A Cyclic Porphyrin Trimer as a Receptor for Fullerenes

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ABSTRACT
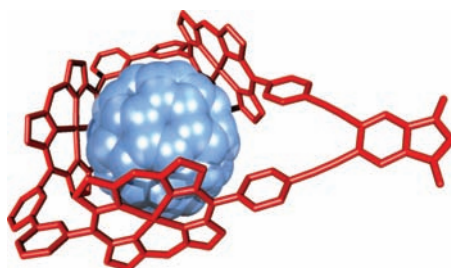
A cyclic porphyrin trimer has been synthesized which has a high affinity for fullerenes. It forms 1:1 complexes with C_{60} and C_{70} with association constants of 2×10^6 and 2×10^8 M^{-1}, respectively, in toluene. Its affinities for C_{86} and La@C_{82} are too strong to measure by fluorescence titration. The solvent dependence of the association constants shows that solvation of both the guest and the host influence the binding strength.

Paramagnetic endohedral fullerenes are well-known for their long coherence times (T_2); for example, N@C_{60} has a T_2 of 300 μs, which is an order of magnitude longer than those of other molecular radicals.[1] This property makes them promising qubits for quantum information processing.[2] In order to develop materials for this application, we need a way of holding several endohedral fullerene units in precise spatial arrangements, so that the entanglement between their spins can be manipulated. A molecular framework functionalized with noncovalent fullerene receptors would be the ideal scaffold because it could bind the fullerene quantitatively at

the final stage of the synthesis, while scarcely perturbing the environment around the endohedral paramagnetic atom. Such receptors will need to have high affinities for fullerenes to achieve quantitative binding in dilute solution. Here we report the synthesis of a receptor designed for this application. A single phthalimide connection point is rigidly attached to the receptor, so that in the future several such receptors can be linked together to create multispin arrays with precise geometries. This receptor has a high binding affinity for C_{60} in toluene, and the affinity increases by at least 2 orders of magnitude on moving to larger fullerenes (C_{70}, C_{86}, and La@C_{82}). These results imply that receptor **1** will bind strongly to other endohedral fullerenes such N@C_{60}.

Among the wide range of receptors for fullerenes reported in the literature,[3] those based on porphyrins display the highest binding affinities.[4,5] Many structures with a single

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porphyrin−fullerene interaction have been characterized in the solid state,[4,6,7] but these complexes readily dissociate in solution, and most solution-phase receptors utilize two or more porphyrin units.[5,8−12] We reasoned that a cyclic porphyrin trimer in which three porphyrins are preorganized to chelate to the same fullerene guest might provide very strong binding. No covalent macrocyclic receptors have previously been reported that exhibit this type of tridentate porphyrin−fullerene interaction, although 3:1 coordination geometries have been reported in solid-state complexes,[7] metal-coordinate self-assemblies,[11] and complexes of tripodal porphyrin trimers.[12] Four-coordinate complexes, in which two porphyrin dimers chelate to the same fullerene molecule have also been reported.[13]

Molecular mechanics calculations on a variety of potential receptors identified porphyrin trimer **1** as a promising target. In the calculated structure of the **1**·C_{60} complex (Figure 1),
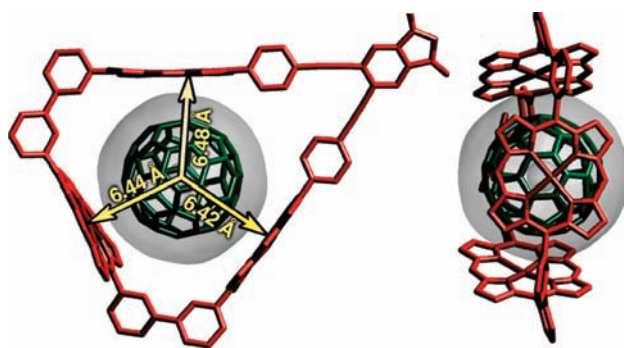

Figure 1. Calculated structure of the C_{60}·**1** complex (MM+, Hyperchem 8.0). Distances shown from the centroid of the porphyrins to the centroid of the fullerene.

the distances from the centroid of the fullerene to the centroids of the three porphyrins are 6.42, 6.44, and 6.48 Å.

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A search of the Cambridge Structural Database shows that the mean value of this C_{60} centroid to porphyrin centroid parameter is 6.28 ± 0.08 Å (mean for 21 zinc porphyrin C_{60} interactions).[14] We calculate that the D_{3h} symmetric analogue of receptor **1** with 3,3′-biphenyl links, at all three corners, would have a cavity centroid to porphyrin centroid distance of 5.91 Å, making it too small to accommodate C_{60}. Thus the roles of the phthalimide unit in the design of **1** are to expand the cavity and to provide a rigid attachment point.

Cyclic porphyrin trimer **1** was synthesized by Sonogashira coupling of 3,4-diiodophthalimide **2**[15] and the alkyne-terminated linear porphyrin trimer **3** (Scheme 1). The linear trimer **4** was prepared by Suzuki coupling of porphyrins **5** and **7** and deprotected to give **3**. Porphyrin monomers **6** and **7** were obtained by statistical reaction of with dipyrromethane **8** with aldehydes **9** and **10**.[16] The most difficult part of this synthesis turned out to be preparation of the porphyrin bisboronic acid **5**. After testing several routes to this compound, it was obtained in 25% yield from **6** by palladium-catalyzed boronylation.

The ^{1}H NMR spectrum of the cyclic porphyrin trimer **1** confirms its C_{2v} symmetry. Its purity and identity were established by ^{1}H NMR, ^{13}C NMR, [1]H−[1]H NOESY, GPC, MALDI-TOF MS, and UV−vis spectroscopy (see Supporting Information).

Boyd and co-workers have shown that fullerene−porphyrin interactions are highly solvent-dependent, and that the strengths of these interactions can be maximized by selecting solvents in which C_{60} has a low solubility.[9c] Thus we chose to investigate the interaction of trimer **1** with C_{60} in a variety of solvents covering a wide rage of C_{60} solubilities. UV−vis titrations were carried out in THF, cyclohexane, carbon tetrachloride, toluene, and *o*-dichlorobenzene. In all cases, the formation of a 1:1 complex with a red-shifted Soret band was detected.[17,18] A typical set of titration spectra is shown in Figure 2a, and the binding constants measured in these five solvents are summarized in Table 1.

The solubility data[19] provide a good measure of the ability of each solvent to solvate C_{60}. As expected, the worst solvent (cyclohexane) gives the highest binding constant [(2.1 ± 0.3) × 10^7 M^{-1}], while the best solvent (*o*-dichlorobenzene) gives the lowest binding constant [(2.2 ± 0.2) × 10^4 M^{-1}]. However, THF and carbon tetrachloride do not fit the trend: they give weaker binding constants than expected based on

(14) See Supporting Information for an analysis of zinc porphyrin C_{60} interactions from the Cambridge Crystallographic Database.

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(17) Analysis of titration data was carried out using Specfit/32 software v3.0.38; see Supporting Information.

(18) Formation of the **1**·C_{60} complex is accompanied by the appearance of a weak charge-transfer band at 650−800 nm ($\varepsilon \approx$ 1000 M^{-1} cm^{-1}, in toluene) as reported for other C_{60}−porphyrin complexes; see: Imahori, H.; Tkachenko, N. V.; Vehmanen, V.; Tamaki, K.; Lemmetyinen, H.; Sakata, Y.; Fukuzumi, S. *J. Phys. Chem. A* **2001**, *105*, 1750–1756.

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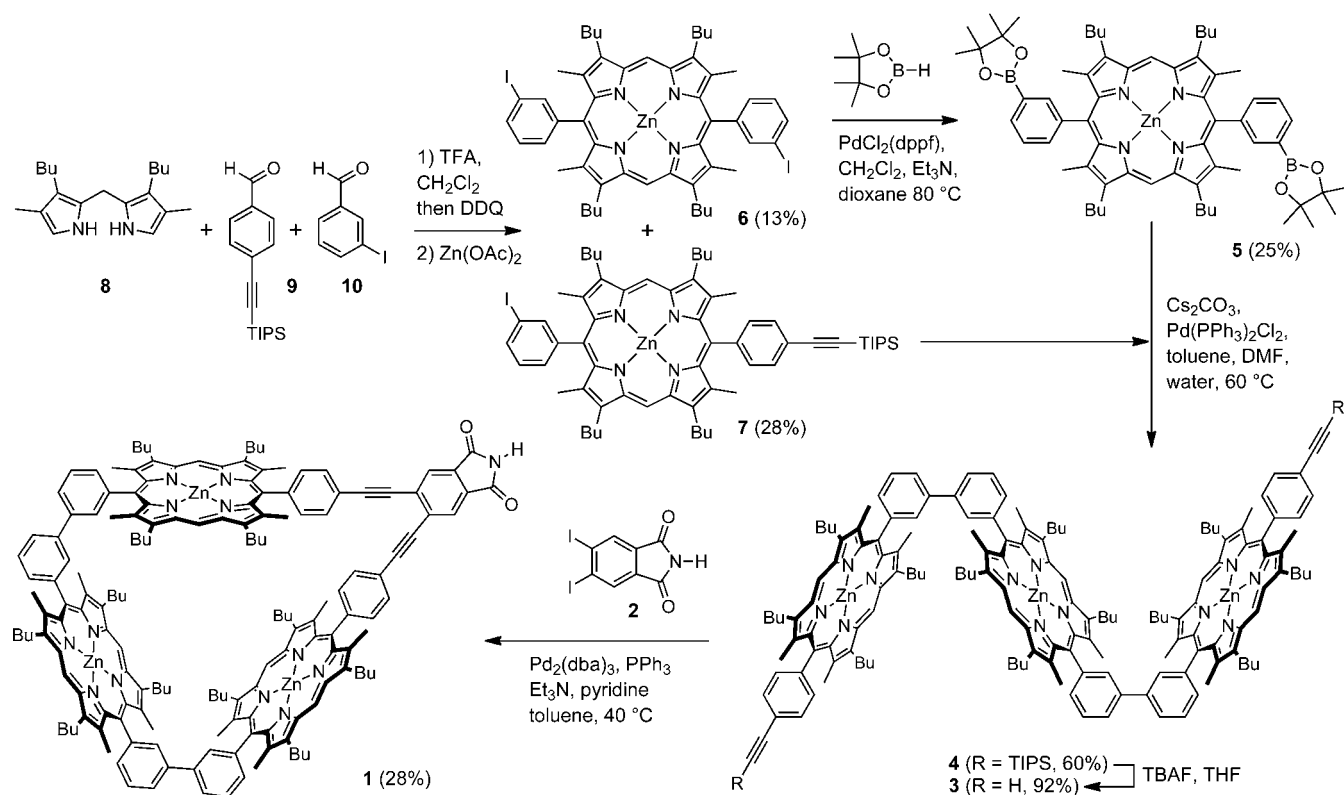**Scheme 1.** Synthesis of the Cyclic Porphyrin Trimer **1**

fullerene	solvent	K (M^{-1})^a	solubility (mg/mL)[19]
C_{60}	cyclohexane	$(2.1 \pm 0.3) \times 10^7$	0.036
C_{60}	THF	$(3.3 \pm 1.5) \times 10^5$	0.06
C_{60}	CCl$_4$	$(9.1 \pm 2.4) \times 10^5$	0.32
C_{60}	toluene	$(1.6 \pm 0.7) \times 10^6$	2.8
C_{60}	o-dichlorobenzene	$(2.2 \pm 0.2) \times 10^4$	27
C_{70}	toluene	$(1.6 \pm 0.7) \times 10^8$	1.1
C_{86}	toluene	$>10^9$	–
La@C_{82}	toluene	$>10^9$	–

^{a} All association constants were measured at 298 K; values for C_{60} were measured by UV−vis titration, whereas those for the higher fullerenes were measured by fluorescence titration.

their C_{60} solubility data, probably because they are good solvents for zinc porphyrin units.[20] The variation in binding constant with solvent reflects the strength of solvation of both the host and the guest.

This solvent study enabled us to identify toluene as the best compromise in terms of high association constant [(1.6

(20) The data in Table 1 imply that 1 equiv of receptor **1** increases the solubility of C_{60} in cyclohexane by a factor of 1050 ± 150. We have observed that the presence of **1** increases the solubility of C_{60}, but we have not measured the solubility of the 1:1 complex. Other receptors have previously been reported to enhance the solubility of fullerenes; see: Pantos, G. D.; Wietor, J.-L.; Sanders, J. K. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 2238–2240.

$\pm$ 0.7) $\times$ 10^6 M^{-1}], satisfactory solubility of both components and ease of comparison with published work on other receptor−fullerene complexes. Preliminary experiments with the higher fullerenes (C_{70}, C_{86}, and La@C_{82}) showed that their complexes with **1** in toluene are all too strong to quantify by UV−vis titration, so we switched technique to fluorescence titration to enable stronger association constants to be measured by working at lower concentrations. Binding to fullerenes quenches the fluorescence of the receptor (Figure 2b), presumably via photoinduced electron transfer from the receptor to the fullerene. The fluorescence titration of **1** with C_{60} gave an association constant of $(8.3 \pm 0.7) \times 10^5$ M^{-1}, which is acceptably close to the value from UV−vis titration. The results for the higher fullerenes are summarized in Table 1. The C_{70}·**1** complex is 2 orders of magnitude more stable than C_{60}·**1** (i.e., $K_{C_{70}}/K_{C_{60}} \approx 100$), while C_{86}·**1** and La@C_{82}·**1** are too stable to measure by fluorescence titration ($K > 10^9$ M^{-1}). Strong binding to C_{70} and C_{86} was confirmed by mass spectrometry: when a MALDI-TOF mass spectrum was recorded for an equimolar mixture of C_{60}, C_{70}, C_{86}, and receptor **1**, peaks were observed for C_{70}·**1** and C_{86}·**1**, but not for C_{60}·**1** (see Supporting Information).

Comparison with published work on other fullerene receptors[8] reveals that cyclic timer **1** binds C_{60} in toluene slightly more strongly than cyclic zinc porphyrin dimers, indicating that the presence of the third porphyrin unit has a small but positive influence on the affinity for C_{60}. However, the cooperative effect of the third porphyrin becomes
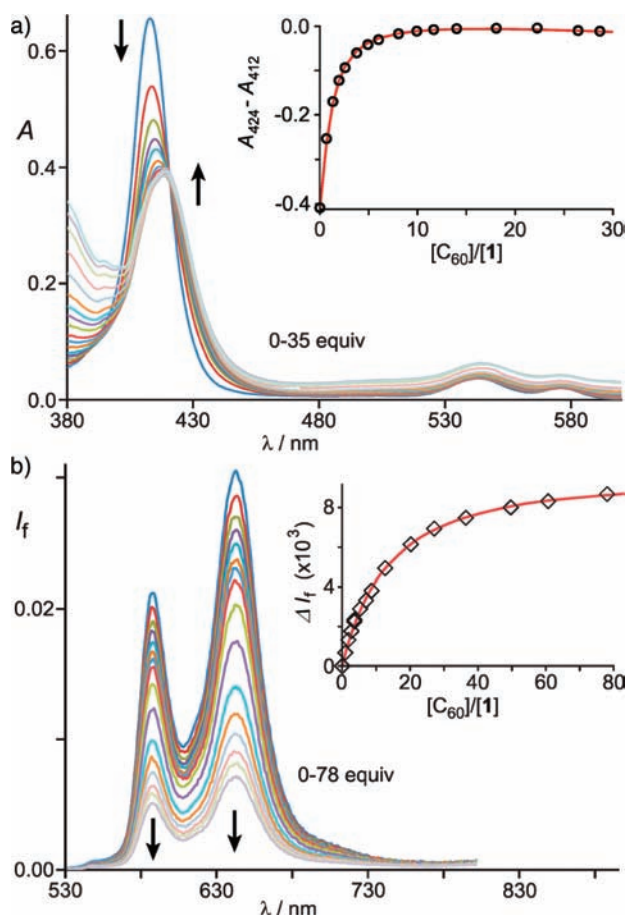
C_{70}, C_{86}, and La@C_{82} enables them to interact well with all three walls of the receptor. The electronic polarization of La@C_{82} may also contribute toward its strong binding.[21] The surprisingly large value of $K_{C_{70}}/K_{C_{60}}$ for receptor **1** indicates that its cavity is slightly too large for binding C_{60}, as deduced above from molecular modeling and crystallographic data.

In conclusion, a cyclic trimer of porphyrins **1** has been synthesized, and its binding to C_{60} has been studied in a range of solvents. There is no clear trend relating the solubility of C_{60} in each solvent to the affinity of C_{60} for receptor **1** in that solvent, but desolvation of the host and of the guest is evidently important. The highest value for the binding constant to C_{60} is obtained in cyclohexane. Other fullerenes (C_{70}, C_{86}, and La@C_{82}) show very high binding constants to receptor **1** in toluene. The value of K for C_{70}·**1** is 1×10^8 M^{-1}, which is substantially higher than those of previous receptors based on zinc porphyrins. The affinities for C_{86} and La@C_{82} are beyond the limit of the fluorescence titration techniques ($K > 10^9$ M^{-1}). To the best of our knowledge, this is the first report of binding of endohedral fullerenes to a molecular receptor.[21] It is well-known that metalloporphyrins such as those of rhodium(III) bind fullerenes much more strongly than zinc porphyrins,[3,5,8b,13] thus changing the metal in **1** should lead to even higher fullerene affinities. The high affinity for La@C_{82} displayed by receptor **1** in toluene indicates that covalently linked assemblies, decorated with multiple copies of this receptor, should be capable of complexing multiple spin-active fullerenes, providing a promising system for studying spin entanglement.

Supporting Information Available: NMR spectra, detailed experimental procedures, UV−vis and fluorescence titration data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Figure 2. (a) Absorption spectral change of **1** (0.77 μM) in toluene at 298 K upon titration with C_{60} (0−27 μM), 10 mm path length. Inset: plot of ($A_{424} - A_{412}$) against number of equivalents of C_{60}: circles = experimental data. (b) Fluorescence spectra during the titration of **1** (0.093 μM) with C_{60} (0−7.2 μM) in toluene at 298 K (λ_{ex} = 413 nm). Inset: plot of ΔI_{615} against number of equivalents of C_{60}: diamonds = experimental data. All titrations were performed at constant receptor concentration.

dramatic with the higher fullerenes. The stability of the C_{70}·**1** complex is much higher than those of previously reported zinc porphyrin receptors (which typically have $K_{C_{70}}/K_{C_{60}} \approx$ 10).[8,9] We are not aware of previous binding results with C_{86} or endohedral fullerenes. Evidently, the greater size of

(21) Elution profiles on porphyrin-functionalized silica indicate that the interaction of La@C_{82} with porphyrins is stronger than those of C_{60} or C_{70}: Xiao, J.; Savina, M. R.; Martin, G. B.; Francis, A. H.; Meyerhoff, M. E. *J. Am. Chem. Soc.* **1994**, *116*, 9341–9342.