HOMO = highest occupied molecular orbital, LUMO = lowest unoccupied molecular orbital). Furthermore, the electrochemical analyses proved the size dependence of the HOMO–LUMO energy gap.^[5b] However, the structural effects of substituted CPPs on their electronic properties has not been studied despite several reports on the synthesis of these derivatives.

Pyrene is one of the most widely used chromophore in materials science and technology.^[12] Despite the structural similarity between biphenyl and pyrene, they have a completely different electronic structure (see below). Therefore, the effect of the cyclic structure of oligopyrenes on their electronic properties would be of great interest. Furthermore, compared to CPP, the cyclic oligomers of pyrene should be better precursors for the bottom-up synthesis of structurally

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uniform armchair CNTs.^[13] Therefore, their synthesis and evaluation of their electronic properties would significantly improve the future design of cyclic π -conjugated molecules.

Herein, we report the synthesis of a cyclic tetramer of pyrene, [4]cyclo-2,7-pyrenylene ([4]CPY, Figure 1c), starting from pyrene and using the platinum-mediated assembly route developed by our group. The theoretical calculations and electrochemical analyses established the unique electronic properties of [4]CPY compared to those of the linear oligomers of pyrene. The results obtained in this study clearly showed a novel effect of cyclic structure on modulating the molecular properties of π -conjugated molecules, namely, the change in orbital topology induced by the cyclic structure. Recently, Itami et al. reported the synthesis of a [16]CPP derivative containing two pyrene units.^[14] However, the synthesis of CPP derivatives consisting of only pyrene units has not been reported. Also, the effect of cyclic structure on the electronic properties has not been investigated.

First, the effects of the cyclic structure of oligopyrenes were estimated by density functional theory (DFT) calculations at the B3LYP/6-31G* level of theory. Pyrene can be drawn as bis-2,2'- and 6,6'-ethynylene bridged 1,1'-biphenyl (**A**) as one of its resonance structure (Figure 2a). However, the frontier orbitals of pyrene are completely different from those of biphenyl and better expressed as a resonance hybrid of the [14]annulene structures **B** and **C** (Figure 2b versus c). Müllen and co-workers experimentally established that this difference in the electronic structure of pyrene was preserved in its oligomers. In sharp contrast to oligoparaphenylenes, the pyrene units in 2,7-linked pyrene dimer and trimer were electronically isolated with negligible π - π interactions because the 2- and 7-positions of pyrene do not have orbital coefficients in both the HOMO and LUMO.^[15] The theoretical calculations of a linear pyrene tetramer supported the

results obtained by Müllen and co-workers. The HOMO of tetra-2,7-pyrene was degenerate, and both the HOMOs were localized on the pyrene ring located at the end, thus preserving the same orbital topology as that of the parent pyrene (Figure 2d). HOMO-2, located 0.03 eV below the HOMO, has orbital coefficients on the two pyrene rings in the middle. However, the lack of orbital coefficients at the 2 and 7-positions of each pyrene unit indicates no electronic interactions between the two pyrene units. The orbital coefficients of LUMO, +1 and +2, also indicate that all the pyrene units have no electronic interactions.

In contrast, the HOMO and LUMO of [4]CPY are fully conjugated and delocalized throughout the entire molecule (Figure 2e). In particular, the distribution and topology of orbital coefficients of [4]CPY are almost identical to those of [8]CPP (Figure 2f), and the distribution of orbital coefficients at the peripheral ethynylene moiety was almost negligible. This orbital modulation must be an important effect of the cyclic structure in π -conjugated oligomers.

The HOMO and LUMO energies of [4]CPY (-5.18 eV and -1.70 eV, respectively) are higher and lower than those of linear pyrene tetramer (-5.39 eV and -1.60 eV, respectively), respectively, because of the strain-induced increase of the quinoidal contribution as observed in CPPs.^[5b,6b] Thus, the HOMO-LUMO gap of the former (3.48 eV) is narrower than that of the latter (3.82 eV). This important effect of the cyclic and strained structure observed in CPPs is preserved in [4]CPY.

The strain energy of [4]CPY was calculated to be 392 kJ mol⁻¹, which is significantly higher than that of [8]CPP (307 kJ mol⁻¹). The sp²-carbon atoms considerably deviated from planarity. The π -orbital axis vector analysis^[16] shows that the pyramidalization angle around C2 and C10b (also C7 and C10c) are 5.5° and 2.9°, respectively.

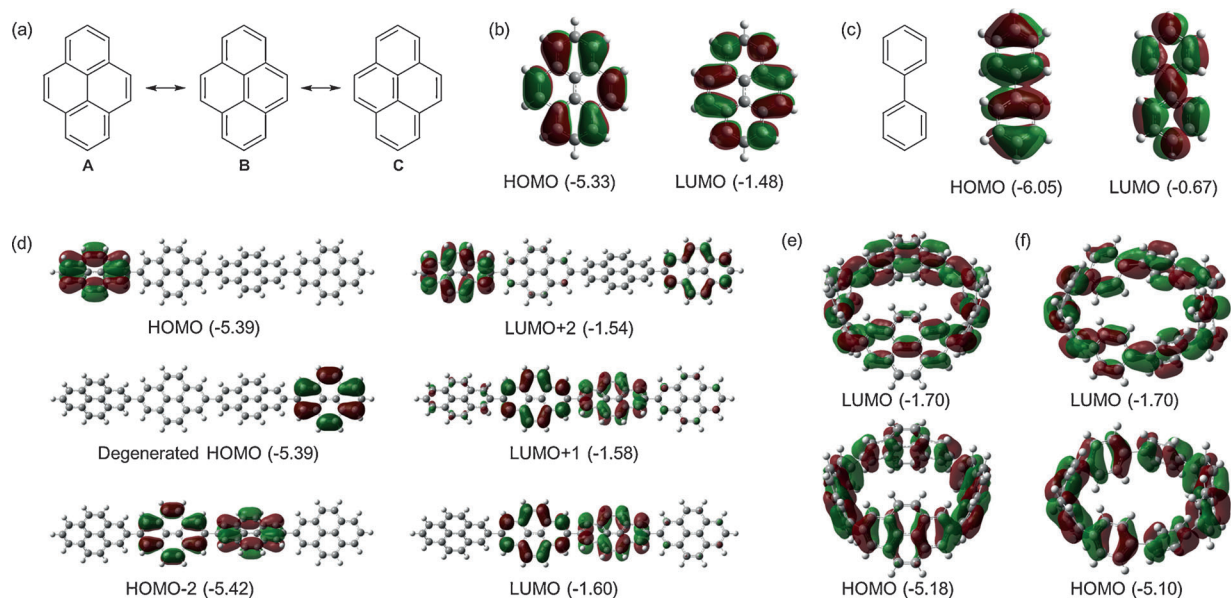
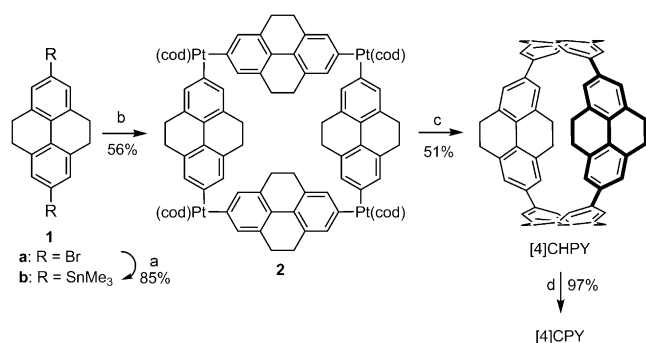


Figure 2. a) Representative resonance structures and b) HOMO and LUMO of pyrene. c) Structure and HOMO and LUMO of biphenyl. HOMO and LUMO of d) tetra-2,7-pyrene, e) [4]CPY, and f) [8]CPP. Orbital energies calculated at the B3LYP/6-31G* level of theory are shown within parentheses.



Scheme 1. Synthesis of [4]CHPY and [4]CPY. Reaction conditions:

a) 1. BuLi (2.05 equiv), THF, -41°C , 1 h. 2. Me₃SnCl (2.1 equiv), THF, -41°C to RT, 11 h. b) [Pt(cod)Cl₂] (1.0 equiv), THF, reflux, 18 h. c) PPh₃ (10 equiv), toluene, 100°C , 21 h. d) Pd/C, 1,2-dichlorobenzene, 150°C , 55 h. cod = 1,5-cyclooctadiene.

The synthesis of [4]CPY was next examined. 2,7-Dibromo-4,5,9,10-tetrahydropyrene (**1a**), which was prepared in two steps and 78% yield from pyrene on large scale ($>10\text{ g}$),^[17] was transformed into the corresponding bis(trimethylstannyl) compound **1b** in 85% yield (Scheme 1). Next, the reaction of **1b** with [Pt(cod)Cl₂] (cod = cycloocta-1,5-diene) in tetrahydrofuran (THF) afforded the tetranuclear platinum complex **2** in 56% yield. The structure of **2**, initially determined by NMR spectroscopy, was unambiguously established by X-ray crystallographic analysis (see Figure S10 in Supporting Information).^[18] The complex **2** is almost square in shape, and the two sets of diagonal C-Pt-C angles were 87.6 and 91.1° .

Heating **2** in the presence of PPh₃ (10 equiv)^[10a,19] at 100°C reductively eliminated platinum, thus affording [4]cyclo-4,5,9,10-tetrahydro-2,7-pyrenylene ([4]CHPY) in 51% yield (Scheme 1). The bromine-induced reductive elimination of platinum in our previous synthesis of CPPs^[5a,b,d] afforded a mixture of cyclic products, including partially 4,5- and/or 9,10-dehydrogenated products, in about a 10% combined yield as determined by NMR and MS analyses. The structure of [4]CHPY, initially determined by ^1H and ^{13}C NMR spectroscopy, and matrix-assisted laser desorption/ionization mass spectrometry (MALDI-TOF MS), was finally and unambiguously established by the X-ray crystallographic analysis of a crystal obtained by the slow evaporation of a solution of [4]CHPY in CH₂Cl₂ (Figure 3).^[20] In the

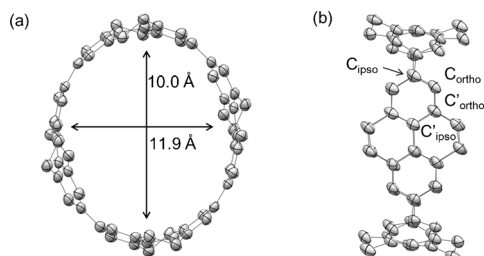


Figure 3. X-ray structures of [4]CHPY from the top (a) and side (b). Thermal ellipsoids are shown at 50% probability. Solvent molecules and hydrogen atoms are omitted for clarity.

crystalline state, [4]CHPY adopted an ellipsoidal shape, in which the short axis was 16% shorter than the long axis. This large deformation is most probably due to the packing forces associated with the highly elastic character of CPPs.^[8b] The average C-C bond lengths of aromatic six membered rings are 1.38 (C_{ipso}-C_{ortho} and C'_{ipso}-C'_{ortho}), 1.48 (C_{ipso}-C_{ipso} and C'_{ipso}-C'_{ipso}), and 1.39 Å (C_{ortho}-C_{ortho} and C'_{ortho}-C'_{ortho}), and were almost identical to those obtained by the DFT calculations (C_{ipso}-C_{ortho} = 1.41, C_{ipso}-C_{ipso} = 1.48, and C_{ortho}-C_{ortho} = 1.39 Å).

Finally, [4]CPY was synthesized by the dehydrogenation of [4]CHPY, with Pd/C in 1,2-dichlorobenzene at 150°C , in nearly quantitative yield (Scheme 1).^[21] The structure of [4]CPY was confirmed by two singlet signals at $\delta = 7.74$ and 8.06 ppm in the ^1H NMR spectrum, five signals in the ^{13}C NMR spectrum ($\delta = 123.76, 125.13, 127.55, 131.92$, and 136.76 ppm), and MALDI-TOF MS ($m/z = 800.2496$). The [4]CPY was stable in air and soluble in many organic solvents, such as CHCl₃, CH₂Cl₂, and toluene in contrast to linear oligopyrenes.^[15]

The photophysical properties of [4]CPY were measured in CHCl₃ (Figure 4a).^[21] The UV/visible spectrum of [4]CPY

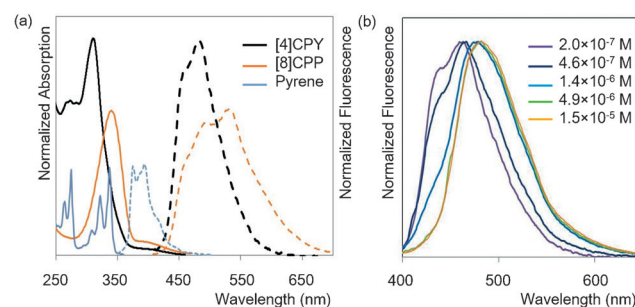


Figure 4. a) UV/visible absorption and fluorescence spectrum of the solutions of [4]CPY ($2.0 \times 10^{-7}\text{ mol L}^{-1}$), [8]CPP ($8.2 \times 10^{-6}\text{ mol L}^{-1}$), and pyrene ($5.0 \times 10^{-5}\text{ mol L}^{-1}$) in CHCl₃. b) Concentration-dependent fluorescence of [4]CPY in CHCl₃. The fluorescence spectra were obtained by exciting the sample at $\lambda = 370\text{ nm}$.

showed the maximum absorption (λ_{max}) at 311 nm with an absorption coefficient (ϵ) of $1.7 \times 10^4\text{ mol L}^{-1}\text{ cm}^{-1}$, which was blue-shifted from that of [8]CPP. The characteristic vibration bands of parent pyrene were not observed. The time-dependent DFT (TD-DFT) calculations indicate that the HOMO→LUMO transition is symmetry forbidden as observed in CPPs.^[5b] The λ_{max} of [4]CPY was derived from the sum of many transitions, and further studies are needed to clarify this point.

The [4]CPY exhibited concentration-dependent fluorescence behavior (Figure 4b). The maximum fluorescence significantly red-shifted with increasing concentration, and a structureless emission band at $\lambda \approx 500\text{ nm}$ was observed at a concentration of greater than $4.9 \times 10^{-6}\text{ mol L}^{-1}$. The fluorescence quantum yield (Φ_F) at $2.0 \times 10^{-7}\text{ mol L}^{-1}$ was 0.05, which was similar to that of [8]CPP ($\Phi_F = 0.08$).^[6a] The concentration dependence indicated that the formation of intermolecular excimers, despite the loss of planarity of the pyrene units, due to the large deformation.

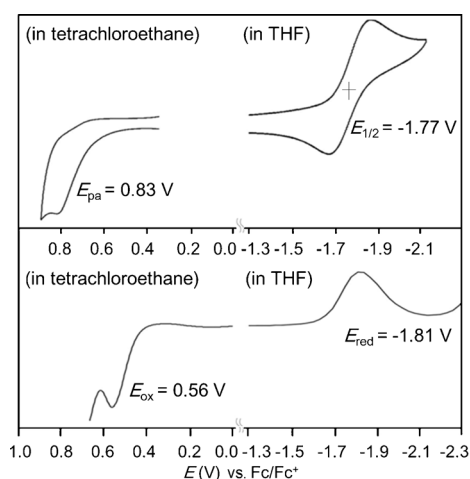


Figure 5. Cyclic voltammograms (upper figure) and differential pulse voltammograms (lower figure) of [4]CPY with $0.1 \text{ mol L}^{-1} \text{ Bu}_4\text{NPF}_6$ as the supporting electrolyte at a scan rate of 0.1 V s^{-1} .

The electrochemical analysis of [4]CPY was analyzed by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in Bu_4NPF_6 solutions of tetrachloroethane or THF (Figure 5). The [4]CPY exhibited irreversible oxidation wave by the CV. The oxidation potential was determined to be 0.56 V (vs. Fc/Fc^+) by the DPV. This value was almost identical to that of [8]CPP (0.59 V). The result was consistent with the similar HOMO energy levels of [4]CPY and [8]CPP obtained by the DFT calculation.

A reversible reduction wave for [4]CPY was observed at -1.77 V in THF. No further reduction wave was observed even when the anodic sweep was further extended to -2.3 V . Müllen and co-workers reported that 2,7-linked linear bi- and tripyrene exhibited two and three reduction waves, respectively, and corresponded to the reduction of each pyrene unit because each pyrene unit was not electronically connected as discussed above.^[15] Therefore the difference between [4]CPY and oligopyrenes should be attributed to the delocalization of the π orbital as suggested by the calculations.

In summary, [4]CPY was synthesized in high yield by the platinum-mediated assembly of **1b**, reductive elimination of platinum from the resulting complex **2**, thus forming [4]CHPY, and subsequent dehydrogenation. Both the theoretical and electrochemical studies showed that the topology of the frontier orbitals of [4]CPY was completely different from that of the corresponding linear oligopyrenes, but was similar to that of [8]CPP. The results clearly illustrate the novel effect of the cyclic structure in π -conjugated oligomers, namely, the modulation of the frontier orbital topology induced by the change in the structural topology. Besides the fascinating electronic character of [4]CPY, this compound along with [4]CHPY would be useful starting materials for the bottom-up synthesis of structurally uniform CNTs.

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- [21] Use of 2,7-bis(trimethylstannyl)pyrene as a precursor of [4]CPY was unsuccessful because of its low solubility to common solvents.
- [22] See the Supporting Information for the physical properties of [4]CPHY. The electronic structure of [4]CPHY was virtually identical to that of [8]CPP.