ORGANIC LETTERS

2002
Vol. 4, No. 6
925–928

Cooperative C_{60} Binding to a Porphyrin Tetramer Arranged around a *p*-Terphenyl Axis in 1:2 Host–Guest Stoichiometry

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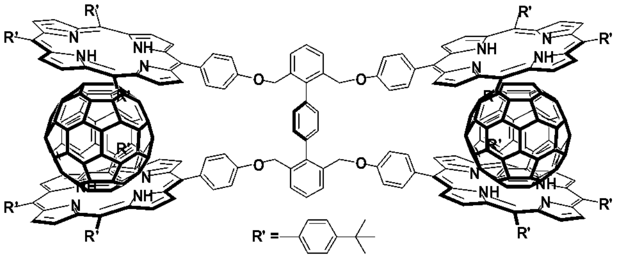
Received December 26, 2001

ABSTRACT



Porphyrin tetramer 1 was newly designed and synthesized to construct a novel cooperative [60]fullerene (C_{60}) binding system. Compound 1 has a *p*-terphenyl axis, which is expected to act as a scaffold for a guest-binding information transducer. In toluene, 1 can bind 2 equiv of C_{60} to produce a 1:2 1/C_{60} complex with association constants of 5800 M^{-1} (K_1) and 2000 M^{-1} (K_2). These values are significantly greater than those for control porphyrin dimers such as 2 and 3.

Fullerene and its derivatives are a fascinating class of molecules that have been applied to many research areas such as chemistry, material science, biology, etc.[1] Development of specific receptors for fullerenes is of great importance in constructing fullerene-based functional materials, photosynthetic systems, and photonic devices. Such host molecules designed so far are concave molecules such as calixarene,[2] resorcarene,[3] cyclotrivertriene,[4] and cyclodextrin.[5] Exploring a novel host molecule, Aida et al. recently demonstrated that the strapped bis-porphyrin macrocycle is a novel platform for fullerene binding with the largest association constant reported so far.[6] Reed et al. showed that palladium-linked bis-porphyrin (jaws porphyrin) also binds fullerenes.[7] So far, many research groups have paid much attention to the pursuit of new host molecules for fullerene, which frequently brings

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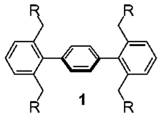
10.1021/ol017299q CCC: $22.00

forth new photochemical and/or electrochemical properties.[2–7] In this Letter, we describe synthesis and binding properties of the novel porphyrin tetramer **1** for C_{60} where four porphyrins are arranged around a *p*-terphenyl rotational axis via methylene spacers. We have already found that the subunits for guest binding, which are rationally arranged around the rotational axis, such as metal ion,[8] C−C bond,[9] or butadiynylene,[10] work cooperatively to bind guest molecules in a nonlinear fashion (positive homotropic allosterism). Furthermore, it was shown that positive homotropic allosterism can be utilized not only to realize the nonlinear guest binding but also to attain higher guest affinity which cannot be achieved by conventional 1:1-type guest binding.[8–10] Thus, if two porphyrins sandwich one C_{60} molecule,[6,7,11] two pairs of porphyrin tweezers in **1** are expected to bind 2 equiv of C_{60} in an allosteric manner to attain high affinity for C_{60}. Compounds **2** and **3** were used for control experiments.



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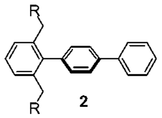

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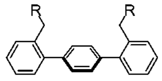

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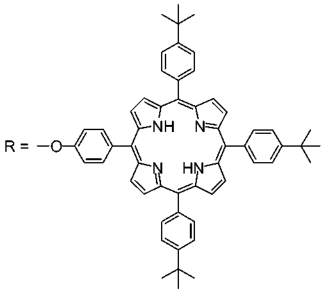

Compound **1** was obtained in 29% yield by the reaction of 5,10,15-tris(4-*tert*-butylphenyl)-20-(4-hydroxyphenyl)porphyrin with 2,6,2″,6″-tetrakisbromomethyl[1,1′;4′,1″]terphenyl in DMF. Each compound was identified by ^{1}H NMR, ^{1}H−^{1}H COSY, and MALDI-TOF MS spectroscopic evidence and elemental analysis.[12]

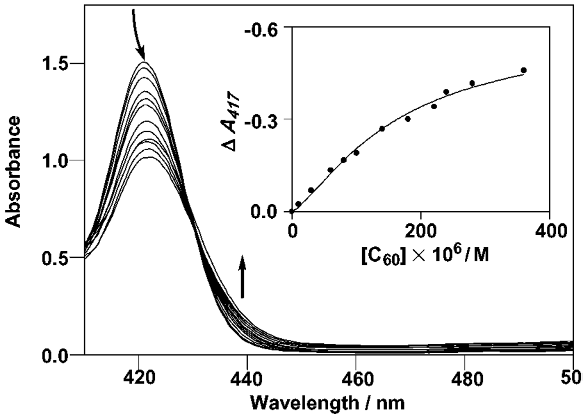

Figure 1. Concentration dependence of the UV−vis spectra: [**1**] = 1.00 μM, [C_{60}] = 0−3.50 mM, toluene, 25 °C. Inset: plot of absorbance change versus C_{60} concentration at 417 nm.

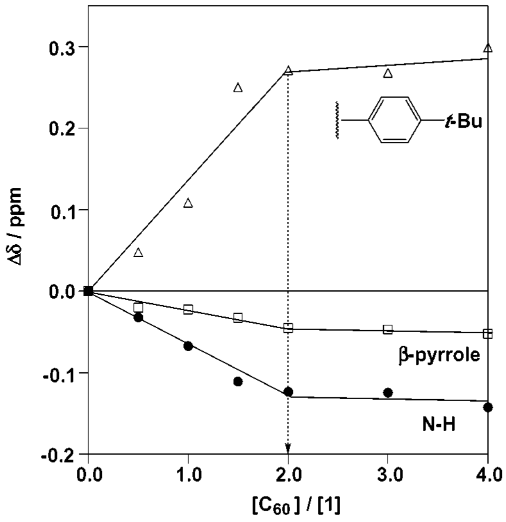

Figure 2. Plots of chemical shift change versus [C_{60}]/[**1**]: 600 MHz, toluene-d_8, 25 °C.

The Soret band of **1** and control compounds **2** and **3** (1.00 μM) in toluene appeared at 421.0 nm, which is same as that of 5,10,15-tris(4-*tert*-butylphenyl)-20-(4-hydroxyphenyl)porphyrin, indicating that porphyrins in **1**−**3** do not interact with each other intramolecularly. Upon addition of C_{60} to the solution of **1** (1.00 μM) in toluene at 25 °C, the Soret band of **1** shifted from 421.0 nm to longer wavelength with a hypochromic effect (Figure 1), which is coincident with the results of recent porphyrin−C_{60} host−guest systems.[6,7] To estimate the stoichiometry between **1** and C_{60} by ^{1}H NMR spectroscopy, ^{1}H NMR spectra for [**1**]:[C_{60}] = 1:0−1:4 in toluene-d_8 at 25 °C were measured ([**1**] = 0.500 mM). *meso*-Aryl protons shifted to a lower magnetic field, whereas β-pyrrole protons and pyrrole NH protons shifted to a higher magnetic field by C_{60} addition (Figure 2). Complex-induced chemical shift changes were saturated at [C_{60}]/[**1**] = 2, showing that the stoichiometry of this system is 1:2. In the ^{13}C NMR spectra, the ^{13}C signal of C_{60} shifted from

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143.2 to 142.7 ppm due to the porphyrin ring current effect (Figure 3). These trends in C_{60}- and porphyrin-induced chemical shift changes in ^1H and ^{13}C NMR spectra are very consistent with those of recent reports on porphyrin−C_{60} systems.[6,7]

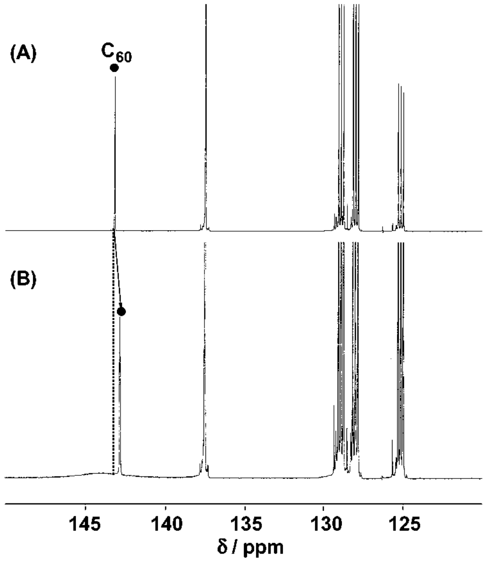

Figure 3. Partial ^{13}C NMR spectra of C^{13}-enriched C_{60} (1.50 mM) in the absence (A) and presence (B) of **1** (0.50 mM): 150 MHz, toluene-d_8, 25 °C.

A plot of the absorbance change at 417.0 nm vs [C_{60}] featured a sigmoidal curvature (although weakly), indicating that the binding of C_{60} to **1** occurs cooperatively (inset of Figure 1). This guest binding profile was tentatively analyzed with the Hill equation:[13] $\log(y/(1 - y)) = n \log[\text{guest}] + \log K$, where K and n are the association constant and Hill coefficient, respectively, and $y = K/([\text{guest}]^{-n} + K)$. From the slope and the intercept of the linear plot, we obtained $\log K = 5.0$ (1:2 **1**/C_{60} complex) and $n = 1.3$. The results show that the K value is relatively large but the cooperativity expressed by the n value ($1 < n \leq 2$) is not so strong. This trend implies that K_1 is not sufficiently smaller than K_2, as in the case of typical positive homotropic systems.[8−10] Hence, the plot was reanalyzed by a nonlinear least-squares method, assuming a two-step binding mechanism with K_1 and K_2. The K_1 and K_2 values for **1** were evaluated to be 5800 and 2000 M^{-1}, respectively (correlation coefficient 0.998). In a 1:2 host−guest cooperative binding system, $K_2 > 1/4K_1$ should be necessary.[13a] Therefore, the results also supports the view that the binding of C_{60} to **1** is taking place cooperatively (with weak positive homotropic allosterism). The K_1 and K_2 values are almost same as that for Reed's palladium-linked bis-porphyrin[7] but smaller are than that for Aida's bis-porphyrin macrocyclic system.[6]

Compound **1** has two different kinds of porphyrin tweezers: one composed of proximal porphyrins in the same phenyl ring (type A in Figure 4) and the other composed of distal porphyrins in the different phenyl ring (type B). The question of which tweezer pairs contribute to this cooperative 1:2 binding system was addressed by control experiments using **2** and **3**. Compounds **2** and **3** are corresponding monotweezers by which one can investigate the binding mode of C_{60} to **1**. When **2** and **3** are titrated with C_{60} in toluene, the bathochromic shift of the Soret band and clear isosbestic points are observed as already shown in the case of **1** with C_{60}. From a plot of ΔA_{417} vs [C_{60}], one can evaluate the association constants, $K = 154\ M^{-1}$ (correlation coefficient 0.994) and $K = 566\ M^{-1}$ (correlation coefficient 0.997) for the 1:1 complexes of C_{60} with **2** and **3**, respectively. Since the K value for **3** is much larger than that for **2**, one can conclude that two pairs of distal porphyrins (type B) in **1** work as cooperative binding sites for C_{60}: that is, the first binding to a pair of distal porphyrins would facilitate the second one by suppressing the *p*-terphenyl axis of rotational freedom in the molecular recognition process of 2 equiv of C_{60} (Figure 4).

Association constants K_1 and K_2 obtained for the **1**/C_{60} system are significantly larger than those for **2** and **3**. In other words, porphyrin tweezer **1** coupled with the concept of "allosterism" exhibits a larger affinity toward C_{60} than those of the corresponding monotweezers, **2** and **3**. It is particular worth emphasizing that positive homotropic allosterism can be utilized as a new strategy to attain higher guest affinity, which cannot be attained by the conventional 1:1-type guest binding.

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(12) **1**: mp >300 °C (decomp), MALDI TOF MS (dithranol) *m/z* 3446.66 ($[M + H]^+ = 3446.78$). Calcd for $C_{243}H_{224}N_{16}O_4 \cdot CHCl_3$: C, 82.14; H, 6.36; N, 6.28. Found: C, 82.42; H, 6.56; N, 6.04. ^1H NMR (600 MHz, $CDCl_3$, TMS, 25 °C) d/ppm (J/Hz) −2.78 (s, 8H), 1.59 (s, 108H), 5.23 (s, 8H), 7.16 (d, $J = 8.8$, 8H), 7.47 (d, $J = 7.8$, 16H), 7.59 (d, $J = 7.5$, 2H), 7.73 (d, $J = 8.0$, 8H), 7.80 (d, $J = 7.6$, 4H), 7.83 (s, 4H), 7.89 (d, $J = 7.8$, 16H), 7.98 (d, $J = 8.2$, 8H), 8.11 (d, $J = 8.0$, 8H), 8.64 (d, $J = 4.4$, 8H), 8.71 (d, $J = 4.4$, 8H), 8.76 (d, $J = 4.1$, 8H), 8.82 (d, $J = 4.1$, 8H).

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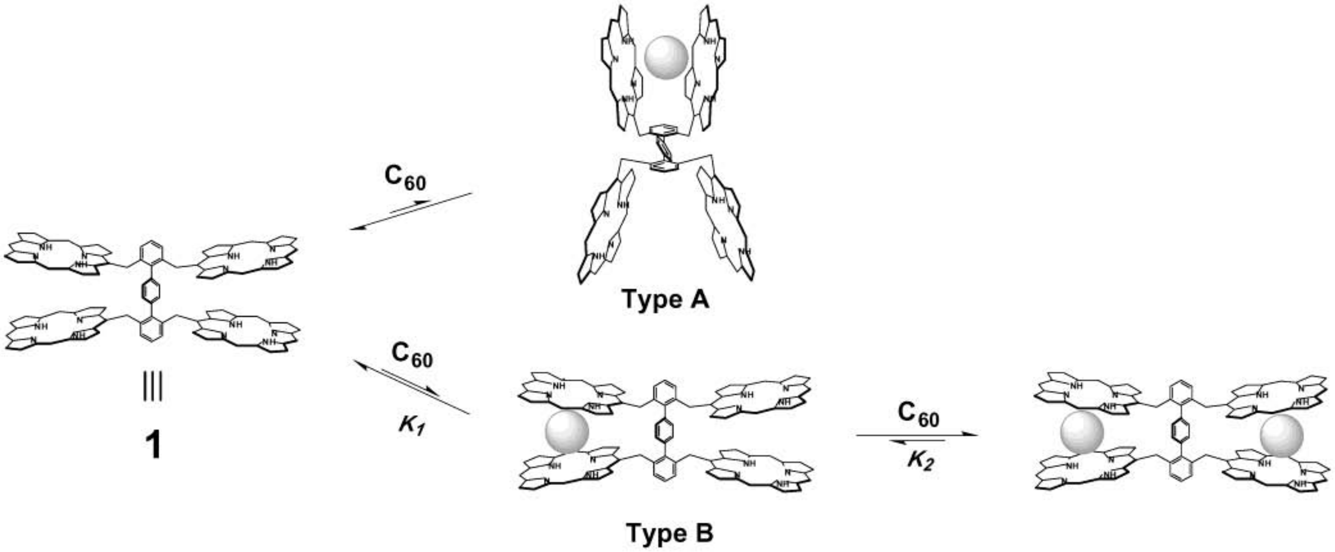

Figure 4. Schematic illustration of cooperative binding of two C_{60} molecules to porphyrin tweezer **1**.

In conclusion, we have demonstrated that compound **1** binds C_{60} cooperatively in toluene to produce the 1:2 complex. As far as we are aware, this is the first example of allosteric 1:2 host−C_{60} complex formation. One can readily apply this basic scaffold to molecular design of oligo- or poly(*p*-phenylene) systems where fullerenes can be ordered around the polymer chain.[14] These studies are now in progress in our group.

Acknowledgment. This work was partially supported by a Grant-in-Aid for COE Research “Design and Control of Advanced Molecular Assembly Systems” from the Ministry of Education, Science and Culture, Japan.

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