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A β-to-β 2,5-Thienylene-bridged Cyclic Porphyrin Tetramer: Its Rational Synthesis and 1:2 Binding Mode with C_{60}

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A β-to-β 2,5-thienylene-bridged cyclic porphyrin tetramer was rationally synthesized via a concise synthetic route. The tetraporphyrin exhibits a positive cooperative binding ability of C_{60} to demonstrate a new potential of the nonplanar, distorted cyclic porphyrin arrays.

Since the crystal structure of LH2 was elucidated to be circularly arranged chromophoric assemblies, many efforts have been devoted towards the synthesis of cyclic porphyrin arrays to study the excitation energy transfer (EET) and electronic coupling along the wheel. These cyclic porphyrin arrays are also interesting in host–guest chemistry, single molecule photochemistry, nonlinear optical (NLO) materials and so on. Cyclic porphyrin arrays are constructed either by means of covalent bonds, noncovalent bonds, or metal coordination bonds. Although there are some reports on covalently bonded cyclic porphyrin arrays, most of them were constructed through meso-to-meso bridging ways. As rare examples, we have recently reported several β-to-β bridged cyclic porphyrin arrays with a 1,3-butadiyne, a 2,6-pyridyl, and a 2,5-thienyl spacer. This double bridging strategy secures a rigid conformation and substantial electronic interaction, which induce significant enhancements of two-photon absorption (TPA) properties.
We have achieved the one-pot synthesis of 2,5-thienylene-bridged cyclic porphyrin dimer 2H and trimer 3H previously. In this reaction we found the formation of a small amount of tetramer 4H in 1% yield (Scheme 1). We then examined a stepwise rational synthetic route to 4H (Scheme 2).

**Results and Discussion**

Coupling of 7 equiv of β,β'-diborylated porphyrin 1 with 2,5-dibromothiophene provided borylated porphyrin dimer 2B, which was then coupled with an excess amount of 2,5-dibromothiophene to furnish 2Br in 48% yield in 2 steps.

β,β'-Diborylated porphyrin 2B was cross-coupled with 2Br in the presence of a palladium catalyst and bases to afford 2,5-thienylene-bridged tetraporphyrin 4H in 52% yield. The 1H NMR spectrum of 4H exhibits a singlet signal for the meso-protons, one singlet and two doublet peaks for β-protons, and a single peak for the thiophene protons, suggesting the high symmetry of 4H. The parent ion peak of 4H was observed at m/z = 3821.30 (calcd for C_{294}H_{396}N_{10}S_{4} = 3821.26 [M]+) in its MALDI-TOF mass spectrum. Then nickel(II) and zinc(II) complexes 4Ni and 4Zn were quantitatively obtained through insertion of nickel and zinc ions into the free base porphyrin 4H.
C₆₀ binding ability

Due to the outstanding chemical and physical properties of C₆₀, the molecular design of C₆₀ receptors is a growing research area.²⁷ For the crystal state and in solution, several articles have shown that porphyrin derivatives form the 1:1 complexes with C₆₀ because of an attractive force between a C₆₀ and a porphyrin-ring. Some other cases exhibited elegant cooperative binding mode for the formation of 1:2 or 1:3 complexes.²⁸ However, none of examples demonstrated such 1:2 complex in the solid state. The totally nonplanar, distorted structure of 4Zn encouraged possible encapsulation of two large molecules such as fullerenes in its wide void π-surrounded spaces.

Although the interactions of 4Zn and 4H with C₆₀ were observed, the complicated spectral changes hampered the detailed analysis. On the other hand, the formation of the 4Ni-C₆₀ complex in toluene was clearly indicated by titration using the UV-vis absorption spectra (Figure 2). The λmax of the Soret band (438 nm) was shifted to longer wavelength (442 nm) with a tight isosbestic point (480 nm in Soret band region). The spectral characteristics are analogous to those of other porphyrin-C₆₀ complexation systems.¹⁹ To estimate the stoichiometry between 4Ni and C₆₀, ¹H NMR spectra for [4Ni]:[C₆₀] = 1:0 to 1:4 at 25°C were measured in toluene-d₈ ([4Ni] = 0.50 mM). The resonance signals of the meso-protons and thiophene protons shifted downfield on C₆₀ addition (see Figure S14 in Supplementary Information; SI). As shown in Figure S15, a plot of Δδ versus [C₆₀]/[4Ni] has a clear inflection point at [C₆₀]/[4Ni] = 2.0. This value supports the view that the complex is formed with a 1:2 4Ni:C₆₀ stoichiometry. The Job's plot also supported 1:2 stoichiometry (Figure S13).

This guest-binding profile was analyzed with the Hill equation: \( \log(y/(1-y)) = n \log([C₆₀]) + \log(K) \), where \( K \) and \( n \) are the association constant and Hill coefficient, respectively, and \( y = (\text{Abs}_{\text{obs}} - \text{Abs}_{\text{so}})/(\text{Abs}_{\text{a}} - \text{Abs}_{\text{so}}) \) where \( \text{Abs}_{\text{so}} \) is \( \text{Abs}_{\text{abs}} \) at C₆₀ = 0 and infinite, respectively.²¹ From the curve-fitting of the plots, we obtained \( \log K = 7.7 \pm 0.6 \) for 1:2 4NiC₆₀ complex and \( n = 1.6 \). The binding of the first C₆₀ holds the flipping of two complexing porphyrin rings and consequently keeps two other opposite porphyrin rings in an appropriate position for binding of the second C₆₀. In fact, the K value is sufficiently large and the Hill coefficient is close to 2.0, indicating a positive cooperative binding of two C₆₀ guests. Fortunately, the complex structure was unambiguously confirmed by single-crystal X-ray diffraction analysis (Figure 3). In the solid state, the porphyrin units have a structure similar to that of 4Zn with respect to the dihedral angles of the thiophene to the adjacent pyrrole rings (29-45°), and the Ni—Ni distances (12.4 and 13.1 Å). As shown in Figure 3, two C₆₀ molecules are nicely captured within the void space with an average distance of 3.2–3.4 Å. Closer inspection of the crystal structure revealed that the one set of constitutional ruffled porphyrins keeps concave face inside to wrap the one C₆₀ up in a cooperative manner, the other set protrudes their convex faces toward the interior void space, which interacts with additional C₆₀. To the best of our knowledge, this is the first crystal structure that achieves a 1:2 binding mode of the...
porphyrin oligomer with C₆₀ in the solid state. Interestingly, the porphyrin 4Ni in the crystal is interconnected through an extracapsular C₆₀ molecule that interacts with its concave faces, hence forming an infinite alternative chain structure (Figure 4).

Conclusions

In summary, a porphyrin tetramer with thiophene as a linker was rationally synthesized via a concise synthetic route. The authors thank Prof. H. Maeda and Mr. Y. Takagi, Nagoya University, Chikusa-ku, Nagoya 463-8503, Japan. Fax: +81-52-789-3113; E-mail: hshino@apchem.nagoya-u.ac.jp

Notes and references

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4. Electronic Supplementary Information (ESI) available: Experimental details of the synthesis and spectroscopic analytical data of new compounds. See DOI: 10.1039/b000000x/
5. Crystallographic data for 4Zn: C₆₀H₈₉N₅S₄Zn₄M, M = 4074.94, tetragonal, space group I-4d (122), a = 41.392(14), c = 22.518(7) Å, V = 383800(22) Å³, T = 90(2) K, Z = 4, reflections measured 87359, 14251 unique. The final R was 0.0860 (>2σ), and the final R on F² was 0.2413 (all data), GOF = 0.71. CCDC 801517. 4Ni-C₆₀: C₆₀H₈₉N₅S₄Zn₄(C₆H₄Cl)₄, M = 6791.88, monoclinic, space group C2/c (15), a = 25.617(4), b = 71.860(12), c = 26.909(5) Å, β = 92.466(4)°, V = 49490(14) Å³, T = 90(2) K, Z = 4, reflections measured 115352, 36533 unique. The final R was 0.1191 (>2σ), and the final R on F² was 0.3194 (all data), GOF = 0.991. CCDC 801516. The contributions to the scattering arising from the presence of the disordered solvents in the crystals of 4Zn and 4Ni-C₆₀ were removed by use of the utility SQUEEZE in the PLATON software package.


