

A Porphyrin Nanobarrel That Encapsulates C₆₀Jianxin Song,[†] Naoki Aratani,^{*,†,‡} Hiroshi Shinokubo,^{*,§} and Atsuhiko Osuka^{*,†}

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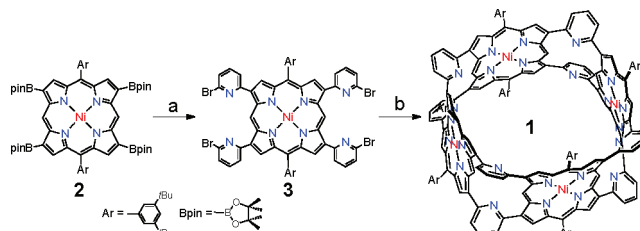
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Abstract: A porphyrin nanobarrel, **1**, that can encapsulate C₆₀ effectively was prepared via a concise coupling route. The structures of both **1** and C₆₀@**1** were confirmed by single-crystal X-ray diffraction analysis.

The bottom-up “designed organic synthesis” of benzene-based nanocarbon materials such as fullerenes¹ and single-walled carbon nanotubes (SWNTs)² has been extensively attempted, as such a synthetic approach would allow for tailored fine-tuning of the structures, properties, and functions of these materials. These attempts are also important in view of bent aromatic molecules.³ Such distorted aromatic systems are expected to display novel electronic properties that are not shared by normal planar aromatic molecules. Porphyrin is a representative planar and aromatic macrocycle that serves as a key chromophore or catalyst in both the natural and chemical worlds. In recent years, it has been increasingly realized that porphyrins are structurally and electronically rather flexible, depending upon perturbations such as peripheral substitution and steric congestion, as exemplified by extensively conjugated cases and extremely distorted or bent examples.⁴

The finding that bacterial photosynthetic light-harvesting antenna LH2 are supramolecular wheel-shaped assemblies has stimulated synthetic efforts directed toward large porphyrin wheels for use in the study of excitation energy transfer and electronic coupling within the wheel.⁵ As a consequence, many porphyrin wheels have been explored. However, with a few exceptions,⁶ the vast majority lack a whole π conjugation, and none of the reported examples involve a doubly linked wheel bearing a void space that is comparable to fullerenes and SWNTs. When these structural requirements are met, the porphyrin wheel may be regarded as a porphyrin nanotube. Quite recently, we reported the synthesis of β,β' -doubly 2,6-pyridylene-bridged Ni(II)–porphyrin belts,⁷ which exhibit remarkably bent conformations due to constraints arising from the β,β' -double 2,6-pyridylene bridges. These structures have strongly encouraged the synthetic extension to cyclic porphyrin tubes.⁸

Here we report the synthesis of porphyrin nanobarrel **1** via consecutive cross-coupling reactions at multiple sites starting from a simple monomer. Our synthetic strategy involves the use of Suzuki–Miyaura cross-coupling reactions for construction of the tubular framework. Specifically, tetraborylporphyrin **2**⁹ and an excess amount of 2,6-dibromopyridine were treated with 6 mol % Pd catalyst in DMF/toluene at reflux under an inert atmosphere to give tetra(6-bromopyridyl)porphyrin **3** in 50% yield; **3** was then coupled with **2** to furnish porphyrin barrel **1** in 10% yield (Scheme

Scheme 1. Synthetic Route to **1**^a

^a Conditions: (a) 2,6-dibromopyridine, Pd₂(dba)₃, PPh₃, Cs₂CO₃, CsF, toluene, DMF, reflux, 22 h; (b) **2**, Pd₂(dba)₃, PPh₃, Cs₂CO₃, CsF, toluene, DMF, reflux, 48 h.

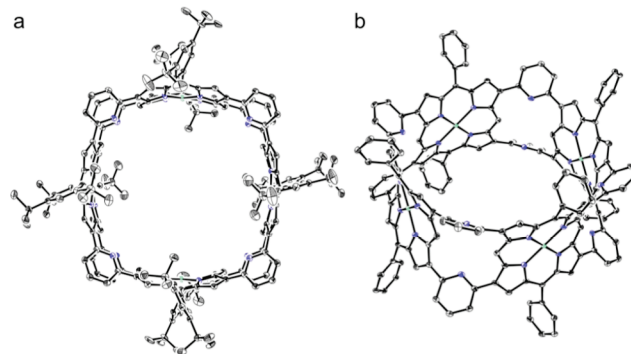


Figure 1. X-ray crystal structure of **1**: (a) top view; (b) perspective view. Thermal ellipsoids represent 50% probability. Hydrogen atoms and solvent molecules in both views and the *tert*-butyl groups in the perspective view have been omitted for clarity.

1). The matrix-assisted laser desorption/ionization time-of-flight (MALDI–TOF) mass spectrum of **1** displays the parent ion peaks at m/z 3574.501 (calcd for C₂₃₂H₂₁₆N₂₄Ni₄, m/z 3574.512 [M]⁺). The ¹H NMR spectrum of **1** in CDCl₃ at –25 °C reveals only a single set of signals that consists of two singlet peaks at 10.42 and 8.64 ppm due to the meso and β protons, respectively, and signals due to the other aromatic protons in the range 8.23–6.97 ppm. These data indicate that the porphyrin barrel **1** takes a *D*_{4h}-symmetric structure in solution.

The final structural proof was obtained from single-crystal X-ray diffraction analysis (Figure 1). The tetramer **1** displays a barrel structure with a diameter of ~14 Å (Ni–Ni distance). The constitutional porphyrins take a ruffled structure, forming a concave wall. The pyridyl bridges are held tilted to the neighboring pyrroles with an average dihedral angle of 43.5° and pyridine–pyrrole bond lengths of ~1.47 Å. The tilted pyridyl bridges seemingly serve as a conjugative mediator to cause overall moderate π conjugation. The inside of the barrel was filled with many solvent molecules of THF and chloroform (Figure S8 in the Supporting Information).

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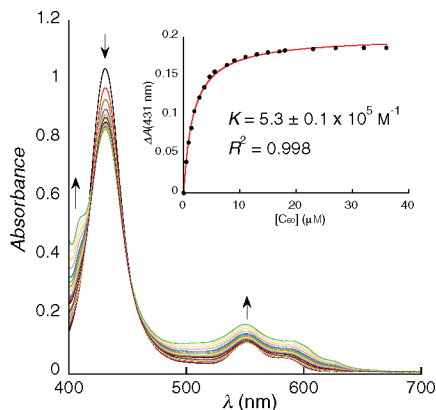


Figure 2. UV–vis absorption spectra of **1** (2.0 μM) in toluene in the presence of various amounts of C_{60} ($0 < [\text{C}_{60}] < 36 \mu\text{M}$) at 25 $^{\circ}\text{C}$. Arrows indicate the changes in absorption with increasing $[\text{C}_{60}]$. Inset: plot of $\Delta A_{431\text{nm}}$ vs $[\text{C}_{60}]$.

The UV–vis absorption spectrum of **1** is spread over a wide range of the visible region relative to that of the monomer, indicating the effective electronic interaction between the porphyrin units through the pyridyl bridges (Figure 2).

In the next step, the encapsulation of C_{60} into **1** was examined, as the diameter of the interior cavity of **1** is $\sim 14 \text{ \AA}$, which is nicely fit to the diameter of C_{60} .¹⁰ Actually, the addition of C_{60} into a toluene solution of **1** changed the absorption spectrum as a result of electronic interactions between the two components (Figure 2). The encapsulation was also confirmed by ^{13}C NMR spectroscopy: a 1:1 mixture solution of **1** and C_{60} in CDCl_3 showed a signal at 139.6 ppm that was distinctly different from the signal of free C_{60} observed at 143.1 ppm and hence assignable to $\text{C}_{60}@\mathbf{1}$. The complexation stoichiometry was determined to be 1:1 on the basis of the Job's plot, and the association constant of $\text{C}_{60}@\mathbf{1}$ was estimated from the UV–vis absorption changes to be $(5.3 \pm 0.1) \times 10^5 \text{ M}^{-1}$, which is certainly large but comparable to or slightly smaller than those reported for cyclic porphyrin dimers^{11a,b} and a cyclic porphyrin timer.^{11c}

Fortunately, the complex structure was unambiguously confirmed by single-crystal X-ray diffraction analysis (Figure 3). In the solid state, the porphyrin units of $\text{C}_{60}@\mathbf{1}$ have a structure similar to that of **1** with respect to the pyridine–pyrrole distance ($1.45\text{--}1.50 \text{ \AA}$), the dihedral angles of the pyridines with respect to the porphyrins ($50\text{--}53^{\circ}$), and the void space (14 \AA diameter). As shown in Figure 3, a C_{60} molecule is nicely captured within the void space with an average distance of $\sim 3.6 \text{ \AA}$. Closer inspection of the crystal structure revealed that the constitutional ruffled porphyrins protrude their convex faces toward the interior void space, which interacts with C_{60} in a cooperative manner. Interestingly, the porphyrin barrels in the crystal are interconnected through extracapsular C_{60} molecules that interact with their concave faces, forming an infinite three-dimensional grid structure (Figure S9).

In summary, the porphyrin barrel **1** was synthesized via a concise synthetic route. This barrel exhibits an effective electronic interaction over the molecule as well as an encapsulating ability toward

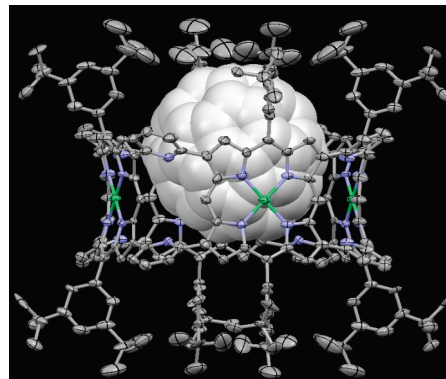


Figure 3. X-ray crystal structure of $\text{C}_{60}@\mathbf{1}$. For clarity, only one isomer of encapsulated C_{60} molecules is shown. Thermal ellipsoids represent 50% probability. The C_{60} molecule is depicted as a sphere model. Solvent molecules, two extracapsular C_{60} molecules, and hydrogen atoms have been omitted for clarity.

C_{60} . We are currently exploring the synthesis of free-base and Zn(II) counterparts of $\text{C}_{60}@\mathbf{1}$ and their electron-transfer chemistry.

Supporting Information Available: Preparation and analytical data for samples and crystallographic data (CIF) for **1** and $\text{C}_{60}@\mathbf{1}$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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