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Synthesis and Properties of Cycloparaphenylene-2,5-pyridylidene: A Nitrogen-Containing Carbon Nanoring

Katsuma Matsui, Yasutomo Segawa, and Kenichiro Itami*

Department of Chemistry, Graduate School of Science, Nagoya University,
Nagoya 464-8602, Japan

itami.kenichiro@a.mbox.nagoya-u.ac.jp

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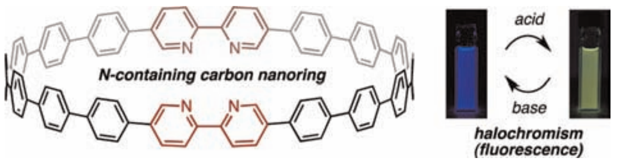
ABSTRACT



The first synthesis of a nitrogen-containing cycloparaphenylene, cyclo[14]paraphenylene[4]2,5-pyridylidene ([14,4]CPPy), has been achieved. A palladium-catalyzed stepwise assembly of 2,2′-bipyridine, benzene, and L-shaped cyclohexane units, followed by NaHSO$_4$/*o*-chloranil-mediated aromatization, successfully provided [14,4]CPPy. While the absorption and fluorescence properties of [14,4]CPPy were somewhat similar to those of cycloparaphenylenes (λ_{abs} = 344 nm, $\varepsilon = 7.3 \times 10^4$ cm^{-1} M^{-1}, λ_{em} = 427 nm, Φ_F = 0.80), it was found that [14,4]CPPy possesses an interesting halochromic property.

Cycloparaphenylene (CPP) is a simple conjugated carbon nanoring consisting solely of benzene rings with para linkage (Figure 1). Although CPP has attracted the interest of chemists for a long time,[1−3] the chemical synthesis of CPP has become feasible only recently.[4−7] Moreover [12]CPP, prepared by the procedure developed in our group, has become commercially available.[8] Adding to its structural simplicity and beauty, CPP has a number of interesting properties such as unique cyclic conjugation,[3] photophysical properties,[4,5e,6,7] and guest-encapsulating properties.[5c,d,9] Moreover, as CPP represents the shortest sidewall segment of armchair carbon nanotube (CNT) structures, there is great expectation that CPP might

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(8) [12]CPP is now commercially available from Tokyo Chemical Industry Co., Ltd. (TCI), catalog no. C2449.

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function as a precursor or seed in the preparation of structurally uniform armchair CNT.[1]

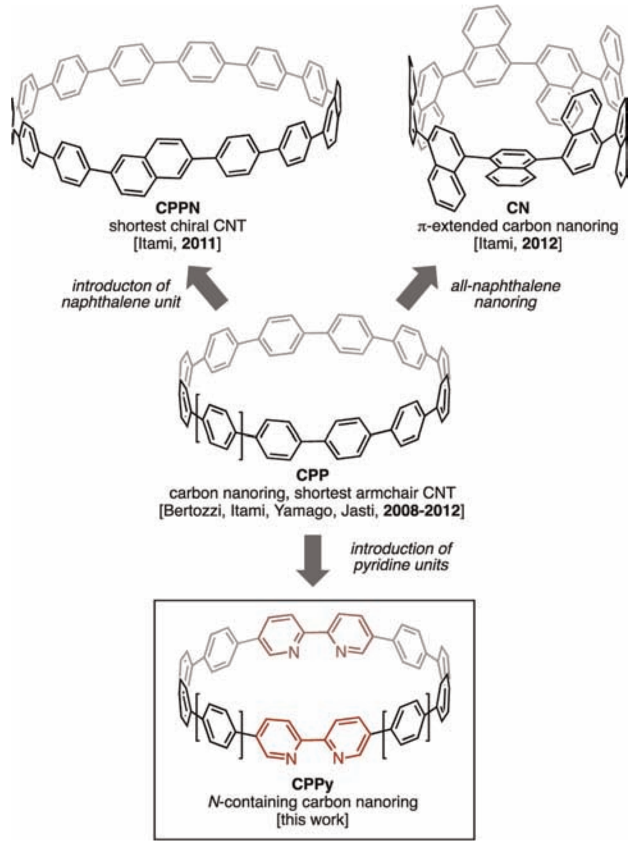
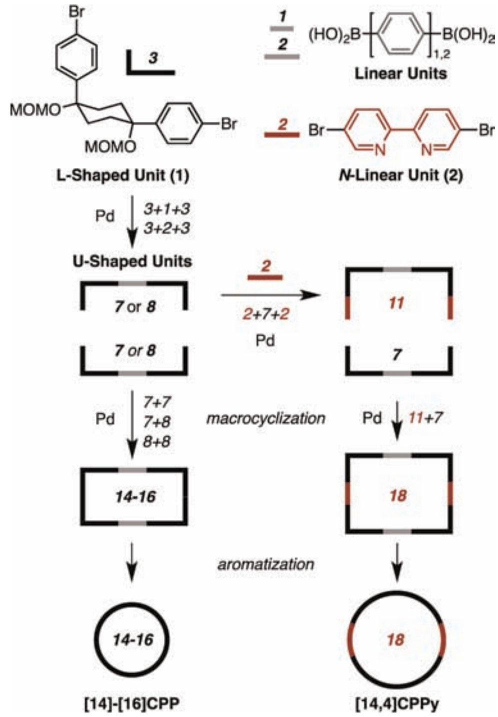


Figure 1. Structures of CPP and related carbon nanorings.

In relation to these studies, other carbon nanorings have recently been synthesized (Figure 1).[10−12] For example, we have designed acene-inserted CPPs as short sidewall segments of chiral CNT structures and synthesized one of the chiral carbon nanorings, [13]cycloparaphenylene-2,6-naphthylene ([13]CPPN).[10,11] More recently, we accomplished the first synthesis of a π-extended carbon nanoring, [9]cyclo-1,4-naphthylene ([9]CN), and uncovered a number of unique structural features such as large dihedral angles, slow arene rotation, chirality, and a racemization process.[12] In addition to these hydrocarbon-based materials, carbon nanorings that bear heteroatoms are of significant interest for numerous potential applications.[3h] We herein report the synthesis and some interesting properties of cyclo[14]paraphenylene[4]2,5-pyridylidene ([14,4]CPPy), a nitrogen-containing CPP.

We decided to apply our general synthetic strategy using a benzene-convertible L-shaped cyclohexane unit to the synthesis of CPPy. Among various routes and conditions for making carbon nanorings,[5,10,12] we envisioned that the stepwise Pd-catalyzed cross-coupling method useful in making relatively large CPPs would be suitable (Scheme 1).[5b] In our previous synthesis of [14]−[16]CPP, the 2:1 cross-coupling of a *cis*-1,4-bis(4-bromophenyl)cyclohexane unit (**1**) and 1,4-diborylbenzene or 4,4′-diborylbiphenyl derivative (linear unit) furnished the corresponding U-shaped dibromide. The counterpart U-shaped diboronates were synthesized from the dibromides by a Pd-catalyzed Miyaura borylation reaction. The cyclizative dimerization of these U-shaped units and follow-up aromatization led to [14]CPP (7 + 7), [15]CPP (7 + 8), and [16]CPP (8 + 8).

Scheme 1. Synthetic Strategy for [14,4]CPPy



We envisaged that [14,4]CPPy, a bipyridine-inserted CPP, would be synthesized by a 2:2 cross-coupling of a U-shaped 7-benzene unit and 5,5′-dibromo-2,2′-bipyridyl (**2**) in a stepwise fashion (2 + 7 + 2 then 11 + 7) followed by aromatization (Scheme 1). The outcome of our investigations based on this strategy is the first synthesis of [14,4]CPPy shown in Scheme 2.

The key 7-benzene U-shaped diboronate **3** was synthesized in four steps from commercially available reagents following our previously established method.[5b] The treatment of **3** (1.0 equiv) with an excess amount of **2** (10 equiv) in the presence of $PdCl_2(dppf)$ (3 mol %) and $n\text{-}Bu_4NBr$ (1.0 equiv) in toluene/H_2O afforded bipyridine-containing U-shaped unit **4** in 79% yield (Scheme 2). Then **4** was subjected to the cyclizative cross-coupling with **3** catalyzed by the $PdCl_2(dppf)/n\text{-}Bu_4NBr$ system to furnish the box-shaped macrocycle **5** in 48% yield. Good yield in the macrocyclization may be a consequence of the nice match

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(11) Isobe also reported the synthesis of [4]cyclo-2,8-chrysenylene as another short sidewall segment of chiral CNT structures. Hitosugi, S.; Nakanishi, W.; Yamasaki, T.; Isobe, H. *Nat. Commun.* **2011**, *2*, 492.

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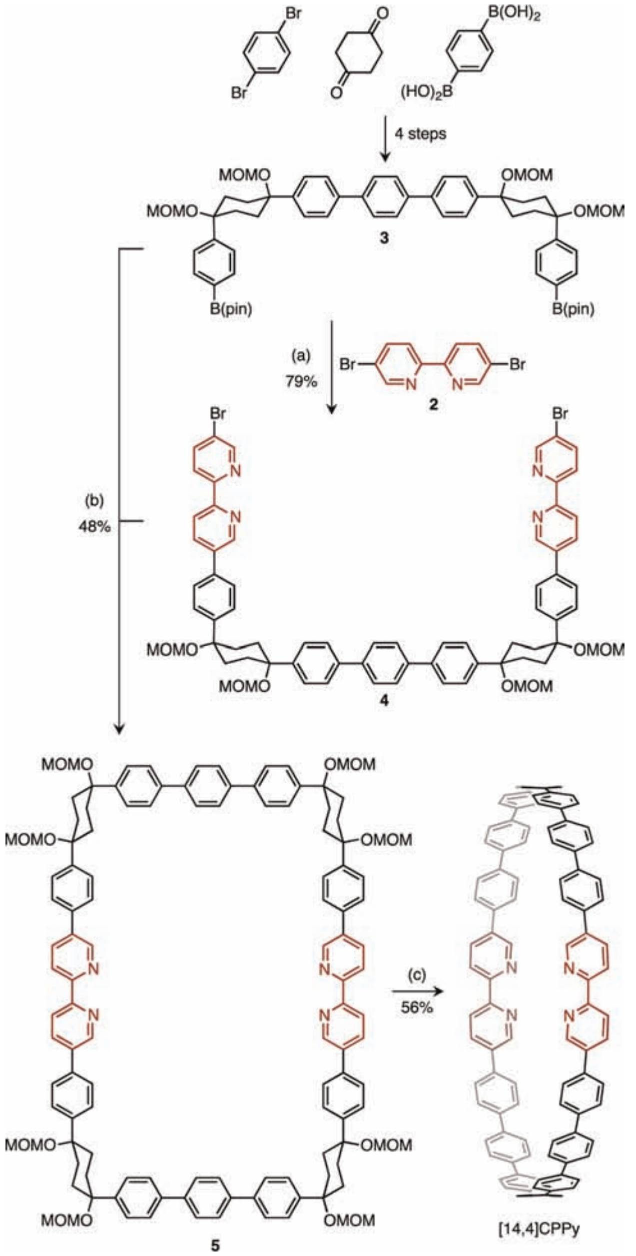
Scheme 2. Synthesis of [14,4]CPPy[a,b]



[a] Reaction conditions: (a) $PdCl_2(dppf)$, Na_2CO_3, n-Bu_4NBr, toluene/H_2O, reflux. (b) $PdCl_2(dppf)$, Na_2CO_3, n-Bu_4NBr, toluene/H_2O, reflux. (c) $NaHSO_4 \cdot H_2O$, o-chloranil, m-xylene/DMSO, 150 °C. [b] MOM = methoxymethyl, B(pin) = 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl, dppf = 1,1′-bis(diphenylphosphino)ferrocene, DMSO = dimethylsulfoxide.

between the “arch widths” of two U-shaped units (**3** and **4**). The conditions based on the $Pd(OAc)_2$/XPhos system, which we optimized and used in the modular synthesis of [n]CPPs,[5b] were not effective in this case. Finally, the macrocycle **5** was subjected to aromatization with $NaHSO_4$ (20 equiv) and o-chloranil (5.0 equiv) in DMSO/m-xylene at 150 °C to afford [14,4]CPPy as a light tan solid in 56% yield (Scheme 2). In the ^1H NMR spectrum of [14,4]CPPy, three typical signals of pyridyl hydrogen atoms were observed: δ = 8.05 (dd, J = 8.4, 1.6 Hz, 4H), 8.45 (d, J = 8.4 Hz, 4H), 8.97 (d, J = 1.6 Hz, 4H) ppm in $CDCl_3$. The ring size of [14,4]CPPy (ca. 25 Å) is almost identical to that of [18]CPP, which is the largest CPP synthesized to date.[4]

With the target nanoring in hand, we subsequently investigated the UV−vis absorption and fluorescence properties of [14,4]CPPy to elucidate the effect of pyridine rings on the electronic nature of CPP. Shown in Figure 2a are these spectra of [14,4]CPPy taken as a dichloromethane solution. The most intense absorption maximum (λ_{abs}) was observed at 344 nm with the molecular absorption coefficient (ε) of 7.3×10^4 cm^{-1} M^{-1}. Interestingly, the shape of the absorption spectrum of [14,4]CPPy turned out to be very similar to those of large CPPs.[5e]

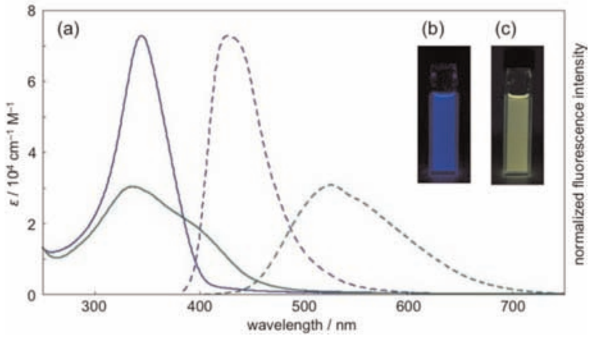


Figure 2. (a) UV−vis absorption (solid lines) and fluorescence spectra (broken lines) of dichloromethane solution of [14,4]CPPy (blue lines) and after adding HCl (green lines). (b) Fluorescence of [14,4]CPPy. (c) Fluorescence of [14,4]CPPy + HCl.

Similar to [18]CPP, [14,4]CPPy showed intense blue photoluminescence with the emission maxima (λ_{em}) at 427 nm. The absolute fluorescence quantum yield (Φ_F), determined by a calibrated integrating sphere system, was found to be quite high (Φ_F = 0.80).[13] According to the quantum yield and fluorescence lifetime (τ_s = 1.2 ns), radiative and nonradiative decay rate constants ($k_r = 6.8 \times 10^8$ s^{-1}, $k_{nr} = 1.7 \times 10^8$ s^{-1}) were determined based on the following equations: $\Phi_F = k_r \times \tau_s$ and $k_r + k_{nr} = \tau_s^{-1}$. These values are comparable to those of [12]CPP ($k_r = 4.0 \times 10^8$ s^{-1}, $k_{nr} = 5.0 \times 10^7$ s^{-1}).[5e]

To determine the nature of excitation of [14,4]CPPy, a TD-DFT study was performed at the B3LYP/6-31G(d) level. Shown in Figure 3 are the energy diagrams and pictorial representations of six frontier MOs of [14,4]CPPy. Unlike in the case of CPP, the orbital energies of [14,4]CPPy are not degenerate because of lower symmetry. However, the shapes and energy levels of frontier MOs of [14,4]CPPy are very similar to those of [18]CPP. This is reflective of the fact that the contribution of lone pairs on nitrogen atoms to HOMO, HOMO−1, and HOMO−2 become negligible in [14,4]CPPy due to the effective π-conjugation.[14] Similarly to the case of CPP, the oscillator strength (f) of the HOMO→LUMO transition (S_1) is virtually not allowed. The observed intense

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(13) The Φ_F values of [12]- and [14]−[16]CPP are in a range of 0.88−0.90. See ref 5e.

absorption should be the excitations of the ground state to the second and third excited states S_2 (HOMO−1→LUMO, HOMO→LUMO+2) and S_3 (HOMO−2→LUMO, HOMO→LUMO+1) with high *f* values (3.15 and 2.16).

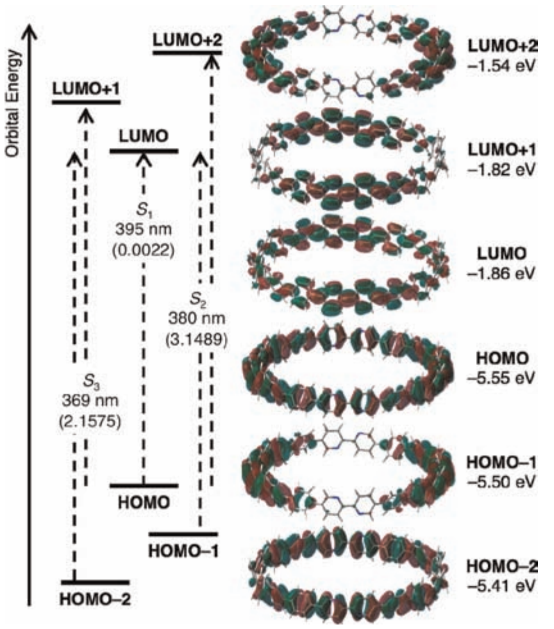

Figure 3. Energy diagrams and pictorial representations of the frontier MOs of [14,4]CPPy, calculated at the B3LYP/6-31G(d) level of theory. Excitation energies were computed by TD-DFT at the same level. Values in parentheses represent oscillator strengths (*f*).

While the absorption and fluorescence properties of CPPy were somewhat similar to those of CPP, the introduction of nitrogen atoms may append additional properties. Those include acid–base chemistry as well as a metal-binding property. We herein report some preliminary results on this topic. We found that the addition of hydrochloric acid to a diluted solution of [14,4]CPPy in dichloromethane changes the optical properties (fluorescence in particular) of [14,4]CPPy. The absorption and fluorescence spectra of [14,4]CPPy with HCl are shown in Figure 2a as green lines. An obvious broadening and a red shift were observed in both absorption and fluorescence. These bathochromic shifts might be due to the emergence of an intramolecular charge transfer excited state upon the protonation of bipyridine units in [14,4]CPPy. By adding HCl, otherwise blue emissive [14,4]CPPy displayed greenish yellow fluorescence. Interestingly, neutralization of the solution with Et_3N reproduced the blue fluorescence of [14,4]CPPy. This acid/base-induced reversible fluorescence change (halochromism) is a novel function added to CPP. By preliminary experiments, we also observed the feasibility of metal complexation of [14,4]CPPy with Pd(II).[15] We greatly expect that CPPy would function as a key component for a new class of supramolecular nanotubes and belts by taking advantage of its metal-coordinating ability.[16]

In summary, the first synthesis of a nitrogen-containing CPP has been achieved. A palladium-catalyzed stepwise assembly of 2,2′-bipyridine, benzene, and L-shaped cyclohexane units, followed by $NaHSO_4$/*o*-chloranil-mediated aromatization successfully provided [14,4]CPPy. While the absorption and fluorescence properties of [14,4]CPPy were somewhat similar to those of CPP (λ_{abs} = 344 nm, ε = 7.3×10^4 cm^{-1} M^{-1}, λ_{em} = 427 nm, Φ_F = 0.80), it was found that [14,4]CPPy possesses an interesting halochromic property. The applications of [14,4]CPPy for various purposes and the synthesis of other heteroatom-containing carbon nanorings are the focus of ongoing work.

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Supporting Information Available. Experimental procedures, characterization data for all new compounds, and details of photophysical and computational studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.