A β-to-β 2,5-thienylene-bridged cyclic porphyrin tetramer: its rational synthesis and 1 : 2 binding mode with C60

Author(s)
Song, Jianxin; Aratani, Naoki; Shinokubo, Hiroshi; Osuka, Atsuhiro

Citation
Chemical Science (2011), 2(4): 748-751

Issue Date
2011-01

URL
http://hdl.handle.net/2433/156623

© The Royal Society of Chemistry 2011; This is not the published version. Please cite only the published version. この論文は出版社版ではありません。引用の際には出版社版をご確認ご利用ください。
A β-to-β 2,5-Thienylene-bridged Cyclic Porphyrin Tetramer: Its Rational Synthesis and 1:2 Binding Mode with C₆₀

Jianxin Song,¹ Naoki Aratani,¹ a,b Hiroshi Shinokubo*, c and Atsushi Osuka* a

Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X
First published on the web Xth XXXXXXXXX 200X
DOI: 10.1039/b000000x

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 C₆₀ 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,¹-³ 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.⁴ These cyclic porphyrin arrays are also interesting in host–guest chemistry,⁵ single molecule photochemistry,⁶ nonlinear optical (NLO) materials⁷ and so on.⁸-¹² Cyclic porphyrin arrays are constructed either by means of covalent bonds, noncovalent bonds, or metal coordination bonds.⁸-¹² 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,¹³ a 2,6-pyridyl,¹⁴ and a 2,5-thienyl¹⁵ spacer. This double bridging strategy secures a rigid conformation and substantial electronic interaction, which induce significant enhancements of two-photon absorption (TPA) properties.¹³-¹⁵

We have achieved the one-pot synthesis of 2,5-thienylene-bridged cyclic porphyrin dimer 2H and trimer 3H previously.¹⁵ 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

Synthesis

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 thiopeene protons, suggesting the high symmetry of 4H. The parent ion peak of 4H was observed at m/z = 3821.30 (calcd for C₂₉₄H₄₃₂N₁₆S₄ = 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.

Scheme 1. One pot synthesis of 2,5-thienylene-bridged cyclic porphyrin arrays.

Definitive structural assignment has been accomplished through single crystal X-ray diffraction analysis of 4Zn, which unveiled a 1,3-alternate conformation (Figure 1), being totally different from the planar structures of the corresponding dimer 2Ni and trimer 3Ni.¹⁵ The thiophene bridges are tilted by ca. 40° with respect to the adjacent pyrrole rings.
The spectral characteristics are analogous to those of C₄₀ binding ability

Due to the outstanding chemical and physical properties of C₄₀, the molecular design of C₄₀ receptors is a growing research area. For the crystal state and in solution, several articles have shown that porphyrin derivatives form the 1:1 complexes with C₄₀ because of an attractive force between a C₄₀ and a porphyrin ring. Some other cases exhibited elegant cooperative binding mode for the formation of 1:2 or 1:3 complexes. 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 C₄₀ were observed, the complicated spectral changes hampered the detailed analysis. On the other hand, the formation of the 4Ni-C₄₀ 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-C₄₀ complexation systems. To estimate the stoichiometry between 4Ni and C₄₀, ¹H NMR spectra for [4Ni]:[C₄₀] = 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 C₄₀ addition (see Figure S14 in Supplementary Information; S1). As shown in Figure S15, a plot of Δθ versus [C₄₀]/[4Ni] has a clear inflection point at [C₄₀]/[4Ni] = 2.0. This value supports the view that the complex is formed with a 1:2 4Ni:C₄₀ stoichiometry. The Job's plot also supported 1:2 stoichiometry (Figure S13).

Figure 1. X-ray crystal structure of 4Zn. tert-Butyl groups and hydrogen atoms are omitted for clarity. The ellipsoids are scaled to the 15% probability.

Figure 2. Concentration dependence of the UV-vis absorption spectra: [4Ni] = 2.0 μM, [C₄₀] = 0–16 μM, toluene, 25°C. Inset: a titration curve of 4Ni under various concentration of [C₄₀].

This guest-binding profile was analyzed with the Hill equation: log(y/(1−y)) + nlog[C₄₀] = log K, where K and n are the association constant and Hill coefficient, respectively, and y = (Absobs − Abs0)/(Abs − Abs0) where Abs₀. Abs is Absobs at C₄₀ = 0 and infinite, respectively. From the curve-fitting of the plots, we obtained log K = 7.7 ± 0.6 for 1:2 4Ni-C₄₀ complex and n = 1.6. The binding of the first C₄₀ 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 C₄₀. In fact, the K value is sufficiently large and the Hill coefficient is close to 2.0, indicating a positive cooperative binding of two C₄₀ 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 C₄₀ 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 C₄₀ up in a cooperative manner, the other set protrudes their convex faces toward the interior void space, which interacts with additional C₄₀. To the best of our knowledge, this is the first crystal structure that achieves a 1:2 binding mode of the...
porphyrin oligomer with C_{60} in the solid state.\textsuperscript{22} Interestingly, the porphyrin 4Ni in the crystal is interconnected through an extracapsular C_{60} molecule that interacts with their concave faces, hence forming an infinite alternative chain structure (Figure 4).

**Figure 3.** X-ray crystal structure of 4Ni-C_{60}. tert-Butyl groups, solvent molecules, disordered isomer and outside C_{60} molecules, and hydrogen atoms are omitted for clarity. The ellipsoids are scaled to the 30% probability.

**Figure 4.** A columnar array of the fullerene molecules along the a-axis shown as a space-filling model. For clarity, 4Ni units are shown as a ball-and-stick model. The blue C_{60} molecules directly interconnect face-to-face with two (C_{60})@4Ni, and purple C_{60} molecules through the two dichlorobenzene molecules. tert-Bu groups are omitted for clarity.

**Conclusions**

In summary, a porphyrin tetramer with thiophene as a linker was rationally synthesized via a concise synthetic route. The tetraporphyrin exhibits a cooperative binding ability of C_{60} to demonstrate a new potential of the nonplanar, distorted cyclic porphyrin arrays. Examination of the photophysical properties of these complexes and the electron conduction properties are actively in progress and will be reported elsewhere.

**Acknowledgements**

This work was partly supported by Grants-in-Aid for Scientific Research (No. 18685013, Nos. 19205006 (A) and 20108001 "pi-Space") from MEXT, and by JST PRESTO program. The authors thank Prof. H. Maeda and Mr. Y. Haketa (Ritsumeikan University) for MALDI-TOF MS measurement.

**Notes and references**

\textsuperscript{*} Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan. Fax: +81-75-753-3970. Tel: +81-75-753-4008; E-mail: aratanai@kuchem.kyoto-u.ac.jp, osuka@kuchem.kyoto-u.ac.jp.

\textsuperscript{1} PRESTO, Japan Science and Technology Agency, Japan.

\textsuperscript{2} Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Chikusa-ku, Nagoya 463-8503, Japan. Fax/TeL: +81-52-789-3113; E-mail: ishino@apchem.nagoya-u.ac.jp.

\textsuperscript{3} Electronic Supplementary Information (ESI) available: Experimental details of the synthesis and spectroscopic analytical data of new compounds. See DOI: 10.1039/b000000x/.

\textsuperscript{4} Crystallographic data for 4Zn: C_{60}H_{48}N_{2}S_{2}Zn_{2}, M = 4074.94, tetragonal, space group I-42d (No.122), a = 41.392(14), c = 22.518(7) Å, F’ = 385800(22) Å^2, T = 90(2) K, Z = 4, reflections measured 87559, 14251 unique. The final R on F’ was 0.2413 (all data), GOF = 0.715. CCDC 801517. 4Ni-C_{60}: C_{60}H_{48}N_{2}S_{2}Zn_{4}(C_{6}H_{5}Cl)_{6}, M = 6791.88, monoclinic, space group C2/c (No.15), a = 25.617(4), b = 71.860(12), c = 26.909(5) Å, β = 92.466(4)°, F’ = 49490(14) Å^2, T = 90(2) K, Z = 4, reflections measured 115358, 36533 unique. The final R on F’ was 0.1191 (+2σ(F’)), and the final R on F 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-C_{60} were removed by use of the utility SQUEEZE in the PLATON software package.\textsuperscript{21}


