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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.

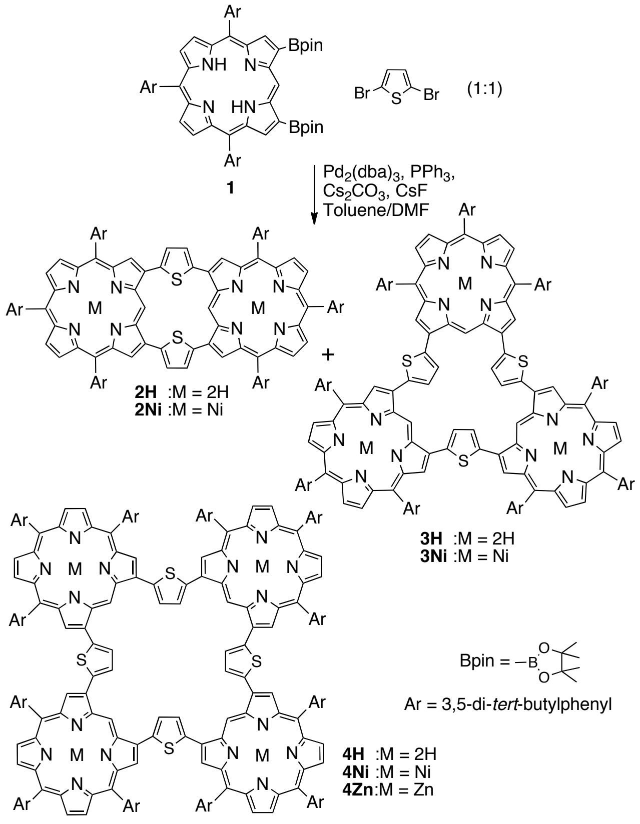
Since the crystal structure of LH2 was elucidated to be circularly arranged chromophoric assemblies,[1-3] many efforts have been devoted towards the synthesis of cyclic porphyrin arrays to study the excitation energy transfer (EET) and electronic coupling along the wheel.[4] These cyclic porphyrin arrays are also interesting in host–guest chemistry,[5] single molecule photochemistry,[6] nonlinear optical (NLO) materials[7] 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-thienyl[15] 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

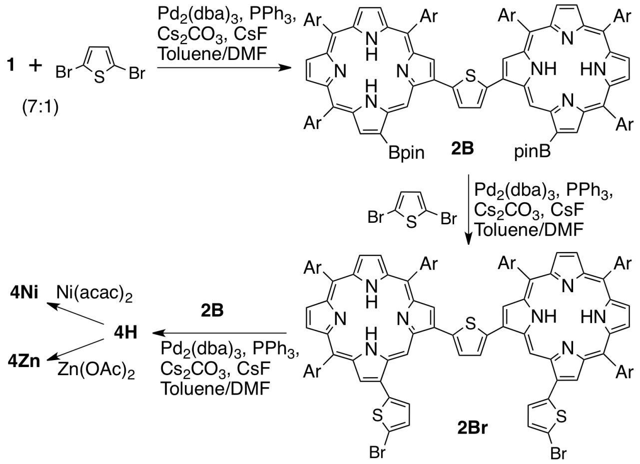
Synthesis

Coupling of 7 equiv of β,β'-diborylated porphyrin **1**[16] 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'-Diboryl 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 ^{1}H 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 $C_{264}H_{296}N_{16}S_4$ = 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**.



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.



Scheme 2. Rational synthesis of 2,5-thienylene-bridged cyclic porphyrin tetramer.

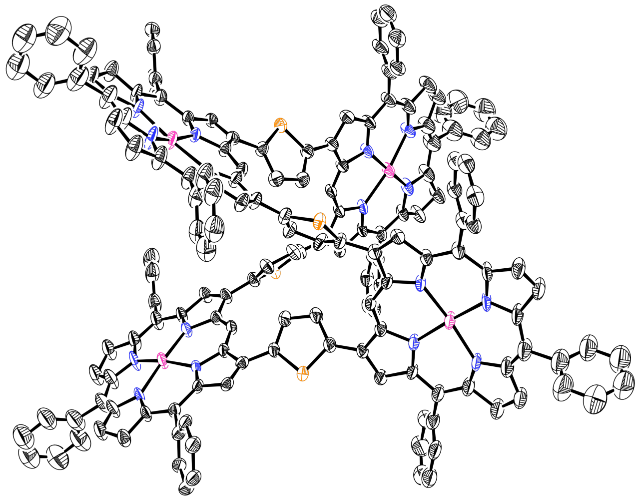


Figure 1. X-ray crystal structure of **4Zn**. *tert*-Butyl groups and hydrogen atoms are omitted for clarity. The ellipsoids are scaled to the 15% probability.

C_{60} binding ability

Due to the outstanding chemical and physical properties of C_{60}, the molecular design of C_{60} receptors is a growing research area.[17] For the crystal state[18] and in solution,[19] several articles have shown that porphyrin derivatives form the 1:1 complexes with C_{60} because of an attractive force between a C_{60} and a porphyrin-ring. Some other cases exhibited elegant cooperative binding mode for the formation of 1:2 or 1:3 complexes.[20] 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 C_{60} were observed, the complicated spectral changes hampered the detailed analysis. On the other hand, the formation of the **4Ni**-C_{60} complex in toluene was clearly indicated by titration using the UV-vis absorption spectra (Figure 2). The λ_{max} 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-C_{60} complexation systems.[19] To estimate the stoichiometry between **4Ni** and C_{60}, ^{1}H NMR spectra for [**4Ni**]:[C_{60}] = 1:0 to 1:4 at 25°C were measured in toluene-d_8 ([**4Ni**] = 0.50 mM). The resonance signals of the *meso*-protons and thiophene protons shifted downfield on C_{60} addition (see Figure S14 in Supplementary Information; SI). As shown in Figure S15, a plot of $\Delta\delta$ versus [C_{60}]/[**4Ni**] has a clear inflection point at [C_{60}]/[**4Ni**] = 2.0. This value supports the view that the complex is formed with a 1:2 **4Ni**:C_{60} stoichiometry. The Job's plot also supported 1:2 stoichiometry (Figure S13).

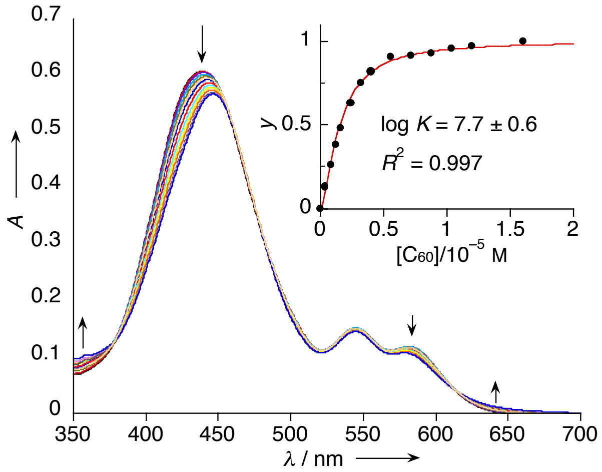


Figure 2. Concentration dependence of the UV-vis absorption spectra: [**4Ni**] = 2.0 μM, [C_{60}] = 0–16 μM, toluene, 25°C. Inset: a titration curve of **4Ni** under various concentration of [C_{60}].

This guest-binding profile was analyzed with the Hill equation: $\log(y/(1-y)) + n\log[C_{60}] = \log K$, where K and n are the association constant and Hill coefficient, respectively, and $y = (\mathrm{Abs}_{obs} - \mathrm{Abs}_0)/(\mathrm{Abs}_\infty - \mathrm{Abs}_0)$ where Abs_0, Abs_∞ is Abs_{obs} at C_{60} = 0 and infinite, respectively.[21] From the curve-fitting of the plots, we obtained log K = 7.7 ± 0.6 for 1:2 **4Ni**-C_{60} complex and n = 1.6. The binding of the first C_{60} 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 C_{60}. In fact, the K value is sufficiently large and the Hill coefficient is close to 2.0, indicating a positive cooperative binding of two C_{60} 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 C_{60} 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 C_{60} up in a cooperative manner, the other set protrudes their convex faces toward the interior void space, which interacts with additional C_{60}. 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.[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).

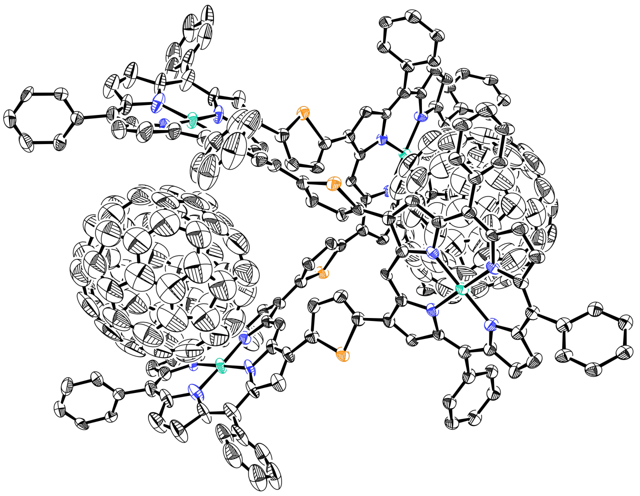


Figure 3. X-ray crystal structure of **4Ni**-C_{60}. *tert*-Butyl groups, solvent molecules, disordered isomer and outside C_{60} molecules, and hydrogen atoms are omitted for clarity. The ellipsoids are scaled to the 30% probability.

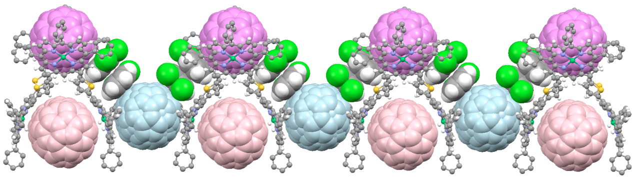


Figure 4. A columnar array of the fullerene molecules along the *a*-axis shown as a space-filling model. For clarity, **4Ni** units are shown as a ball-and-stick model. The blue C_{60} molecules directly interconnect face-to-face with two $(C_{60})_2$@**4Ni**, and purple C_{60} molecules through the 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.

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Notes and references

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‡ Crystallographic data for **4Zn**: $C_{264}H_{288}N_{16}S_4Zn_4$, M = 4074.94, tetragonal, space group $I\text{-}42d$ (#122), a = 41.392(14), c = 22.518(7) Å, V = 38580(22) Å^3, T = 90(2) K, Z = 4, reflections measured 87359, 14251unique. The final R_1 was 0.0860 ($>2\sigma(I)$), and the final $_wR$ on F^2 was 0.2413 (all data), GOF = 0.715. CCDC 801517. **4Ni**-C_{60}: $C_{264}H_{282}N_{16}Ni_4S_4\cdot(C_{60})_3\cdot(C_6H_4Cl_2)_4$, 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) Å^3, T = 90(2) K, Z = 4, reflections measured 113582, 36533 unique. The final R_1 was 0.1191 ($>2\sigma(I)$), and the final $_wR$ on F^2 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.[23]

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