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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 and showed high affinity for fullerenes and differentiated rates of binding 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 modification 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 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 requires multiple steps and often has 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 fullerene receptors, high and differentiated binding affinity was definitely achieved.[16] We report herein a cage-structured receptor synthesized *via* a facile "click" approach that is easier to synthesize and modify and showed a high affinity for fullerenes (Fig. 1).

Previously, we have reported that the porphyrin cage **1** is a good receptor for recognizing azide anions.[17] However, 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 length of the linkers to adjust the porphyrin–porphyrin distance of the porphyrin cage to accommodate fullerenes. The larger porphyrin cage **2** can be synthesized directly from two readily accessible

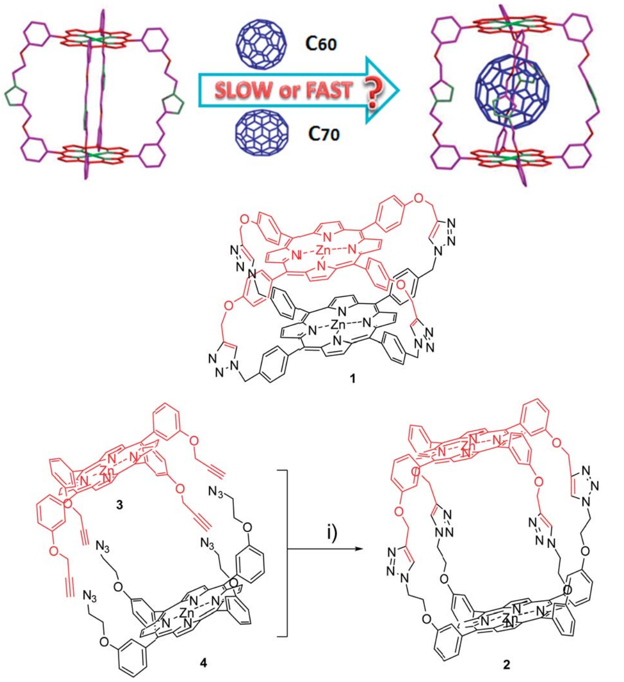

Fig. 1 Top: schematic illustration of porphyrin cage with different binding rates for fullerenes; bottom: synthesis of the porphyrin **2**: (i) CuI, DBU, toluene, pseudo high-dilution condition, dropwise, 75 °C, 24 h, yield: 33%.

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porphyrin-based precursors, **3** and **4**, in one step using a CuAAC click reaction (Fig. 1, bottom). 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 the ESI†).

The first indication of the ability of the porphyrin cage **2** to bind to 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 (shown in Fig. S1 and 2†). No peaks corresponding to aggregates of other stoichiometries were found.

The second point of evidence in support of the formation of C_{60}@**2** and C_{70}@**2** complexes was obtained from the analysis of their ^{1}H NMR spectra. We briefly studied the interaction of the porphyrin cage **2** with C_{60} and C_{70} by means of ^{1}H NMR titration experiments (Fig. 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 cage **2**. This new set of signals was assigned to the C_{60}@**2** complex. With the addition of increased amounts of C_{60}, the signals of the cage **2** decreased continuously, while a new set of signals increased correspondingly (Fig. 2a).

Compared to the interaction of C_{60} with 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 the cavity so quickly that signal splitting was observed immediately and the phenomenon did not change with additional time. However, 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 the cavity more slowly than C_{60}, requiring more than 20 minutes to enter the cavity completely. There are two possible reasons for this observation. One is that C_{70} has an ellipsoidal shape with a volume larger than that of C_{60}, and second, 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 to add one equivalent of C_{70} in CS_2 all at once, and the ^{1}H NMR data were collected at intervals of 5 minutes. Along with the change in time, the ^{1}H NMR signals assigned to cage **2** became weaker and the ^{1}H NMR signals assigned to C_{70}@**2** became correspondingly stronger. Such observations indicated that C_{70} can enter the cavity of cage **2** at a slower rate (shown in Fig. 2b).

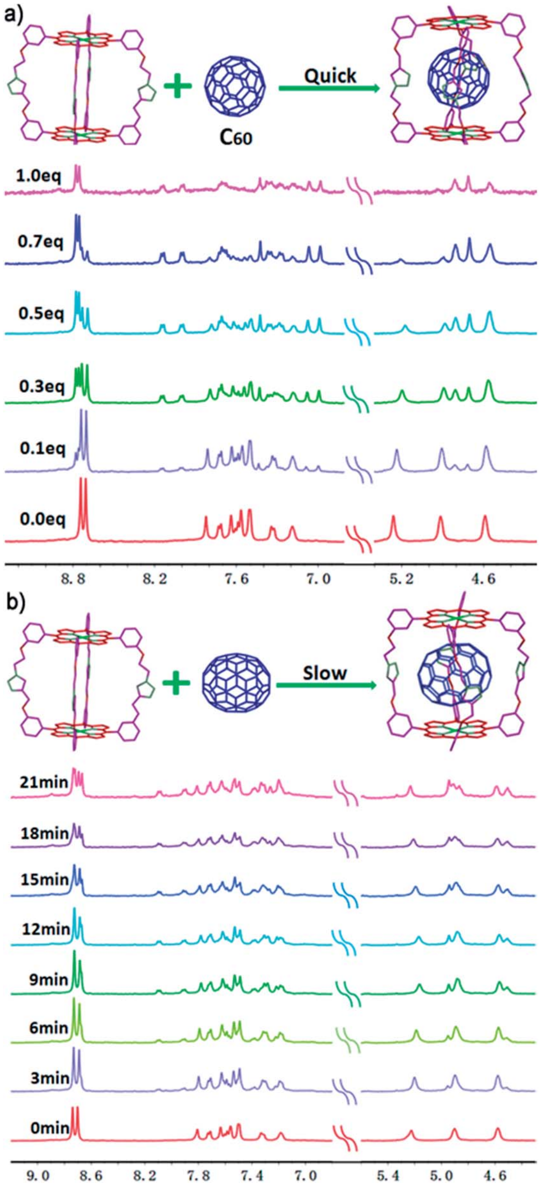

Fig. 2 (a) Partial ^{1}H NMR spectrum of cage **2** in 1,2-dichloroethane-d4 at 298 K upon titrational addition of C_{60} in CS_2. (b) Partial ^{1}H NMR spectrum of cage **2** in 1,2-dichloroethane-d4 + C_{70} in CS_2 (1 : 1) at 298 K with time as the basis.

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 larger with the increasing addition of a CS_2 solution of C_{60} (shown in Fig. S3a†), and the new spot for C_{70}@**2** also became larger with the change in time (shown in Fig. S3b†). The spots for cage **2** were fluorescent, but the spots for C_{60}@**2** and C_{70}@**2** were not 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 with 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 using the Gaussian 09 package.[18] The geometrical structures of the studied cage **2** and C_{60}@**2**, and C_{70}@**2** complexes were optimized fully using the DFT methods at the 6-31G basis set with the exchange potential of Becke[19] and correlation function of Lee, Yang, and Parr (B3LYP).[20] In the calculated structures for the C_{60}@**2** and C_{70}@**2** complexes (Fig. 3), the distances from the top panel of the porphyrin cage **2** to the bottom panel increased from 12.78 Å initially to 13.27 Å and 13.48 Å, respectively. Due to the excellent flexibility of cage **2**, a more obvious change in the distance between the 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.

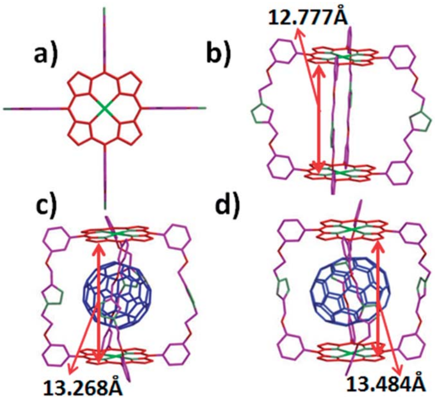

Fig. 3 Calculated structures of cage **2**, C_{60}@**2**, and C_{70}@**2**, ((a), a top view of cage **2**; (b), the side view of cage **2**; (c), C_{60}@**2**; (d), C_{70}@**2**). The distance is shown from the top porphyrin panel to the bottom porphyrin panel.

Upon addition of C_{60} to the solution of cage **2** in toluene, the Soret band of cage **2** in the UV-vis spectrum shifted markedly 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 ESI†). 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 a K_a of 1.7×10^6 M^{-1} was obtained (shown in Fig. 4a and Fig. S4†). Replacement of C_{60} with C_{70} at the same concentration caused no change in the absorption spectrum of cage **2**, because the binding affinity of cage **2** to C_{70} is too strong to be quantified by UV-vis titration. At the investigated concentration, the mixtures of the model porphyrin system (cage **1**) and fullerenes unable to form a supramolecular complex did not show fluorescence quenching. 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 is the main reason.[21] Fluorescence titration[22] was used to measure the association constant (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} (shown in Fig. S5 and 6†). Compared with previous fullerene receptors,[11,23] cage **2** was a competition receptor with a dramatic affinity for C_{70} ($K_a = 1 \times 10^8$ M^{-1}) and a relatively high affinity for C_{60} ($K_a = 1.7 \times 10^6$ M^{-1}), which is easier to be synthesized and modified. Such high binding constants with C_{60} or C_{70} are due to the flexible cage structure, which enables fullerene to interact well with the two porphyrin panels of the receptor (Fig. 4).

In summary, we successfully synthesized a new zinc porphyrin cage through simple steps, and its 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 with C_{70} at a relatively slower rate. The affinities of cage **2** for C_{60} or C_{70} are competitive among those of the best-performing fullerene receptors reported so far, but cage **2** is more easily synthesized and modified.

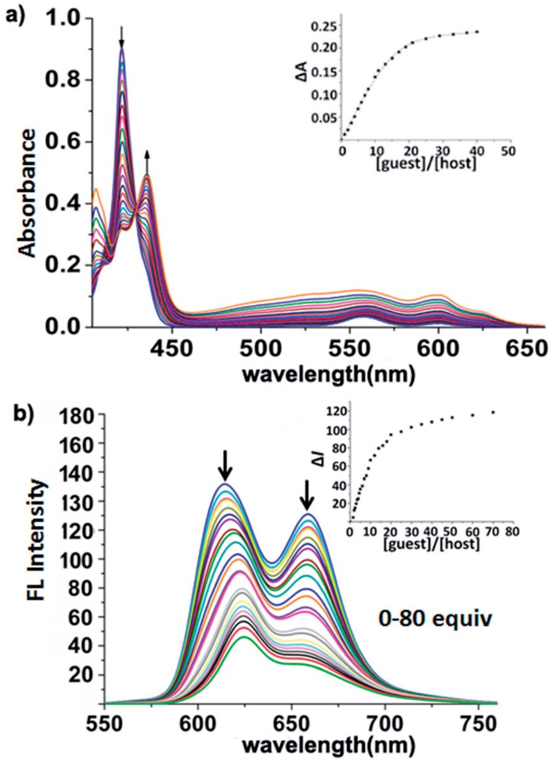

Fig. 4 (a) Absorption spectral change of **2** (1 μM) in toluene at 298 K upon titration with C_{60} (0–40 μM). Inset: plot of $\Delta A_{412\text{nm}}$ against number of equivalents of C_{60} added. (b) Fluorescence spectra during the titration of **2** (0.1 μM) with C_{70} (0–80 equiv.) in toluene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

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