JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
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A Highly C_{70} Selective Shape-Persistent Rectangular Prism Constructed through One-Step Alkyne Metathesis

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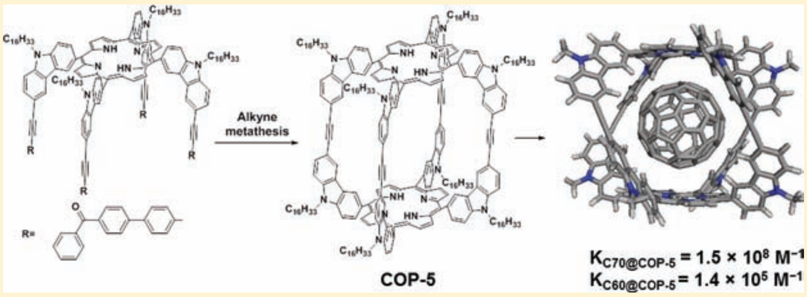
S Supporting Information

ABSTRACT:



Dynamic covalent chemistry (DCC) provides an intriguing and highly efficient approach for building molecules that are usually thermodynamically favored. However, the DCC methods that are efficient enough to construct large, complex molecules, particularly those with three-dimensional (3-D) architectures, are still very limited. Here, for the first time, we have successfully utilized alkyne metathesis, a highly efficient DCC approach, to construct the novel 3-D rectangular prismatic molecular cage **COP-5** in one step from a readily accessible porphyrin-based precursor. **COP-5** consists of rigid, aromatic porphyrin and carbazole moieties as well as linear ethynylene linkers, rendering its shape-persistent nature. Interestingly, **COP-5** serves as an excellent receptor for fullerenes. It forms 1:1 complexes with C_{60} and C_{70} with association constants of $1.4 \times 10^5\ M^{-1}$ (C_{60}) and $1.5 \times 10^8\ M^{-1}$ (C_{70}) in toluene. This represents one of the highest binding affinities reported so far for purely organic fullerene receptors. **COP-5** shows an unprecedented high selectivity in binding C_{70} over C_{60} ($K_{C70}/K_{C60} > 1000$). Moreover, the binding between the cage and fullerene is fully reversible under the acid−base stimuli, thus allowing successful separation of C_{70} from a C_{60}-enriched fullerene mixture (C_{60}/C_{70}, 10/1 mol/mol) through the "selective complexation−decomplexation" strategy.

Three-dimensional (3-D) molecular cages, particularly shape-persistent, covalent organic polyhedrons (COPs) with well-defined pore dimensions, have attracted considerable attention due to their numerous applications in host−guest chemistry,[1,2] chemical sensing,[3,4] catalysis,[5,6] gas adsorption,[7−10] etc. Current synthesis of rigid molecular cages is dominated by supramolecular chemistry, including metal coordination[6,11−13] and hydrogen bonding,[14] which usually provides the target species with high efficiency through the self-assembly process. The growing importance of supramolecular cages in the bottom-up design of novel functional materials has prompted the development of COPs, which usually possess high chemical and thermal stability, as promising candidates for those applications requiring harsh operating conditions (e.g., in the presence of acid or base). While supramolecular cages have been extensively studied, purely organic covalent molecular cages are relatively rare and have only recently received increasing attention. Conventionally, COPs are constructed via irreversible chemical transformations, which usually require enormous synthetic and purification efforts with very low overall yields.[15,16] In great contrast, recent advances in dynamic covalent chemistry (DCC)[17,18] offer convenient pathways to high-yielding synthesis of COPs.[19−24] To date, imine condensation/metathesis is almost the only reversible DCC reaction that has been used in the construction of 3-D molecular architectures.[8,9,24,25] However, the potential drawbacks of imine groups are their sensitivity to acidic conditions and water. Further hydride reduction of imines provides more robust, but also flexible, amino groups, resulting in the loss of certain shape persistency of target structures.

Rigid, shape-persistent 3-D molecular cages[26] are attractive as hosts for selectively binding guest molecules of a certain size and shape. However, the construction of molecular cages with well-defined and large intrinsic cavities, which are not easily altered by the environmental stimuli, still remains a grand challenge. To preserve such shape persistency, the molecules should consist of rigid, noncollapsible scaffolds. In the ocean of conformationally rigid building blocks exists a particularly interesting group of conjugated systems, porphyrins, which have attracted enormous research interest due to their intriguing applications in host−guest chemistry,[27] artificial photosynthesis,[28] and catalysis.[29] Another important group of building blocks with inherent rigidity

Received: October 7, 2011
Published: November 15, 2011

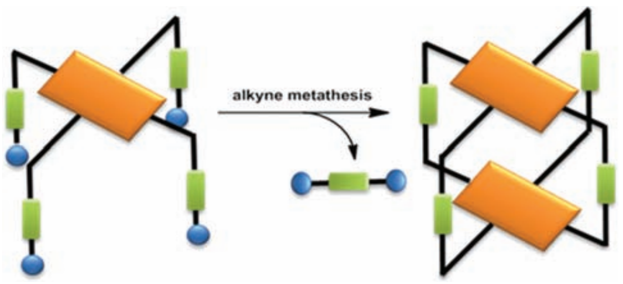


Figure 1. Schematic presentation of constructing a rectangular prism from a tetra-armed precursor through alkyne metathesis.

are arylene ethynylenes, and recent advances in shape-persistent 2-D macrocycles have taken advantage of their angular, rigid geometries and easy synthetic access.[30−33] In this context, alkyne metathesis,[34−36] a DCC approach, has emerged as a powerful synthetic tool for the efficient and versatile construction of shape-persistent molecular architectures and has been elegantly applied to the one-step modular synthesis of a variety of 2-D macrocyclic compounds from simple arylene diacetylene monomers.[37] Such a synthetic approach is remarkable in that it can transform various undesired oligomeric and macrocyclic kinetic intermediates into the thermodynamically most stable product. Shape-persistent 3-D molecular architectures based on rigid arylene ethynylene backbones are synthetically more challenging than their 2-D analogues, and so far they have mainly been obtained through multistep labor-intensive statistical or template-supported oxidative Glaser coupling.[38] Here we present, for the first time, one-step synthesis of a shape-persistent organic rectangular prismatic cage consisting of only aromatic moieties in its backbone structure, via Mo(VI) carbyne catalyzed alkyne metathesis from tetrasubstituted porphyrin monomers, in decent yield (Figure 1). The unique combination of the conjugated system and the rigidity of this cage molecule renders its rapid and selective binding of C_{70} over C_{60}; the cage exhibits a binding interaction with C_{70} compared to C_{60} that is stronger by 3 orders of magnitude. Moreover, the clean release of fullerenes (guest) and regeneration of the cage **COP-5** (host) was realized by simply tuning the pH of the media. Such a "selective complexation−decomplexation" strategy has been successfully applied to the isolation of C_{70} from a C_{60}-enriched fullerene mixture.

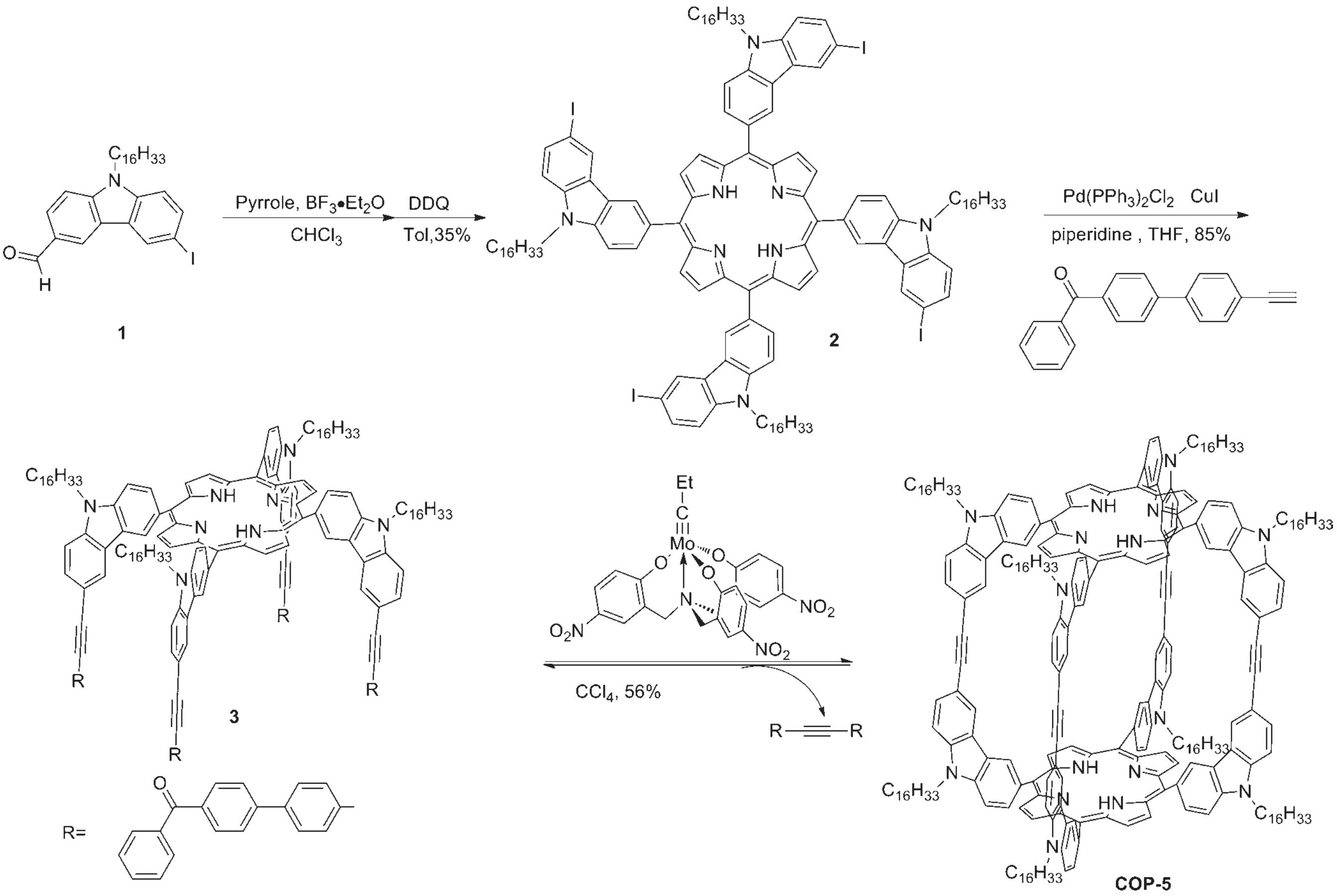
RESULTS AND DISCUSSION

Previously our group has demonstrated that various trigonal-prismatic cage molecules can be constructed through the "panel-pillar-assembly" design strategy via a one-step imine condensation/metathesis reaction followed by further reduction of imines to more chemically robust amino groups.[9] However, these amine-linked molecular cages are semishape-persistent and adopt a distorted-prismatic architecture due to the rotational freedom of the amine bond connections. Although COPs containing methylene, ether, amino, or similar saturated moieties could be shape-persistent to some extent, they are generally considered less conformationally rigid compared to those molecules constructed solely with aromatic fragments in their skeletons. Among functional groups capable of undergoing chemical transformations while retaining their conformational rigidity, the linear ethynylene group seems to be an appropriate robust rigid linker moiety. Given the fact that alkyne metathesis has been successfully utilized in the efficient synthesis of shape-persistent 2-D aryleneethynylene macrocycles,[37] we envisioned this dynamic covalent transformation with "self-correction" nature would be an ideal approach to construct the ethynylene-linked rigid molecular cage. The next challenge for the dynamic covalent construction of a molecular cage was then the identification of a rigid 90° corner piece that would yield a rectangular-prismatic structure with minimum angle strain. Careful examination of the geometrical parameters suggested that the C_4-symmetric carbazole-substituted porphyrin **3**, in which the ethynyl groups are oriented approximately perpendicular to the porphyrin ring, could be a suitable monomer to yield **COP-5** (Scheme 1). Porphyrins are incorporated into the cage structure because of their interesting properties in fullerene binding, which would provide highly efficient donor−acceptor pairs for the photoinduced electron transfer (PET) process.[39,40]

The monomer **3** was prepared from 3-iodo-6-formyl-9-hexadecylcarbazole (**1**) through the Lindsey method to form the 5,10,15,20-tetrakis(carbazolyl)porphyrin **2**, followed by Sonogashira coupling to attach the benzoylbiphenyl acetylene group (Scheme 1). Benzoylbiphenyl was utilized as the end group so that insoluble byproduct diarylacetylenes would be formed along the reaction, thus driving the reversible alkyne metathesis to completion.[37] Our newly developed multidentate Mo(VI) carbyne was utilized as the metathesis catalyst, which has shown superior catalytic activity, broader substrate scope, and longer lifetime in comparison to its monodentate analogue.[41] Given the suitable geometrical shape, rigidity of the building block, and high activity of alkyne metathesis catalyst, the formation of the thermodynamically favored target molecular cage is expected. The reaction was performed at 75 °C under microwave irradiation in CCl_4. After 32 h, the predominant formation of cage **COP-5** was observed (56% isolated yield). The dynamic nature of alkyne metathesis offers the self-correction pathway toward the cage formation. The reaction progress monitored by gel permeation chromatography (GPC) showed the gradual conversion of initial high-molecular-weight oligomeric intermediates into the target cage **COP-5** (Figure S2, Supporting Information). Such a cage is enthalpy favored due to its minimal angle strain and also entropy favored due to its consistent minimal number of building blocks (in comparison to larger oligomeric products). This cage synthesis represents the first time alkyne metathesis has been used to construct a purely organic, shape-persistent molecular rectangular prism with high efficiency.

The cage **COP-5** was fully characterized by ^{1}H and ^{13}C NMR spectroscopy, UV−vis spectroscopy, and GPC, as well as MALDI-TOF mass spectrometry. The ^{1}H NMR spectrum of **COP-5** in $CDCl_3$ shows only one set of singlets corresponding to the porphyrin protons at 8.73 ppm, indicating the high symmetry of the cage structure. The MALDI-TOF mass spectrum shows the desired molecular ion peaks at m/z 3825.80 ($[M + H]^+$ calcd for $C_{272}H_{332}N_{16}$ 3825.66). Additional evidence supporting the rectangular-prismatic structure of **COP-5** was obtained through a diffusion ordered spectroscopy (DOSY) experiment. All the peaks assigned to **COP-5** have the same diffusion coefficients (D values) within the experimental errors ($(4.1 \pm 0.4) \times 10^{-10}$ m^2 s^{-1}). From the Stokes−Einstein equation, the effective hydrodynamic radius R (9.2 ± 1.0 Å) is calculated, which is in good agreement with the calculated radius of gyration 9.7 Å based on the energy-minimized structure in Figure 2. The cage is thermally stable and also exhibits a very high chemical stability even with

Scheme 1. Synthesis of Rectangular Prism COP-5



exposure to water and acids (e.g., trifluoroacetic acid, TFA) for weeks, thus showing a great advantage over those supramolecular cages as well as imine-linked COPs.

One of our major motivations for constructing such rigid, porphyrin-containing molecular cages is to develop a novel class of organic fullerene receptors, which could bind strongly and also selectively with a certain type of fullerene. Although covalent macrocycles[27,42] or supramolecular cages[43] containing porphyrin moieties have been reported to exhibit strong binding interactions with fullerenes, covalently bonded organic cages have rarely been reported as fullerene receptors. Porphyrin—fullerene binding is mainly driven by an electronic effect: i.e., a favored donor—acceptor interaction. With two porphyrin-free base moieties as the top and bottom panels, the cage **COP-5** is expected to strongly bind fullerenes. The computational modeling study (Figure 2) reveals that **COP-5** has a cavity with a height (defined as the distance between the top and bottom porphyrin panels) of 11.9 Å and a diameter of 18.3 Å (defined as the distance between the two ethynylene groups in the diagonal edges), in which a fullerene can be nicely accommodated.

The cage **COP-5** indeed showed a strong binding interaction with fullerenes. The binding of **COP-5** with C_{60} and C_{70} was characterized by UV—vis titration experiments in toluene (Figure 3a,b). With a gradual addition of C_{70} to the cage solution (in toluene), the intensity of the absorption peak of **COP-5** at 428 nm decreases while a new signal at 437 nm arises. The cage—C_{70} complex (C_{70}@**COP-5**) formation is clearly signaled by the substantial intensity decrease (~55%, with 1 equiv of C_{70} added) at 428 nm and the red shift (9 nm) of the porphyrin Soret band in comparison to that of **COP-5** itself. A similar trend in the UV—vis titration curve was also observed when the solution of **COP-5** in toluene was titrated with C_{60}. According to the Job plot, both C_{60} and C_{70} formed a 1:1 host—guest complex with **COP-5** (Figure S4, Supporting Information). Consistent with this observation, when 0.25 equiv of C_{70} was added to the cage solution in toluene, C_{70}@**COP-5** was formed instantaneously, and the ^{1}H NMR spectra (Figure 3c) showed two sets of signals corresponding to the free **COP-5** and C_{70}@**COP-5** complex with an integration ratio of 3:1, further supporting the 1:1 binding mode between **COP-5** and C_{70}. MALDI-TOF spectra (Figure S5, Supporting Information) of cage—fullerene complexes clearly showed peaks with *m*/*z* 4544.20 and 4664.74 corresponding to 1:1 host—guest complexes C_{60}@**COP-5** and C_{70}@**COP-5**, without any other complexes observed.

Additional evidence in support of the fullerene encapsulation inside the cage comes from the analysis of ^{1}H NMR spectra of the cage—fullerene complexes. The chemical shifts of the protons at the 4,5-positions on the carbazole corner pieces, which are pointing to the inside cavity of the cage, moved significantly downfield in both C_{60}@**COP-5** and C_{70}@**COP-5**, while the other protons of the carbazole are not much affected (Figure S6, Supporting Information); such an observation indicates the fullerenes are located inside the cage. On the other hand, the internal N—H protons of the porphyrins at −1.97 ppm shifted

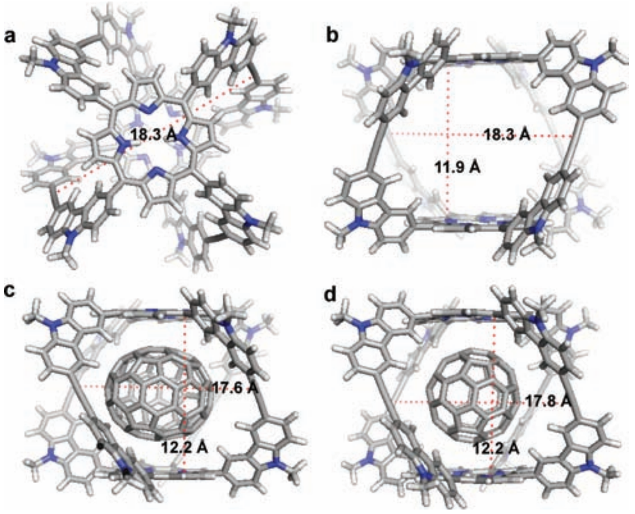


Figure 2. Energy-minimized structures of **COP-5** (a, top view; b, side view), C_{70}@**COP-5** (c), and C_{60}@**COP-5** (d). Methyl groups were used in the calculation instead of hexadecyl chains for simplicity. The height of **COP-5** was defined as the distance between the top and bottom porphyrin panels, and the diameter of the inside cavity of **COP-5** was defined as the distance between the two ethynylene groups in the diagonal edges.

significantly upfield by the influence of the fullerene ring current in C_{70}@**COP-5** (Figure S6), which indicates a strong $\pi-\pi$ interaction between C_{70} and the porphyrin panels of **COP-5**. The simplicity of the NMR signals of the C_{70}@**COP-5** and C_{60}@**COP-5** suggests a highly symmetrical structure of the complexes, further supporting the notion of fullerene binding inside the cage.

On the basis of the 1:1 binding mode and fitting of the UV−vis adsorption changes at 428 nm under different fullerene concentrations, the association constants of C_{60} and C_{70} with **COP-5** were estimated to be 1.4×10^5 M^{-1} (C_{60}) and 1.5×10^8 M^{-1} (C_{70}) in toluene, which are comparable to those best-performing fullerene receptors reported thus far. It has been a great challenge to obtain host molecules that bind fullerenes with association constants higher than 10^5 M^{-1}. To the best of our knowledge, the highest fullerene binding affinity was observed in a Ir(III) metalloporphyrin derivative reported by the Aida group, which showed $K_{assoc} = 1.3 \times 10^8$ M^{-1} in 1,2-dichlorobenzene and $K_{assoc} > 10^9$ M^{-1} in benzene for C_{60}.[44] The Anderson group also reported a cyclic porphyrin trimer with an impressive high affinity for fullerenes with $K_{assoc} = 2 \times 10^6$ for C_{60} and $K_{assoc} = 2 \times 10^8$ for C_{70} in toluene.[42] However, it should be noted that the previously reported best performers are all metalloporphyrins and release of the fullerene guest and regeneration of the valuable host would be difficult, thus making the fullerene separation/purification based on these host molecules impractical.

It is noteworthy that the cage **COP-5**, containing nonmetalated porphyrin moieties, shows a high binding affinity with C_{70}, which is 3 orders of magnitude higher than that with C_{60}. Such a remarkable selectivity in the binding of C_{70} over C_{60} is unprecedented and is significantly higher than those of previously reported fullerene receptors, which are usually lower than 10, with highest being around 100, reported by the Anderson group.[42] In order to further explore the potential of **COP-5** in fullerene separation, we used a mixture of two fullerene guests in a binding competition test. As expected, selective complexation of **COP-5** with C_{70} in a C_{60}-enriched fullerene mixture was observed. When **COP-5** was mixed with a solution of C_{60} (91 mol %) and C_{70} (9 mol %) in toluene, the **COP-5** selectively bound with C_{70} to form C_{70}@**COP-5**. The ^{1}H NMR spectrum clearly shows the major set of proton signals corresponding to C_{70}@**COP-5** (Figure S6).

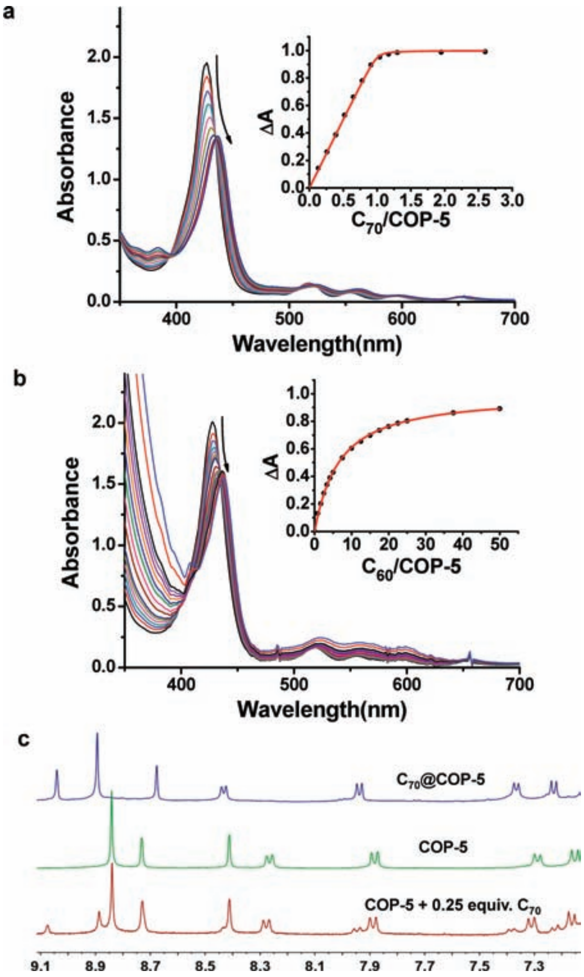


Figure 3. **COP-5**—fullerene (C_{70} and C_{60}) binding studies. (a) UV−vis absorption spectra of **COP-5** (2.0 μM) in toluene in the presence of various amounts of C_{70} (0 → 3 equiv) at 23 °C, while the concentration of **COP-5** was maintained constant. Inset: plot of $\Delta A_{428\ nm}$ vs equivalents of C_{70} added. (b) UV−vis absorption spectra of **COP-5** (2.0 μM) in toluene in the presence of various amounts of C_{60} (0 → 50 equiv) at 23 °C, while maintaining the concentration of **COP-5** constant. Inset: plot of $\Delta A_{428\ nm}$ vs equivalents of C_{60} added. The association constants modeled with a 1:1 equilibrium are $K_{C70@COP\text{-}5} = 1.5 \times 10^8$ M^{-1} ($\Delta G = -11.2$ kcal/mol) for C_{70}@**COP-5** and $K_{C60@COP\text{-}5} = 1.4 \times 10^5$ M^{-1} ($\Delta G = -7.0$ kcal/mol) for C_{60}@**COP-5**. (c) ^{1}H NMR spectra of C_{70}@**COP-5** (blue), **COP-5** (green), and a mixture of **COP-5** with 0.25 equiv of C_{70} (red) in toluene-d_8.

Computational calculations on the energy-minimized structures of **COP-5** and **COP-5**—fullerene complexes provide further insight into the preferential binding of C_{70} versus C_{60}. The Amber 11.0 molecular dynamics program package[45] was used to optimize the structure of the fullerene, the cage, and the cage—fullerene binding complexes. The general Amber force field (GAFF field)[46] was used with the charge parameters computed by the AM1-BCC method.[47] The computational modeling study (Figure 2) reveals that the heights of **COP-5** are slightly increased to 12.1−12.2 Å in C_{60}@**COP-5** and C_{70}@**COP-5** from the initial 11.9 Å in the unoccupied **COP-5**, while the diameters of the cavities are decreased slightly to 17.6−17.8 Å from 18.3 Å. Owing to the high degree of shape persistency of the cage **COP-5**, the size and geometry of the cage do not change much upon fullerene encapsulation. In both C_{60}@**COP-5** and C_{70}@**COP-5** complexes, the shortest atom-to-atom distances between porphyrin panels and fullerenes are similar and are close to 3.2 Å, which leads to an appreciable $\pi-\pi$ interaction in both complexes. It is known that fullerenes also have CH−π interactions with host molecules, and the favored distance for CH−π interactions is around 2.9 Å.[48,49] This type of CH−π interactions also exists in fullerene−**COP-5** complexes. The average distances between fullerenes and those carbazole CH protons, which are pointing toward the inside cavity of the cage, in C_{60}@**COP-5** and C_{70}@**COP-5** are around 3.5 and 3.1 Å, respectively. Since the distance for CH−π interactions in C_{70}@**COP-5** (3.1 Å) is closer to the known favored distance 2.9 Å, the CH−π interactions are presumably stronger in C_{70}@**COP-5** compared to those in C_{60}@**COP-5**. Considering the rigid, noncollapsible nature of the cage **COP-5**, it would be difficult for the cage to adjust the distance between the top and bottom porphyrin panels to achieve stronger binding interactions with fullerene guests. The nonperfect match between the sizes of host and guest would result in a less favored binding interaction of **COP-5** with C_{60}. Given the conformational rigidity, the slight difference in the distance between the host and guest could lead to a large difference in their stabilization energy (4.2 kcal/mol, calculated from the binding constants of C_{70}@**COP-5** and C_{60}@**COP-5**) gained through the host−guest binding interaction and could be the origin of the remarkable binding selectivity.

Intrigued by the impressive differentiating capability of cage **COP-5** in binding C_{60} and C_{70}, and to achieve a clean and efficient separation of C_{70} from fullerene mixtures, we then directed our efforts to the investigation of controlled release of fullerene guests and regeneration of host cage molecules. Since porphyrin−fullerene interactions are based on the attraction between electron-rich (porphyrin) and electron-poor (fullerene) moieties, their interactions could be tuned by changing the electronic properties of either one of them. Unlike the case for metalloporphyrins, the electron density of the porphyrin free base can be easily reduced by simple protonation, and thus the porphyrin−fullerene interactions could be weakened. We envisioned dissociation and release of the guest molecules, and regeneration of the **COP-5** can be realized by simply tuning the pH of the media. Trifluoroacetic acid (TFA) and triethylamine (TEA) were used as the acid and base stimuli. Upon addition of excess TFA (100 equiv) to a solution of C_{70}@**COP-5** (or C_{60}@**COP-5**) in toluene, protonation of the porphyrin ring occurred, and consequently, complete release of the fullerene molecules was observed, as evidenced by the disappearance of the ^{1}H NMR signals corresponding to C_{70}@**COP-5** (or C_{60}@**COP-5**) and the appearance of a new set of signals corresponding to the protonated **COP-5** with an empty cavity. However, the subsequent addition of 100 equiv of triethylamine (TEA) to the above mixture neutralized the porphyrin ring and restored the binding interaction between **COP-5** and fullerenes. As a result, the ^{1}H NMR spectrum of C_{70}@**COP-5** (or C_{60}@**COP-5**) was regenerated, indicating the reversibility of the association/dissociation process. Such a reversible association/dissociation triggered by acid/base stimuli was also confirmed by monitoring the process with UV−vis absorption spectra (Figure 4). In brief, we observed almost the identical UV−vis absorption spectra when we protonated **COP-5** and C_{70}@**COP-5** (or C_{60}@**COP-5**) with 100 equiv of TFA, which indicates the complete dissociation of the cage−fullerene complex upon protonation of the porphyrin-free base center. The regeneration of C_{70}@**COP-5** (or C_{60}@**COP-5**) complex by the addition of 100 equiv of TEA to the mixture of protonated **COP-5** and free C_{70} was evidenced by a UV−vis absorption almost identical with that of the pure C_{70}@**COP-5** (or C_{60}@**COP-5**). The association−dissociation process can be repeated in several cycles without leading to any noticeable change in the absorbance by the alternating addition of TFA and TEA (Figure 4, inset), thus showing that the cage−C_{70} binding is a highly efficient, robust, and fully reversible process.

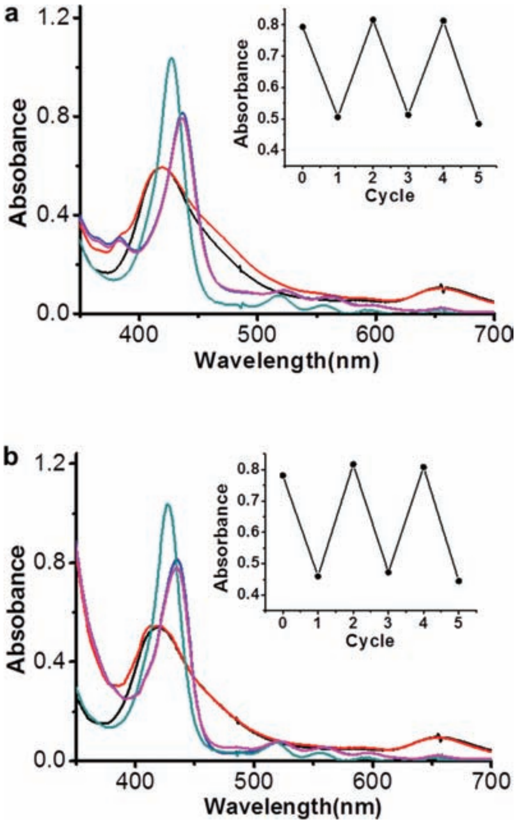


Figure 4. pH-Driven reversible **COP-5**−fullerene binding. **COP-5** concentration was 1.0 × 10^{-6} M in toluene. (a) UV−vis spectra of the free **COP-5** (cyan), of C_{70}@**COP-5** (magenta), after the addition of 100 equiv of TFA to **COP-5** (black), after the addition of 100 equiv of TFA to C_{70}@**COP-5** (red), and after the addition of 100 equiv of TFA, followed by the subsequent addition of 100 equiv of TEA to C_{70}@**COP-5** (blue). Inset: plot of absorption at 437 nm vs repetitive association−dissociation cycles. (b) UV−vis spectra of the free **COP-5** (cyan), of C_{60}@**COP-5** (magenta), after the addition of 100 equiv of TFA to **COP-5** (black), after the addition of 100 equiv of TFA to C_{60}@**COP-5** (red), and after the addition of 100 equiv of TFA followed by the subsequent addition of 100 equiv of TEA to C_{60}@**COP-5** (blue). Inset: plot of absorption at 436 nm vs repetitive association−dissociation cycles.

Fullerene purification has attracted great attention since the 1990s, and people are still actively pursuing a highly efficient and easy process for fullerene separations.[42,50−52] One of the most

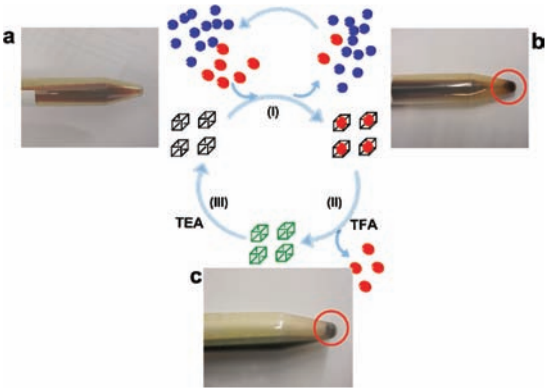


Figure 5. Schematic presentation of the C_{70} isolation process. Step I: to a solution of C_{60} and C_{70} mixture (C_{60}/C_{70} = 10/1, molar ratio) in CS_2 was added a small amount of **COP-5** (equal to or less than the stoichiometric amount of C_{70}), resulting in the favored formation of C_{70}@**COP-5**. After the unbound free fullerenes were separated by precipitation in $CHCl_3$ (precipitates shown in (b)), cage−fullerene complexes (mostly C_{70}@**COP-5**) were collected in the solution phase. Step II: upon the addition of 100 equiv of TFA to the solution collected in step II, fullerene guest molecules (mostly C_{70}) were released as black precipitates and removed to complete one cycle of the isolation process (shown in (c)). Step III: regeneration of **COP-5** was accomplished by the addition of 100 equiv of TEA to the above solution.

common methods aiming at the separation of fullerenes of specific size is based on selective complexation of a particular fullerene from an organic solution of fullerene mixtures.[27,53] However, the difficult release of fullerenes and regeneration of hosts have greatly impeded the practical applications of this method.[52] Given the over 1000 times stronger binding interactions of **COP-5** with C_{70} over C_{60}, and the reversible nature of this host−guest binding triggered by pH, we envisioned that the separation of C_{70} from C_{60} can be achieved with a simple "selective complexation−decomplexation" process (Figure 5). As a proof of concept, we used a C_{60}-enriched C_{60}/C_{70} mixture in the separation study. Carbon disulfide was chosen as the solvent for the encapsulation step, since both C_{60} and C_{70} have good solubility in CS_2. A mixture of **COP-5** and C_{60}/C_{70} in CS_2 was sonicated for 30 s, and the solvent was evaporated. The residue was then dispersed in chloroform. Since fullerenes have very limited solubility in $CHCl_3$, free fullerenes remained as precipitates. The solution phase, which was composed of mostly C_{70}@**COP-5**, was separated from the insoluble fullerene mixtures by centrifugation. Further acidifying the C_{70}@**COP-5** complex with excess TFA followed by sonication (5 min) released C_{70} as a black precipitate, which allowed easy removal by centrifugation. The cage **COP-5** was then regenerated by neutralization with TEA and was recycled for the next round of fullerene separation. The UV−vis absorption showed that the C_{70} abundance of the fullerene mixture increased significantly (∼9-fold increase) from the initial 9 mol % to 79 mol % after only one cycle of separation (Figure S1, Supporting Information). This result clearly demonstrates the simplicity and high efficiency of such a fullerene separation approach by using shape-persistent molecular cages as selective receptors. The "selective complexation−decomplexation" strategy presented here would greatly facilitate the purification of these intriguing graphitic materials and promote their wide application in organic photovoltaics, polymer electronics, and biopharmaceuticals.

■ CONCLUSIONS

In summary, we have successfully synthesized the shape-persistent porphyrin-based molecular cage **COP-5** via efficient alkyne metathesis, which represents the first time such a reversible dynamic covalent approach has been used to construct 3-D molecular cages. Such a DCC approach complements the existing dynamic assembly strategies for the construction of large complex, molecular architectures and would be particularly beneficial for the synthesis and study of noncollapsible, shape-persistent covalent cage molecules. The obtained cage **COP-5** shows an unprecedented high selectivity (>1000/1) in binding of C_{70} over C_{60}. The pH-driven reversible association and dissociation of fullerene−cage complexes enables an easy and efficient separation of C_{70} from a fullerene mixture. Currently the binding behavior of such porphyrin-based molecular cages with higher fullerenes and further assembly of these cage−fullerene complexes into highly ordered 3-D architectures are being investigated in our laboratory and will be reported in due course.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Text and figures giving experimental details, UV−vis spectroscopic data, computation methods, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

This work was supported by the National Science Foundation (Nos. DMR-1055705 and CBET-1033255) and the Defense Advanced Research Projects Agency (DARPA). We thank Dr. Kuthanapillil Jyothish for helpful discussions, Dr. Yinghua (Alice) Jin for help with manuscript writing, and Dr. Richard Shoemaker for NMR assistance. This research used the capabilities of the National Renewable Energy Laboratory Computational Science Center, which is supported by the Office of Energy Efficiency and Renewable Energy of the U.S. Department of Energy under Contract No. DE-AC36-08GO28308.

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