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PAPER

New strapped porphyrins as hosts for fullerenes: synthesis and complexation study†

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New strapped porphyrin-based hosts with different π-conjugated moieties and linkers have been prepared and their ability to bind with fullerenes was studied in dilute solution. We found that the ability of these hosts to bind with fullerenes strongly depends on their chemical nature and more precisely on the substitution pattern of the porphyrin deck. As expected, the more electron-rich hosts containing either an exTTF or a porphyrin unit as the strap bind fullerenes more efficiently with association constants of up to 3.9×10^5 M^{-1}. The results clearly demonstrate the potential of such hosts as a supramolecular scaffold for surface immobilization of pristine fullerenes.

Introduction

Fullerene C_{60} is considered as one of the most important building blocks for the next generation of electronic devices.[1] In addition to being a promising material for non-volatile memory application,[2] C_{60} is also very useful as an n-type, electron-conducting material for organic electronic devices such as field-effect transistors[3] and solar cells.[4] The great interest of the scientific community towards C_{60} comes from its triply degenerate LUMO energy level that can accommodate up to six electrons upon reduction under optimized conditions.[5] However, to be processed in solution, C_{60} has to be made soluble to allow the formation of thin films or monolayers. The most common way to enhance the solubility of C_{60} is to attach organic moieties directly to the cage through covalent bonds. Although very useful, this strategy leads to a significant deterioration of the electronic properties and chemical stability of C_{60} since one pair of π-electrons at the 6 : 6 junction is consumed during the reaction. Therefore, new strategies enabling the processability of pristine C_{60} need to be developed.

An increasingly popular method for processing pristine C_{60} is to use supramolecular interactions between a π-conjugated host and the C_{60} (guest).[6] Among several hosts developed recently, porphyrins[7] and extended tetrathiafulvalene (exTTF)[8] derivatives have attracted a lot of attention. Porphyrins have been widely used to complex with pristine C_{60} because of its high π-electron density and low re-organization energy, while exTTF derivatives offer excellent van der Waals contact with the C_{60} surface owing to its curved conformation. After precise conformational optimization, association constants of up to 10^8 M^{-1} have been obtained in dilute solution for a guest made from porphyrin and/or exTTF.[7d,8g,9]

The next logical step towards the utilization of pristine C_{60} in electronic applications is the creation of an organized, stable two-dimensional network of C_{60} on metallic or semi-conducting surfaces by exploiting the recent advances in the supramolecular chemistry of C_{60}.[1d] To the best of our knowledge, no efficient host fulfilling all the requirements for the surface immobilization of pristine C_{60} has been developed thus far, although many hosts for pristine C_{60} complexation in solution have been developed. Thus, we decided to address the challenge of surface immobilization of C_{60} by preparing a new class of hosts with strapped porphyrin architecture that could be further organized as stable self-assembled monolayers on the surface. In recent studies, Aida *et al.* showed that very high association constants can be obtained when a porphyrin "strapped" by another porphyrin is used as the host for fullerene complexation.[7d,9] Although many research groups reported on the preparation of strapped porphyrins for different purposes, the Aida report is the only one showing the potential of such a molecular architecture for fullerene complexation. However, the use of various π-conjugated moieties (other than porphyrin) as the strap has not been accomplished and an exhaustive study on structure–property relationships for strapped porphyrins as hosts for fullerenes is still lacking.

As the first step towards the development of highly stable supramolecular complexes on the surface, we report herein the synthesis and complexation study of new strapped metalloporphyrin-based hosts for fullerenes (Scheme 1). With this study, we sought to optimize the structural parameters of the hosts in order to increase the association constant between strapped porphyrins and fullerenes. To achieve this goal, different π-conjugated moieties have been used to strap the porphyrin unit and a complexation study using both C_{60} and C_{70} was conducted in dilute solution.

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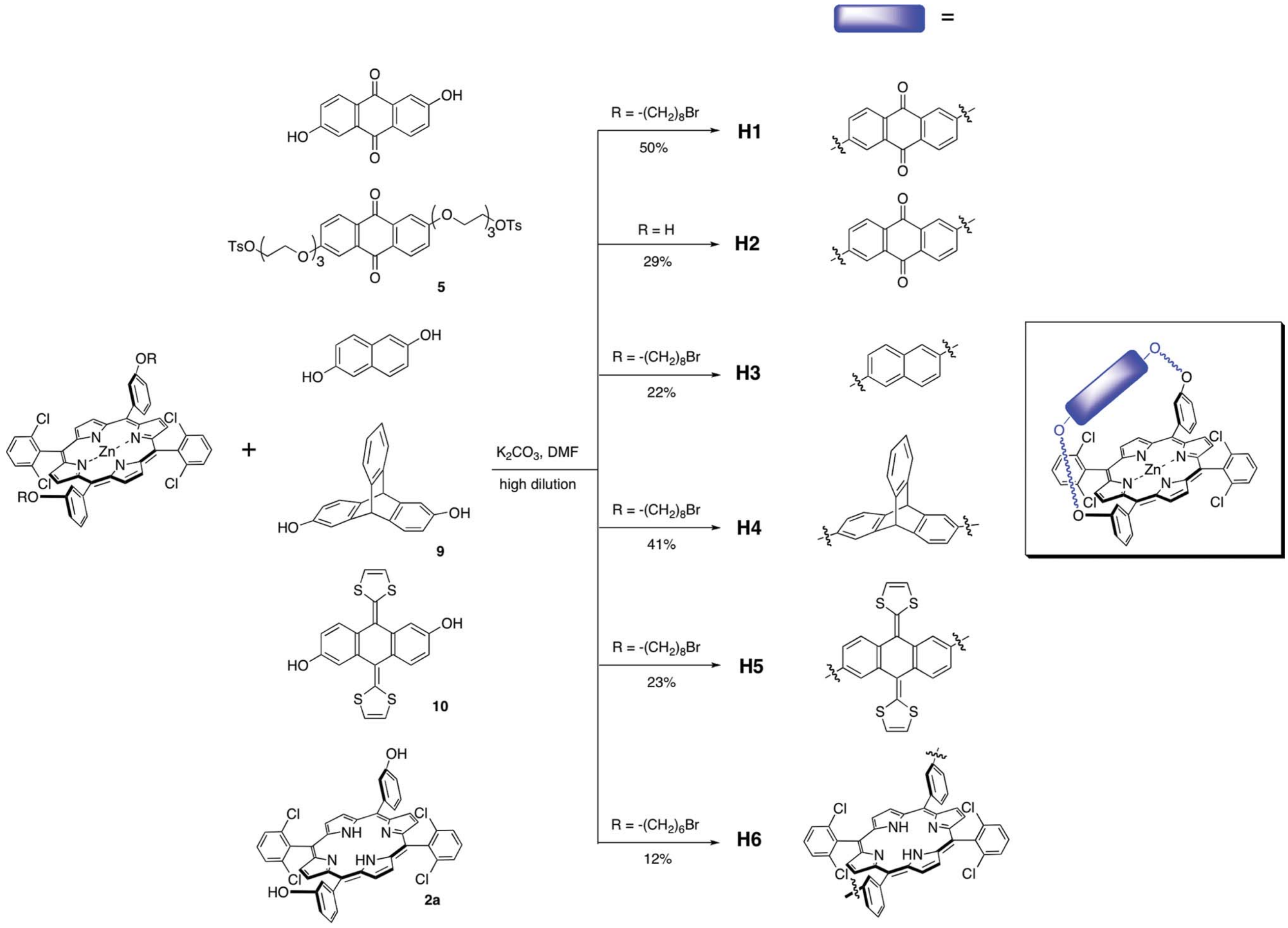


Scheme 1 Synthesis of the hosts **H1–H6**.

Results and discussion

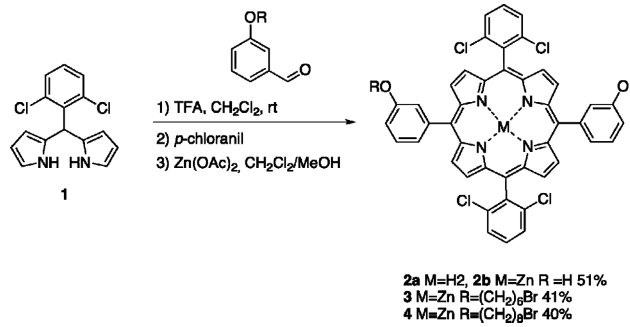
Synthesis of strapped porphyrins

All the hosts, except **H7**, prepared for this study possess the same *meso*-strapped porphyrinic building block, with tethers attached to the *meso*-phenyl rings. To attach the straps, five different π-conjugated moieties have been used, namely 2,6-anthraquinone (**H1** and **H2**), 2,6-naphthalene (**H3**), 2,6-triptycene (**H4**), 2,6-exTTF (**H5** and **H7**) and porphyrin (**H6**) (Scheme 1). Porphyrin with a *trans*-A_2B_2-tetraaryl configuration was used as the scaffold for the synthesis of the strapped porphyrin hosts. This scaffold has been chosen because it is readily accessible *via* classical, non-statistical porphyrin synthesis. In addition, it allows the straightforward preparation of a variety of hosts through the attachment of different linkers and/or π-conjugated bridges directly to the porphyrin scaffold. This post-functionalization approach greatly simplifies the purification of the macrocyclic hosts compared to the route involving the direct formation of strapped porphyrin *via* the condensation of a bis-aldehyde-containing strap.[10] Moreover, this approach allows the introduction of chemically sensitive moieties such as exTTF at the very end of the synthesis.

The acid-catalyzed rearrangement of 5-aryldipyrromethane during the condensation with an aldehyde to form *trans*-A_2B_2 porphyrins can generate a complex mixture of isomers. The rearrangement process, called *scrambling*,[11] dramatically decreases the yield and makes the purification step quite difficult. One way to suppress the scrambling process is to use a sterically hindered dipyrromethane.[15] In our case, however, the functional group on the aryl substituent used to induce steric hindrance has to be carefully chosen since it must not preclude the introduction of fullerenes inside the host's pocket. For this reason, we chose 5-(2,6-dichlorophenyl)dipyrromethane (**1**)[12] over the bulkier 5-mesityldipyrromethane because the van der Waals radii of the chloride atom is smaller than that of the methyl group and should cause less steric hindrance towards further complexation with fullerenes.

As shown in Scheme 2, the synthesis of *meso* substituted *trans*-A_2B_2 porphyrins **2–4** was achieved *via* the condensation of sterically hindered 5-(2,6-dichlorophenyl)dipyrromethane[16] **1** with the corresponding aldehydes[13] under the carefully controlled conditions developed by Lindsey *et al.*[15] giving minimal *scrambling*. Subsequent metallation using zinc acetate afforded the porphyrin building blocks **2a,b–4** in very good yields (40–51%) for porphyrin formation. The incorporation of the zinc atom in the porphyrin center simplified the purification and is necessary for the future surface immobilization *via* axial coordination.

With the porphyrin scaffold on hand, we undertook the preparation of the π-conjugated bridges. We first chose to focus our efforts on the preparation of 2,6-dihydroxy substituted



Scheme 2 Synthesis of the mesoporphyrins.

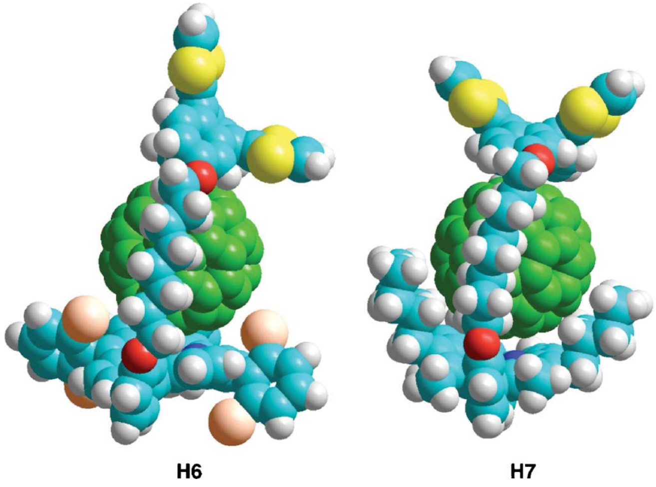
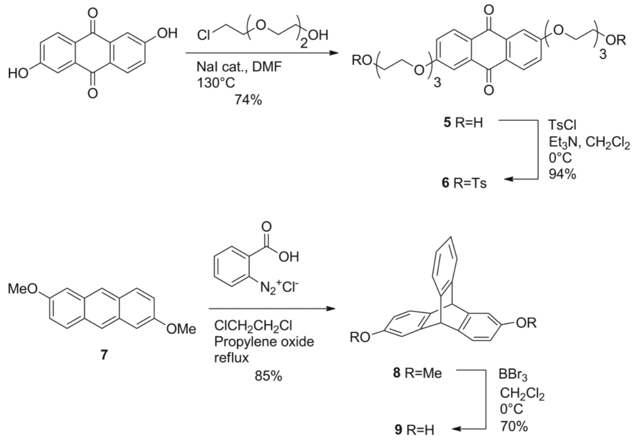


Fig. 1 Energy-minimized structures of **H5** and **H7** complexes with C_{60} (Amber force field using HyperChem^{TM}).

aromatic moieties with alkyl or ethylene oxide chains as linkers. The optimal length for the linkers was determined to be an octyl chain according to geometry optimization performed using molecular modeling (*vide infra*).

Commercially available anthraflavic acid is a useful precursor to prepare a variety of 2,6-substituted aromatic moieties. As shown in Scheme 3, the anthraquinone derivative bearing the ethylene oxide strap **6** was synthesized in two steps. Anthraflavic acid was first alkylated with 2-[2-(2-chloroethoxy)ethoxy]ethanol using a catalytic amount of NaI and K_2CO_3 in DMF to afford compound **5** in 74% yield. The diol **5** was di-tosylated with tosyl chloride and Et_3N in CH_2Cl_2 to afford the bis-tosylated anthraquinone **6** in 94% yield.

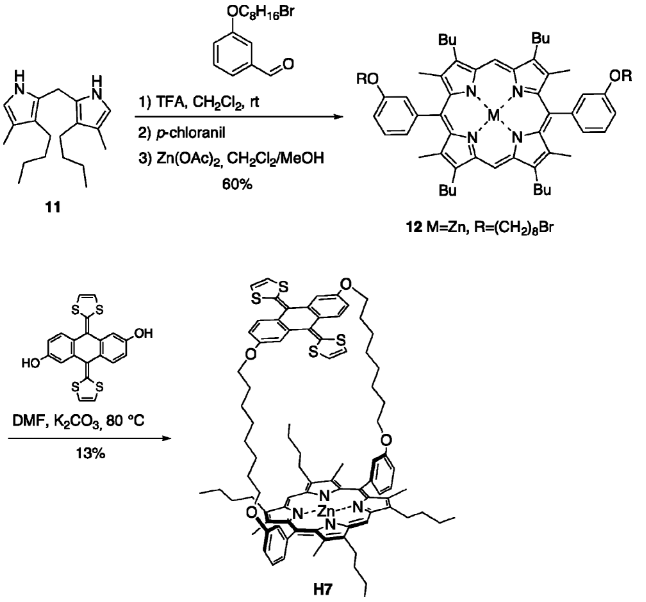


Scheme 3 Synthesis of ethylene oxide chain-containing anthraquinone and triptycene units.

The second building block of interest was prepared *via* a Diels–Alder reaction between 2,6-dimethoxyanthraquinone,[14] prepared from the two-step reduction of 2,6-dimethoxyanthraflavic acid, and an excess of benzyne precursor 2-carboxybenzenediazonium chloride[15] with propylene oxide as an acid scavenger. The racemic C_2-symmetric 2,6-dimethoxytriptycene derivative **8** was thus obtained in 85% yield (Scheme 3). Deprotection of the methoxy groups was achieved with BBr_3 to afford the 2,6-dihydroxytriptycene **9** in 70% yield.

With the porphyrins and aromatic moieties in hand, the next step was to form the strapped porphyrin hosts (Scheme 1). The macrocyclization reactions were performed under classical alkylation conditions using K_2CO_3 as a base in DMF under high dilution conditions (*ca.* 2 mM) and the desired products were purified using standard column chromatography on silica gel. First, the bis-(8-bromooctyloxy)porphyrin **4** was reacted with anthraflavic acid to afford the host **H1** in 50% yield. Likewise, the anthraquinone appended host **H2** bearing the PEO chain was prepared from bis-hydroxy porphyrin **2b** and bis-tosylate anthraquinone **6** in 29% yield. Similarly, the naphthalene appended host **H3** was prepared from porphyrin **4** and 2,6-dihydroxynaphthalene in 22% yield. The same procedure was used to form the triptycene appended host **H4** in 41% yield from the corresponding building blocks **4** and 2,6-dihydroxytriptycene **9**. The exTTF appended host **H5** was synthesized using **4** and reported 2,6-dihydroxy-exTTF[16] **10** in 23% yield. Compound **10** is easily oxidizable and special care has been taken to minimize its exposure to air.

Analogous to Aida's metalloporphyrin cyclic hosts,[6a] the dimeric porphyrin host **H6** bearing both free base and zinc porphyrins was prepared from free base porphyrin **2a** and zinc porphyrin **3** in 12% yield. Following preliminary fullerene complexation results (*vide infra*), we also prepared the less sterically hindered host **H7** (Scheme 4). In a similar fashion to the



Scheme 4 Synthesis of host **H7**.

Table 1 Binding constant K_a (M^{-1}) and selectivity factor ($K_{a,C_{70}}/K_{a,C_{60}}$) for complexation of C_{60} and C_{70} with hosts **H1–H7** in different solvents

Host	Solvent[a]	K_a C_{60}[b] (M^{-1})	K_a C_{70}[b] (M^{-1})	$K_{a,C_{70}}/K_{a,C_{60}}$
H1	PhMe	—	—	—
	PhMe : ACN (1 : 1)	7000	—	—
H2	PhMe	—	—	—
	PhMe : ACN (1 : 1)	—	—	—
H3	PhMe	—	—	—
	PhMe : ACN (1 : 1)	5000	—	—
H4	PhMe	1000	—	—
	PhMe : ACN (1 : 1)	18 000	22 000	1.2
H5	PhMe	4000	—	—
	PhMe : ACN (1 : 1)	31 000	37 000	1.2
H6	PhMe	23 000	29 000	1.3
	PhMe : ACN (1 : 1)	315 000	390 000	1.2
H7	PhMe	9000	20 000	2.2
	PhMe : ACN (1 : 1)	120 000	350 000	2.9

[a] PhMe = toluene, ACN = acetonitrile. [b] UV-visible (298 K). The K_a values were calculated by the nonlinear least-squares method.[19]

above-mentioned porphyrins, the alkyl substituted porphyrin **12** was prepared in 60% yield from the TFA catalyzed condensation of 4,4′-dimethyl-3,3′-dibutyl-2,2′-dipyrrylmethane[17] **11** with 3-(8-bromooctyloxy)benzaldehyde. The analog of host **H5** was synthesized from porphyrin **12** and 2,6-dihydroxy-exTTF **10** under the same macrocyclisation conditions to afford host **H7** in 13% yield.

Complexation study

The ability of these hosts to bind fullerenes was evaluated by measuring the association constant (K_a) between the hosts and two different fullerenes, namely C_{60} and C_{70}. It is well-known that C_{70} generally yields a better K_a value than C_{60} due to its egg shape and flatter surface, allowing increased π contact with the hosts. The K_a values have been calculated in dilute solution in pure toluene and in a 1 : 1 mixture of toluene/acetonitrile. The results are summarized in Table 1. The complexation between two different fullerenes (C_{60} and C_{70}) and **H1–H7** was studied using UV-visible spectroscopy by monitoring the spectral changes at the Soret band (around 425 nm) upon addition of a fullerene solution. In a typical experiment, aliquots of a toluene solution of fullerene (7.5×10^{-4} M) were added to a solution of host (1.5×10^{-6} M) in toluene or in an acetonitrile/toluene mixture.

The first structural parameter studied was the chemical nature of the flexible linker bridging the porphyrin unit and the π-conjugated moiety ("strap"). For this study, we chose to compare the straight alkyl chain and ethylene oxide chain in the anthraquinone-porphyrin hosts, **H1** and **H2**, respectively. Unfortunately, in both cases, we were unable to measure the K_a value in toluene due to the very weak signal lost in UV-visible spectra upon titration with C_{60} and C_{70}. However, when a mixture of toluene and acetonitrile was used, a K_a value of 7.0×10^3 M^{-1} was measured for **H1** with C_{60} while **H2** exhibited very low binding ability for C_{60} and C_{70} ($<1.0 \times 10^3$ M^{-1}). This difference suggests that straight alkyl chains are more suitable than ethylene oxide ones as linkers in our host design. This result is in disagreement with the results published by Martín *et al.*, suggesting that n–π interactions can take place between oxygen atoms and fullerenes.[18] It should be noted that Martín *et al.* used crown ether and not short straight ethylene oxide for their hosts, meaning that more oxygen atoms are involved in such an interaction in their case.

The next step in our investigation was to study the influence of the π-conjugated moiety linked to the porphyrin unit. Thus, we synthesized a host with a small π surface (naphthalene, **H3**) and compared it with different π-conjugated moieties that were expected to show better contact with C_{60} and C_{70}. **H3** shows detectable association only with C_{60} ($K_a = 5.0 \times 10^3$ M^{-1}) in a mixture of toluene and acetonitrile. Quite surprisingly, no association was observed with bigger fullerenes such as C_{70}. The steric hindrance caused by the presence of two chlorine atoms pointing inside the host "pocket" is likely responsible for this lack of association between **H3** and C_{70}. Moreover, the smaller length of the naphthalene unit compared to the other π-conjugated moieties used in this study could be responsible for a significant decrease in the size of the pocket (shorter strap), thus reducing the affinity of this particular host for bigger fullerenes like C_{70}.

In order to increase the K_a value, a host with a triptycene unit (**H4**) was prepared. The triptycene unit was expected to show improved interactions with fullerene due to its concave π surface that complements the convex shape of fullerene. As predicted, **H4** binds fullerenes more efficiently than **H3** in a mixture of toluene and acetonitrile with K_a values of 1.8×10^4 M^{-1} for C_{60} and 2.2×10^4 M^{-1} for C_{70}. Encouraged by these results, we decided to use exTTF as the π-conjugated moiety (**H5**). In addition to having a concave shape, this unit is more electron-rich than triptycene, thus increasing the strength of the interaction between the host and fullerenes. As a consequence of this structural improvement, **H5** exhibits higher K_a values in the toluene/acetonitrile mixture for both C_{60} and C_{70} (3.1×10^4 and 3.7×10^4 M^{-1}, respectively) than **H4**. Finally, we measured the K_a values for **H6**, which is a porphyrin strapped with another porphyrin. Surprisingly, the K_a values in toluene/acetonitrile were one order of magnitude higher than those measured for **H5** (3.15×10^5 for C_{60} and 3.9×10^5 M^{-1} for C_{70}). This result confirms the great ability of porphyrin derivatives to bind to C_{60} in a supramolecular manner.

A very interesting trend observed in this study is the poor selectivity of all the hosts towards either C_{60} or C_{70}. In most of the reports published thus far, the hosts preferentially bind to C_{70} over C_{60} due to its egg shape and flatter surface, which are responsible for stronger interactions with the hosts. Even when very flexible hosts are used, the selectivity factors ($K_{a,C_{70}}/K_{a,C_{60}}$) are generally much higher than 2.[7h] However, for the hosts **H1–H6**, the selectivity factor is close to unity. Because this peculiarity of our system is unlikely to be attributed to electronic effects, we suspected the steric effect to be the cause of this poor selectivity. As mentioned earlier and shown in Fig. 1, the two chlorine atoms pointing inside the cavity of the host induce steric hindrance that reduces the size of the pockets available for the fullerenes. Obviously, this steric effect is expected to be more detrimental to the complexation of C_{70}. To confirm this hypothesis, we synthesized a new strapped porphyrin (**H7**) by removing the chlorine atoms on the *meso*-phenyl units and adding short alkyl chains on the pyrrole units. exTTF was chosen as the π-conjugated moiety. Because alkyl chains are more flexible, they should allow C_{70} to enter the cavity more easily. Interestingly, **H7** binds C_{60} and C_{70} more efficiently than **H5** with a four-fold increase in the K_a values when a mixture of toluene and acetonitrile was used. This significant increase can be attributed to the small increase of the pocket size, but also to the presence of alkyl chains that can cause the porphyrin to bend and adopt a concave conformation due to steric hindrance (Fig. 1).[6a] The selectivity factor was also increased from 1.2 to 2.9 following this simple modification, which supported our initial hypothesis on steric hindrance induce by chlorine atoms.

Another peculiarity of **H7** is its ability to bind with C_{60} only in a 1 : 1 configuration, but with C_{70} in both 1 : 1 and 2 : 1 configurations. As shown in Fig. 2, two isosbestic points at 423 and 442 nm appeared in the UV/vis spectrum when C_{70} was added to a dilute solution of **H7** in a mixture of toluene and acetonitrile. The formation of both types of configuration was assessed using Job plots, which shows a maximum between 0.5 and 0.6 (see ESI†). This phenomenon was reported and studied in detail by Aida *et al.* for similar macrocyclic hosts.[20] The fact that a 2 : 1 complex has been observed for C_{70} but not for C_{60} tends to demonstrate that the alkyl chains we used to link the π-conjugated bridge and the porphyrin deck are long enough for C_{60} complexation, but a bit too short to accommodate the bigger C_{70}. Hence, the short strap forces the host to adopt a more open conformation, leaving one side of the C_{70} available for further complexation by another host molecule.

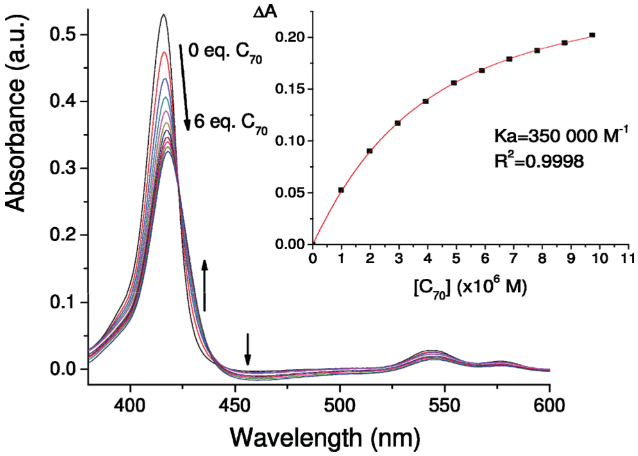


Fig. 2 (a) UV-visible spectral changes of **H7** upon addition of C_{70} in a toluene/acetonitrile (1 : 1) mixture at 298 K. Inset: Plot of the UV-visible changes at 416 nm.

Conclusions

In summary, we prepared seven strapped porphyrin-based hosts for complexation of fullerenes. As the geometrical complementarity between the host and the fullerenes (concave/convex interaction) and the electronic density of the host increase, the association constants increased to a value of up to $3.9 \times 10^5\ M^{-1}$. We also found that the substitution pattern of the porphyrin deck was an important parameter to take into account in the host design. The two best hosts, **H6** and **H7**, are now assembled onto a gold surface and their ability to bind with pristine and reduced fullerenes ($C_{60}^{\bullet-}$) in a stable way is now under investigation.

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