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ARTICLE TYPE

A "clicked" Porphyrin Cage with High Binding Affinity towards Fullerenes

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A cage-structured receptor was synthesized in a facile "clicked"way, which showed high affinity for fullerenes and differentiated binding rate to C_{60} and C_{70}.

Since the group of Ringsdorf reported the first purposely designed hosts for fullerenes which consisted of aza-crown ethers carrying suitable alkyl chains on the nitrogens[1], the design and synthesis of hosts for trapping fullerenes have attracted more and more attention due to their potential application in the extraction, solubilization and chemical modifications of fullerenes[2], light-harvesting devices[3], and molecular conductors or magnets[4]. Tetrathiafulvalenes (TTFs), calixarenes, cyclotriveratrylenes (CTVs) and cyclodextrins as electron donors have been utilized for the design of fullerene receptors[5]. In the past decade, many kinds of excellent host molecules incorporating of porphyrin blocks have been synthesized successfully[6-9]. Recently cyclic receptors with more than two porphyrin units have been reported.[10-12]. Compared to the synthesis of cyclic compounds, the organic cage compounds formed with only covalent bonds are relatively rare because the synthesis of most cage compounds need multiple steps and often have low overall yields. To date, the application of dynamic covalent chemistry makes the synthesis of cage compounds successful in fewer steps and usually higher yields[13-15]. Among these fullerenes receptors, high and differentiated binding affinity was definitely achieved[16]. We report herein a cage-structured receptor synthesized via a facile "click" way which is easier to synthesize and be modified" and which showed a high affinity for fullerenes. (Figure 1).

Previously, we have reported the porphyrin cage **1** that was proved to be a good receptor for recognizing azide anion[17]. But the cavity of the porphyrin cage **1** (the distance between two porphyrin panels is 7.946 Å) is not large enough to accommodate fullerenes. It is possible to change the linkers' length for adjusting the porphyrin–porphyrin distance of the porphyrin cage to accommodate fullerenes. The larger porphyrin cage **2** can be synthesized directly from two readily accessible porphyrin-based precursors **3** and **4** in one step using CuAAC click reaction (Figure 1 down). The ^{1}H NMR spectrum of the porphyrin cage **2** confirms its C_{4v} symmetry. Its purity and identity were established by ^{1}H NMR, MALDI-TOF MS and UV-vis spectroscopy (see Supporting Information).

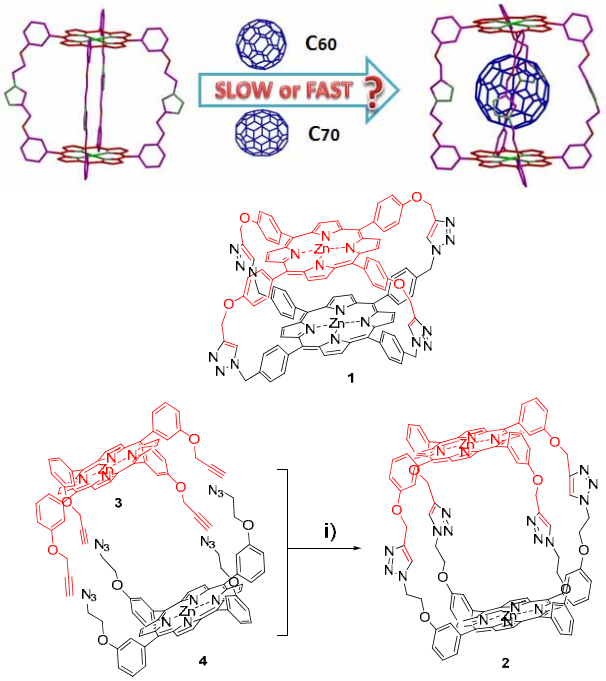

Figure. 1. Top: schematic illustration of porphyrin cage with different binding rate for fullerenes; down: synthesis of the porphyrin **2**: (i) CuI, DBU, toluene, pseudo high-dilution condition, dropwise, 75°C , 24h, yield: 33%.

The first indication of the ability of the porphyrin cage **2** to bind fullerenes came from the MALDI-TOF spectra. When 1:1 mixtures of the porphyrin cage **2** and either C_{60} or C_{70} were analyzed, peaks at m/z 2633.2 and 2753.1, corresponding to C_{60}@**2** (calcd 2633.94) and C_{70}@ **2** (calcd 2753.85) respectively were clearly observed. No peaks corresponding to aggregates of other stoichiometries were found.

The second evidence in support of forming C_{60}@**2** and C_{70}@**2** complexes was obtained from the analysis of their ^{1}H NMR. We briefly studied the interaction of the porphyrin cage **2** with C_{60} and C_{70} by means of ^{1}H NMR titration experiments (Figure 2). Addition of approximately 0.1 equiv of C_{60} in CS_2 to a 1,2-dichloroethane-d4 solution of the cage **2**, resulted in signal splitting of the cage **2**. This new set of signals was assigned to the C_{60}@**2** complex. With the increasing addition of C_{60}, the signals

of the cage **2** decreased continuously while a new set of signals increased correspondingly (Figure 2a).

Compared to the interaction of C_{60} with the cage **2**, the interaction was somewhat different between C_{70} and **2**. When a CS_2 solution of C_{60} was added, C_{60} entered into the cavity so quickly that a signal splitting was observed immediately and the phenomenon did not change with time going by. But when a CS_2 solution of C_{70} was added, the signal splitting was almost not observed due to the fact that C_{70} entered into the cavity more slowly than C_{60} and required more than 20 minutes for the C_{70} to enter the cavity completely. There are two possible reasons for this observation, one is that C_{70} has an ellipsoidal shape whose volume is larger than C_{60} and secondly, the skeleton of the porphyrin cage **2** is flexible requiring time to rearrange in order to accommodate the C_{70}. Therefore, we modified the experimental protocol in which one equivalent of C_{70} in CS_2 was added all at once and the ^{1}H NMR data was collected at intervals of five minutes. Along with the change of time, the ^{1}H NMR signals assigned to the cage **2** became weaker and the ^{1}H NMR signals assigned to C_{70}@ **2** became stronger correspondingly. Such observation indicated that C_{70} can enter the cavity of the cage **2** at slower rate (shown in Figure 2b).

Strong encapsulation of C_{60} or C_{70} by the porphyrin receptors was also supported by TLC (straight-phase thin-layer chromatography), which exhibited a new spot for the complexes. The new spot for C_{60}@**2** became bigger with the increasing addition of a CS_2 solution of C_{60} (shown in Figure S6a), and the new spot for C_{70}@**2** also became bigger with the change of time (shown in Figure S6b). The spots for cage **2** were fluorescent, but the spots for C_{60}@**2** or C_{70}@**2** were none emissive. The TLC results are consistent with the above ^{1}H NMR observations, also suggesting strong electronic interaction between the porphyrin receptors and the fullerene guest.

The energy-minimized structures of Cage **2**, C_{60}@**2**, and C_{70}@**2** were determined using molecular mechanics calculations. They provided us a further understanding of the interactions between Cage **2** and C_{60} or C_{70}. All the electronic structure calculations in this work were carried out by the Gaussian 09 package[18]. The geometrical structures of the studied Cage **2** and complexes C_{60}@**2**, and C_{70}@**2** were optimized fully using the DFT methods at the 6-31G basis set with the exchange potential of Becke[19] and correlation functional of Lee, Yang, and Parr (B3LYP)[20]. In the calculated structure of the C_{60}@**2** and C_{70}@**2** complexes (Figure 3), the distances from the top panel of the porphyrin Cage **2** to the bottom panel increase from the initial 12.78 Å to 13.27 Å and 13.48 Å respectively. Due to the excellent flexibility of Cage **2**, more obvious change of the distance between two panels was observed in the C_{70}@**2** complex and it was about 0.70 Å. The value was about 0.49 Å in the C_{60}@**2** complex.

Upon addition of C_{60} to the solution of cage **2** in toluene, the Soret band of cage **2** in the UV-vis spectra were shifted notably from 421 nm to 436 nm, with a clear isosbestic point at 429 nm. The 1:1 complexes in solution were confirmed by Job's plot analysis (see the Supporting Information). The association constants (K_a) of complexes C_{60}@**2** in toluene were then evaluated on the basis of the 1:1 binding mode, and the K_a of 1.7×10^6 M^{-1} was obtained. Replacement of C_{60} with C_{70} of the identical concentration caused no change in the absorption spectral of cage **2**, because the binding affinity of cage **2** with C_{70}

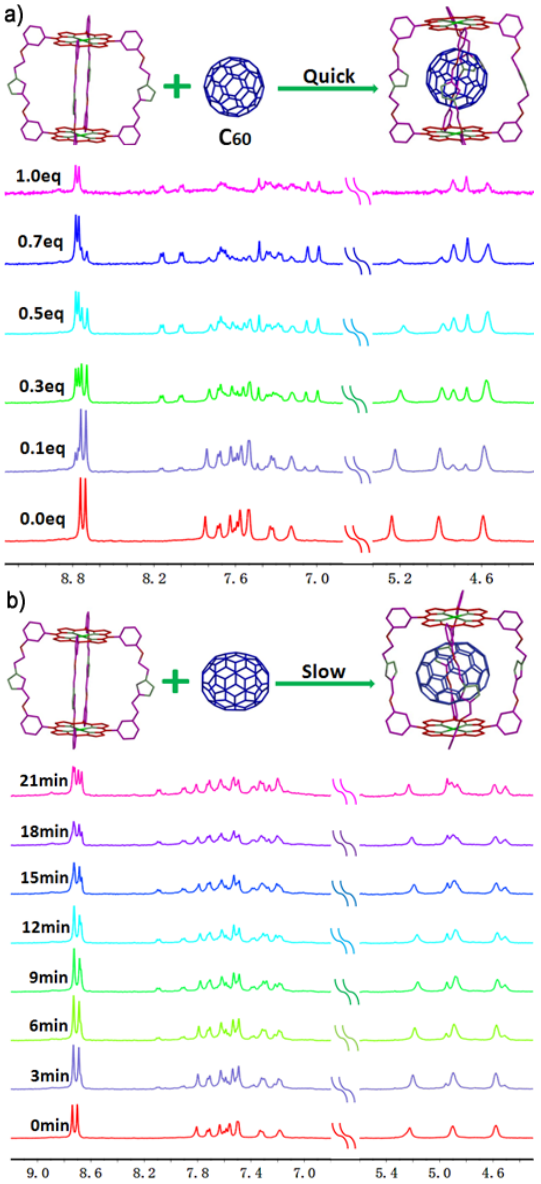

Figure 2. a) Partial ^{1}H NMR spectrum of cage **2** in 1,2-dichloroethane-d4 at 298 K upon titrational addition of C_{60} in CS_2. b) Partial ^{1}H NMR spectrum of cage **2** in 1,2-dichloroethane-d4 + C_{70} in CS_2 (1:1) at 298 K with time as the basis.

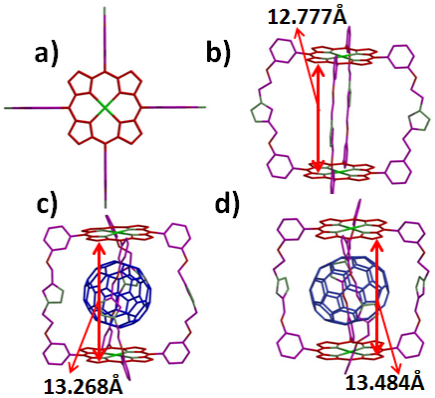

Figure 3. Calculated structures of Cage **2**, C_{60}@**2**, and C_{70}@**2**, (a, a top view of Cage **2**, b, the side view of Cage **2**, c, C_{60}@**2**, d, C_{70}@**2**). The distance shown from the top porphyrin panel to the bottom porphyrin panel.

is too strong to quantify by UV-vis titration. At the investigating concentration, the mixtures of model porphyrin system (cage **1**) and fullerenes unable to form a supramolecular complex didn't show the fluorescence quench. Thus the intermolecular quenching processes can be ignored and the intramolecular quenching of the porphyrin excited state by the fullerene moiety in the supramolecular complex through electron transfer/energy transfer was the main reason[21]. Fluorescence titration[22] was used to measure the association constants (K_a) of the complex C_{70}@**2** (1×10^8 M^{-1}), which indicated that cage **2** exhibited a stronger affinity to C_{70} than to C_{60}. Compared with those previous fullerene receptors[11, 23], cage **2** was a competition receptor with a dramatic affinity for C_{70} ($K_a=1\times10^8$ M^{-1}) and a relatively high affinity for C_{60} ($K_a=1.7\times10^6$ M^{-1}), which is easier to be synthesized and modified. Such high binding constants with C_{60} or C_{70} is due to the flexible cage structure, which enables fullerene to interact well with two porphyrin panels of the receptor.

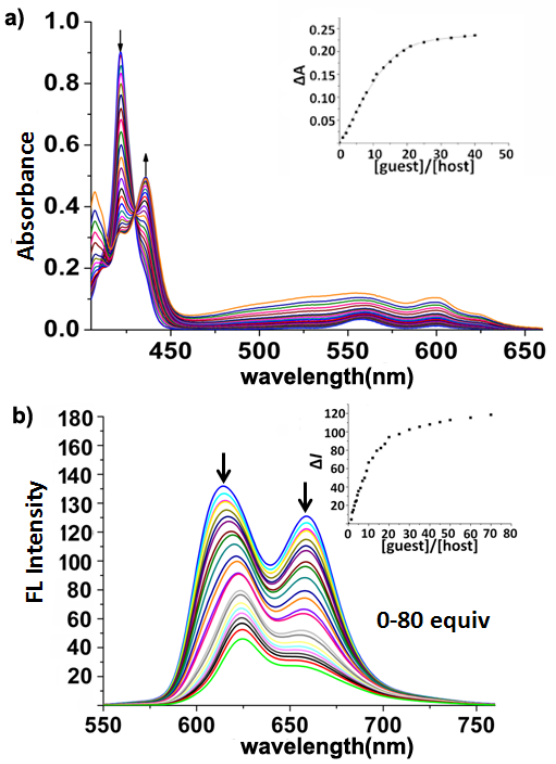

Figure 4. (a) Absorption spectral change of **2** (1 μM) in toluene at 298 K upon titration with C_{60} (0-40 μM). Inset: plot of ΔA_{412nm} against number of equivalents of C_{60} added. (b) Fluorescence spectra during the titration of **2** (0.1 μM) with C_{70} (0-80 equiv) in toluene at 298 K (λ_{ex} =421 nm). Inset: plot of I_{609nm} against number of equivalents of C_{70} added.

In summary, we have successfully synthesized a new zinc porphyrin cage through the simple steps whose flexible skeletons are constructed based on the CuAAC click reaction. We studied the process of interactions between cage **2** and C_{60} or C_{70} by ^{1}H NMR titration experiments and TLC analysis. The results demonstrated that cage **2** interacted with C_{60} quickly and relatively slow when it interacted with C_{70}. The affinities of cage **2** with C_{60} or C_{70} are competitive to those best-performing fullerene receptors reported so far but more easy to be synthesized and modified.

Notes and references

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