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[3]Rotaxane–Porphyrin Conjugate as a Novel Supramolecular Host for Fullerenes

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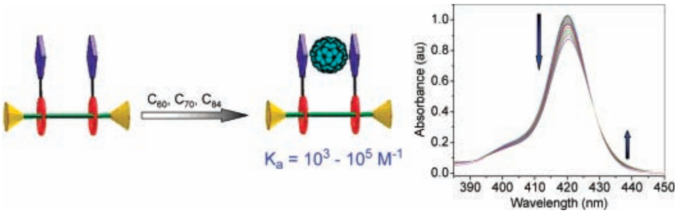
ABSTRACT



A new supramolecular host with good affinity toward fullerenes has been developed. This host having a tweezer-like shape is built on a [3]rotaxane scaffold and contains two free-base porphyrin moieties as recognition units for fullerenes. The ability of this tweezer to bind fullerenes strongly depends on the solvent system used and the size of fullerene.

Supramolecular porphyrin−fullerene complexes[1] have received a great deal of attention in the past decade for different applications, ranging from photocurrent generation[2] to metal-organic framework solids.[3] The remarkably high stability of those supramolecular assemblies is attributed to the strong $\pi-\pi$ and weaker electrostatic interactions,[1a] especially when fullerenes are sandwiched between two porphyrin moieties.[1a] Therefore, several dimeric porphyrin hosts having pocket-like[4] or tweezer-like[5] shape have been developed to study the effect of structural parameters (porphyrin-to-porphyrin distance, metal atom in the porphyrin core, substituents in porphyrin periphery, etc.) on the binding constants.

The most studied scaffold to appropriately orient porphyrin moieties in a tweezer-like configuration is the calix[4]arene derivatives,[5c,6] although numbers of interesting scaffolds such as resorcinarenes,[7] dendrimers,[8] and organometallic complexes[9] have been developed. In most cases, values ranging from 10^4 to $10^8\ M^{-1}$ have been reached for the complexation of C_{60} and higher fullerenes.[4b] One common characteristic of all these receptors is that the porphyrin units are linked together by a covalent bond through different linear or cyclic scaffolds. Covalent attachment is considered important to keep an optimal porphyrin-to-porphyrin distance and to add

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conformational stiffness to the receptors, enabling fullerene complexation. However, there is no report on the complexation of fullerenes with a dimeric porphyrin host mounted on a supramolecular scaffold. We report herein the synthesis and fullerene complexation study of a novel dimeric porphyrin host having a [3]rotaxane scaffold (Figure 1). With the mechanically interlocked structure of [3]rotaxane adding more flexibility to the host compared to calix[4]arene derivatives, we wanted to have a better understanding of the importance of the stiffness on the binding ability of the tweezer-like dimeric porphyrin hosts.

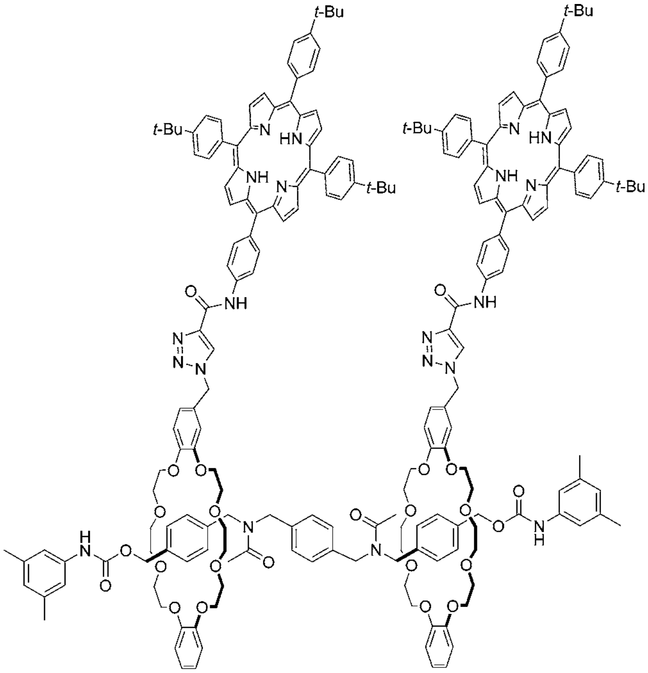
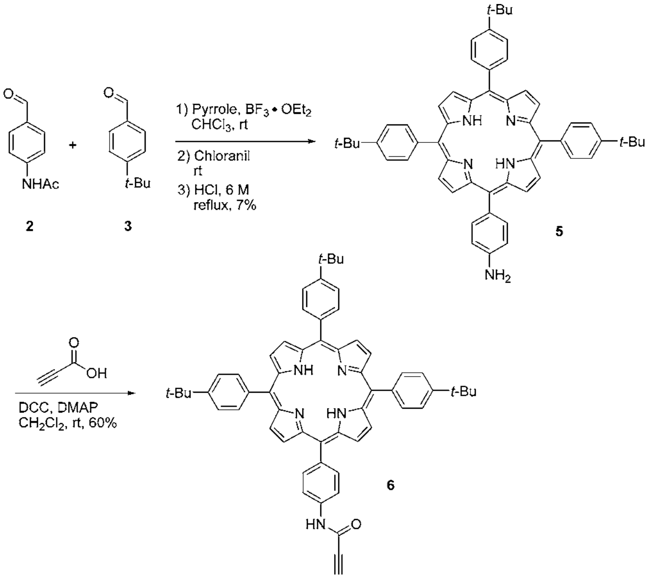


Figure 1. Idealized conformation of the [3]rotaxane-based tweezers.

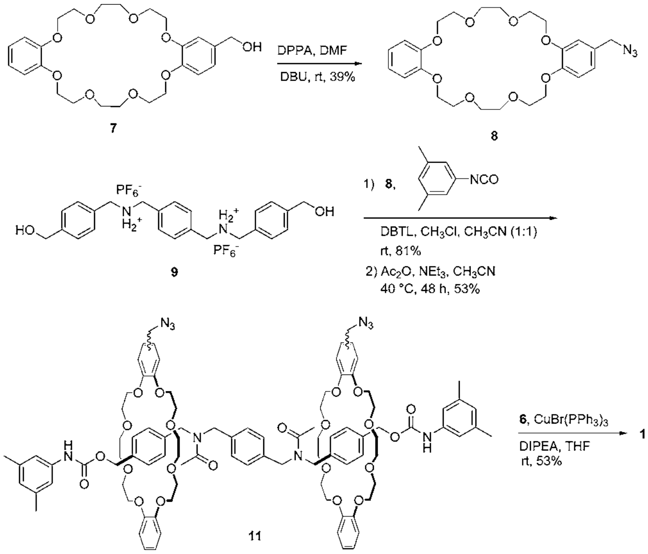
A good host should have sufficient flexibility to form the best complex but with the least loss of entropy. For this reason, the [3]rotaxane scaffold was revealed to be a powerful tool for the construction of a supramolecular host with a tweezer-like shape. The position of the crown ether macrocycles threaded over the bis(amine) rod can be tailored to optimize the porphyrin-to-porphyrin distance, allowing the modulation of the binding capability of the resulting tweezers. Unlike rigid scaffolds, such as calix[4]arene, the distance between porphyrin units is not fixed since the crown ether macrocycles are mechanically interlocked onto the rod, allowing them to slip if necessary, similar to a sliding vice, to adopt the most favorable conformation for guest complexation, thus forming an ideal complex but with a limited loss of entropy. The free rotation of the porphyrin units around the crown ether triazole axis can also contribute to the conformational flexibility of this host. Despite its high conformational flexibility, a [3]pseudorotaxane template was successfully used by Grubbs and Stoddart to accelerate olefin cross-metathesis.[10]

Scheme 1. Synthesis of the Alkyne-Containing Porphyrin Unit



The synthesis of the tweezer **1** is depicted in Schemes 1 and 2. The synthesis of porphyrin **5** was achieved by a traditional statistical method using pyrrole and a 1:3 mixture of benzaldehyde derivatives **2** and **3**. The amino group was then deprotected using HCl to give **5** in 7% yield (two steps) and reacted with propiolic acid in the presence of dicyclocarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) to give porphyrin **6** in 60% yield.

Scheme 2. Synthesis of [3]Rotaxane-Based Tweezers **1**



The crown ether macrocycle **8** was synthesized from **7**[11] using diphenylphosphoryl azide in DMF in 39% yield. The

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[3]rotaxane has been formed in 53% yield by adding 3,5-dimethylphenylisocyanate and a catalytic amount of dibutyltin dilaurate to a solution of **8** and bis(ammonium) rod **9**.[12] Because the crown ether is unsymmetrical, the resulting rotaxane exists as a pair of diastereoisomers (see Supporting Information). The ammonium group was acetylated with acetic anhydride in a triethylamine/acetonitrile mixture to give **11** in 81% yield. Finally, two porphyrin units (**6**) were attached to the [3]rotaxane **11** using copper-catalyzed 1,3-dipolar cycloaddition (or “click chemistry”) in THF to give **1** in 53% yield. Click chemistry was used because it generally proceeds with good yield, minimizing formation of side products, thus enabling the purification of high molecular weight compounds. $Cu(PPh_3)_3Br$ has been chosen as catalyst rather than the widely used copper(II)-based catalytic systems because of solubility issues and to avoid the insertion of copper atom in the porphyrin center. NMR and HRMS analyses of **1** along with comparison between **1** and the metalated analogue of **6** using UV−visible suggest the presence of free-base porphyrin only (see Supporting Information). It is noteworthy that attempts to use click chemistry to couple porphyrins to the [3]rotaxane in its protonated state were unsuccessful for an unknown reason. Different catalytic systems and solvents were tried, but none gave satisfactory results.

The complexation between three different fullerenes (C_{60}, C_{70}, and C_{84}) with **1** was studied using UV−visible spectroscopy by monitoring the spectral changes at the Soret band (419 nm for **1**) upon addition of a fullerene solution. In a typical experiment, aliquots of a toluene solution of fullerene (6×10^{-4} M) were added to a solution of **1** (2.0×10^{-6} M) in toluene or in an acetonitrile/toluene mixture. Examples of UV−visible and fluorescence titration experiments of **1** with C_{70} in a 3:2 acetonitrile/toluene mixture are shown in Figure 2. As expected, addition of a C_{70} solution to **1** induces significant optical changes both in the UV−visible and in the fluorescence spectra. The UV−visible spectrum displayed a clear isosbestic point at 429 nm, indicating a 1:1 host/guest complexation. In addition, Job plots using ^{1}H NMR titration confirmed the formation of a 1:1 complex of the tweezer **1** with fullerenes (see Supporting Information).

The binding constants obtained for **1** with different fullerenes are summarized in Table 1. For C_{60} in toluene, a binding constant of $K_a = 4600 \pm 300\ M^{-1}$ was measured which is similar to the values calculated for most of the dimeric free-base porphyrin hosts mounted on a calix[4]arene scaffold.[5c,6] This result suggests that the high conformational flexibility of the [3]rotaxane is not a drawback to the construction of efficient scaffolds for host−guest chemistry.

As observed for most of the porphyrin-based hosts, the binding constant measured between **1** and C_{70} in toluene ($K_a = 10\,100 \pm 900\ M^{-1}$) is higher than the value measured for C_{60}. This increase in binding affinity can be attributed to the ovoid shape of C_{70} which allows better contact between the C_{70} surface and the porphyrin units.[9] Interestingly, the selectivity factor between C_{70} and C_{60} ($K_{a,C70}/K_{a,C60} = 2.2$) is fairly low compared to that of dimeric porphyrin hosts mounted on other scaffolds (>10). This can be attributed to the higher conformational flexibility of the [3]rotaxane scaffold compared to the more rigid ones,[13] allowing the porphyrin units to adopt the most favorable conformation for the complexation of fullerenes having different sizes.

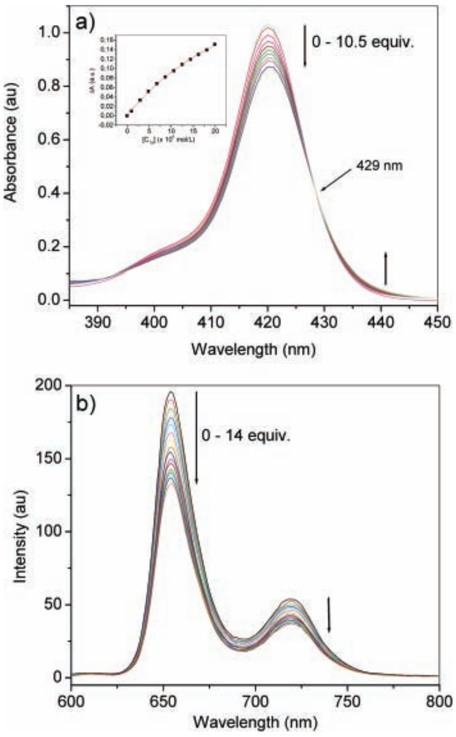

Figure 2. (a) UV−visible and (b) fluorescence spectral changes of tweezers **1** upon addition of C_{70} in an acetonitrile/toluene (3:2) mixture at 298 K. Excitation wavelength = 429 nm (corresponding to the isosbestic point of the UV−visible spectrum). Inset: Plot of the UV−visible changes at 419 nm.

To study the influence of solvent on binding constants, titration experiments of **1** with C_{70} in an acetonitrile/toluene mixture have been achieved. Boyd and co-workers have recently showed that addition of acetonitrile (non-solvent for fullerenes) in complexation experiments between porphyrin units and fullerenes can increase the binding constants by 2 orders of magnitude.[5c] It is noteworthy that titration experi-

Table 1. Binding Constant K_a (M^{-1}) for Complexation of C_{60}, C_{70}, and C_{84} with the Tweezers **1** in Different Solvents

MeCN/PhMe ratio	K_a C_{60} (M^{-1})	K_a C_{70} (M^{-1})	K_a C_{84} (M^{-1})
0	4600 ± 300^a	10100 ± 900^a	
1:1		28400 ± 2200^a	
3:2		32500 ± 1700^a	246700 ± 41000^a
		29000 ± 3300^b	280800 ± 30400^b

[a] UV−visible (298 K). [b] Fluorescence (298 K). The K_a values were calculated by the nonlinear least-squares method.[14]

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ments of **1** with C_{60} in such a mixture were unsuccessful since, unlike the C_{70}, the UV−visible changes were too small to calculate an accurate binding constant in the concentration regime we used. As expected, the binding constants calculated for **1** with C_{70} in an acetonitrile/toluene mixture are higher than those calculated in pure toluene. In a 1:1 and 3:2 acetonitrile/toluene mixture, binding constants of K_a = 28 400 ± 2200 and 32 500 ± 1700 M^{-1} were measured, respectively. These results clearly demonstrate the importance of the desolvation of the fullerenes to the binding constant in dilute solution. It is worth mentioning that the binding constants calculated using the UV−visible spectroscopy give results similar to those calculated using fluorescence spectroscopy.

The influence of the fullerene size was also evaluated by comparing binding constants between **1** and C_{70} and C_{84}. Interestingly, the binding constant measured for C_{84} (K_a = 246 700 ± 41000 M^{-1}) is 1 order of magnitude higher than that calculated for C_{70}. Although this difference is not yet fully understood, it could be explained by three contributing factors. First, C_{84} possesses a section with a rather flat surface owing to its egg shape, allowing better contact with the porphyrin units compared to the smaller C_{70}.[15] Second, the smaller size of C_{70} compared to C_{84} could force the porphyrin units and, consequently, the crown ether macrocycles to be closer and pass over the acetyl-protected amine, thus increasing the steric hindrance along the rod. Third, the difference in binding constant between C_{84} and C_{70} can be attributed to different solvation effect.[5c] Unfortunately, no X-ray crystallography analysis was performed to study the conformation of a 1:1 complex since all our attempts to obtain crystals of **1**/fullerene were unsuccessful.

In summary, a novel dimeric porphyrin host for fullerene complexation mounted on a [3]rotaxane scaffold has been developed. Despite its high conformational flexibility, this host proved to be useful to complex fullerenes with a similar efficiency to those based on a calix[4]arene scaffold. However, the flexibility can be responsible for the relatively low selectivity factors between C_{60} and higher fullerenes compared to other tweezer-like hosts. Research is ongoing in our group to explore the possibility of complexing other molecules with the [3]rotaxane scaffold. Since the crown ether can shuttle along an ammonium-containing rod with an appropriate stimuli to produce translational movement,[16] the molecular tweezers **1** could open the way to the development of new molecular machinery able to move molecules on a distance of a few nanometers.

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Supporting Information Available: Experimental procedures and characterization data for all the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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