A Square Cyclic Porphyrin Dodecamer: Synthesis and Single-Molecule Characterization

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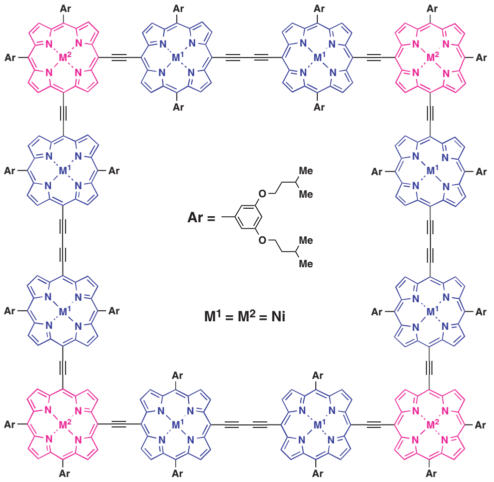
We prepared a square cyclic porphyrin dodecamer via the tetramerization of a trimer shaped like a right angle. The molecule was visualized by scanning tunneling microscopy to be square.

The synthesis of porphyrin oligomers is one of the most attractive topics in contemporary interdisciplinary research.[1] Many molecules with various shapes have been reported so far. Cyclic porphyrin oligomers (CPOs) hold a unique position in this research field.[2] Because the cyclic alignment of porphyrinoid compounds is employed in harvesting light energy in photosynthesis,[3] the evaluation of structure-function relationship has emerged as a new research topic. The CPOs are expected to be used as model compounds for the elucidation of the light harvesting phenomenon, and as advanced host molecules having the capability to incorporate large molecules into their nanosized holes.[2] In this communication, we report the synthesis and characterization of cyclic porphyrin dodecamer **1** in which the porphyrins are connected to each other by acetylenes.



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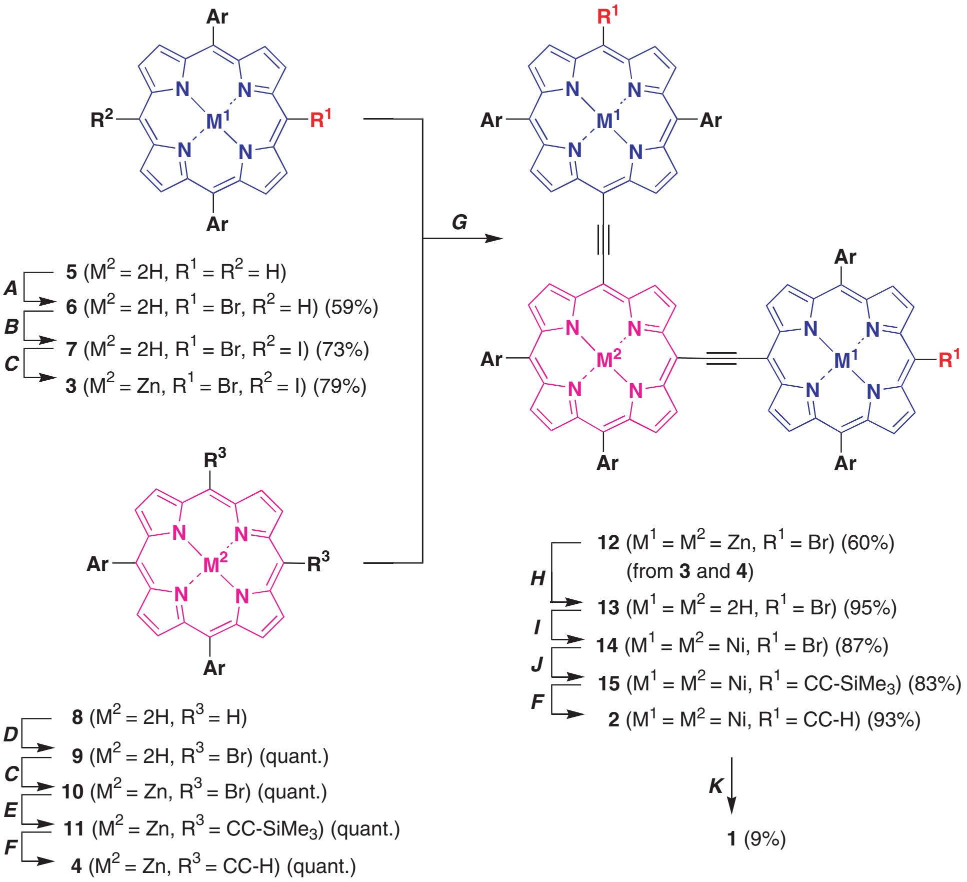
Formula 1. Molecular structures of **1**.

The synthesis of **1** is summarized in Scheme 1. The selection of the incorporated metal is vital to our chemistry. Zinc is required to increase the concentrations of **3** and **4** in the coupling reaction of **12** using THF, because the nickel complexes of **3** and **4** have low solubilities, whereas nickel is required to decrease the aggregation of **1**. An important intermediate, porphyrin trimer **2** having a right angle, was prepared by the coupling reaction of **3** with **4**. Porphyrin **3** having different halogens at the *meso*-positions, bromine and iodine, was prepared by a revised method.[4] Porphyrin **4** functionalized at its 5- and 10-positions was obtained by conventional functional group transformation of the corresponding diarylporphyrin **8**.[2a] The coupling reaction of a 2:1 mixture of **3** and **4** required strictly controlled conditions using a combination of $AsPh_3$ and $Pd_2(dba)_3 \cdot CHCl_3$ in a weakly coordinative solvent, THF, with 16 mM **4** to give **12** in an acceptable yield. After the replacement of the metals and the introduction of acetylenic groups, the protecting groups were removed to afford **2**. The final reaction involved oxidative coupling. Structurally undefined oligomeric and incomplete dimeric and trimeric products were separated by gel permeation chromatography to give dark solid **1** (9%, total yield: 0.007% in 22 steps).

The results of laser desorption time-of-flight mass spectroscopy supported the structure of **1**, $M^+ = 10725.7$, calcd $M^+ = 10725.2$ for $C_{656}H_{696}N_{48}Ni_{12}O_{48}$. The absence of the acetylenic C-H stretching mode of **1**, e.g., the absorption at 3310 cm^{-1} observed for **2**, also supported the cyclic structure of **1**. However, the most reliable evidence supporting the structure of **1** was provided by the direct observation of its molecular shape by ultrahigh-vacuum scanning tunneling microscopy (UHV-STM) (Figure 1). UHV-STM images of **1** were taken in its adsorbed state on a Cu (111) surface, prepared using our pulse injection technique.[5] The molecule was recognized as a square-shaped doughnut with a hole. Each side of the square was approximately 5-nm long, consistent with the molecular size of **1** estimated by molecular geometry calculation (MM3), 5.1 nm.

The UV–Vis spectrum of **1** is composed of two bands: the Q-band-like Band I (13500 cm^{-1}, 743 nm, log $\varepsilon = 5.60$) and the Soret-band-like Band II (20500 cm^{-1}, 488 nm, log $\varepsilon = 5.77$) (in $CHCl_3$). The fact that the relative intensity of Band I to Band II of **1** is higher than those of structurally similar oligomers may indicate the large oscillator strength of Band I as derived from preliminary theoretical considerations. The excitation of Band I may be due to the exciton coupling between the $a_{2u} \rightarrow e_g$ excitations of each porphyrin moiety.

In conclusion, novel cyclic porphyrin dodecamer **1** was prepared and structurally characterized. The molecule is expected to



Scheme 1. Condition A: 1 equiv. NBS/CH_2Cl_2-pyridine. Condition B: I_2, $PhI(CF_3CO_2)_2$/CH_2Cl_2-pyridine. Condition C: $Zn(OAc)_2{\cdot}4H_2O$/$CHCl_3$. Condition D: 2 equiv. NBS/CH_2Cl_2-pyridine. Conditions E: 9 equiv. $Me_3C{\equiv}CH$, $Pd(PPh_3)_4$, CuI/THF-Et_3N. Conditions F: $(n\text{-BuN})^+F^-$/CH_2Cl_2. Condition G: **3** and **4** (=2:1), $Pd_2(dba)_3{\cdot}CHCl_3$, $AsPh_3$/THF-Et_3N. Condition H: CF_3CO_2H/$CHCl_3$-MeOH. Condition I: $Ni(acac)_2$/toluene. Condition J: 40 equiv. $Me_3C{\equiv}CH$, $Pd(PPh_3)_4$, CuI/THF-Et_3N. Condition K: 90 equiv. CuCl, TMEDA, Air/CH_2Cl_2.

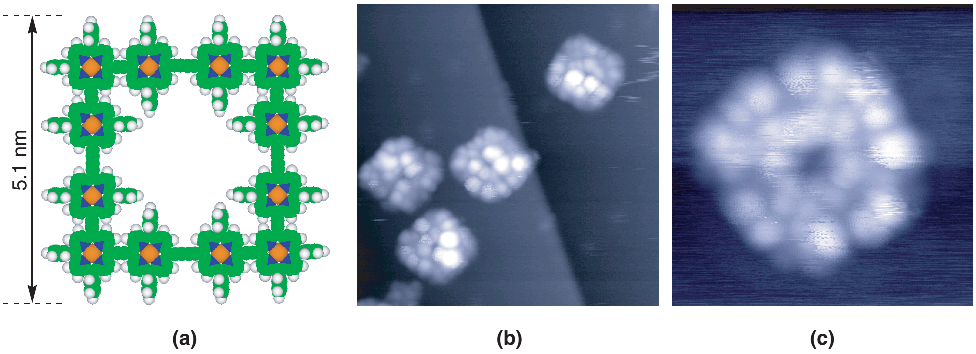


Figure 1. (a) Space filling drawing of **1** obtained by MM3 calculation. Isopentyloxy groups on the phenyl groups were removed for clarity. (b) UHV-STM image ($21 \times 21\,nm^2$) on a Cu (111) surface at liquid nitrogen temperature. The imaging conditions are $I = 2\,pA$ and $V_s = -1.5\,V$. (c) Higher resolution UHV-STM image ($7 \times 7\,nm^2$). The imaging conditions are $I = 2\,pA$ and $V_s = +0.7\,V$.

pave the way to a new field of advanced materials chemistry. We are currently investigating the details of its spectroscopic characteristics and its single-molecule nano-host–guest chemistry using a ca. 2-nm diameter hole of **1**.

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