Theoretical Prediction on a Novel Reduction-Responsive Nanoring Having a Disulfide Group for Facile Encapsulation and Release of Fullerenes C$_{60}$ and C$_{70}$

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**ABSTRACT:** In this work, a novel reduction-responsive disulfide bond-containing cycloparaphenylenes nanoring molecule (DSCPP) with a pyriform shape has been designed. In addition, the interactions between the designed nanoring (host) and fullerenes C$_{60}$ and C$_{70}$ (guests) were investigated theoretically at the M06-2X/6-31G(d,p) and M06-L/MIDI! levels of theory. By analyzing geometric characteristics and host–guest binding energies, it is revealed that the designed DSCPP is an ideal host molecule of guests C$_{60}$ and C$_{70}$. DSCPP presents excellent elastic deformation during the encapsulation of C$_{60}$ and C$_{70}$. The high binding energies suggest that the formation of the two host–guest complexes is thermodynamically spontaneous. In addition, the frontier molecular orbital (FMO) features and intermolecular weak interaction region between DSCPP and fullerene guests are discussed to further understand the structures and properties of the DSCPP fullerene systems. Finally, the ring-opening mechanism of the DSCPP under reduction conditions is investigated.

1. INTRODUCTION

Host–guest chemistry plays a significant role in the development of advanced supramolecular materials.$^{1-3}$ Currently, considerable interest has been focused on the host–guest systems formed with nanoring hosts and fullerene guests because of their good selectivity$^{4-8}$ and high efficiency.$^{9-15}$ On the other hand, the facile release of encapsulated guest molecules from the nanoring host molecule is necessary for the subsequent delivery or utilization of the captured fullerene guest molecules.

Generally, the captured guest molecule can be released from the host by external stimulation of a physical field or by addition of secondary guests in a guest-exchange process. Kishi et al.$^{16}$ designed and prepared a novel coordination-molecular tube (CMT) by using two Ag(I) ions as metal hinges for a curved bispyridine ligand. This kind of CMT can bind fullerene C$_{60}$ at room temperature and subsequently release the captured C$_{60}$ upon UV–vis irradiation. In our previous work,$^{17,18}$ novel photo-responsive nanoring molecules have been designed by introducing azobenzene groups onto the conventional cycloparaphenylenes carbon nanorings (CNRs). By using theoretical calculations, they were predicted to be the ideal hosts for the inverse encapsulation and release of fullerene C$_{60}$ and C$_{70}$ guests under photoirradiation with different wavelengths. Recently, Jasti and co-workers$^{19}$ reported the design and synthesis of two cycloparaphenylenes containing thermally stable cis-azobenzene moieties in the conjugated framework, their behavior upon irradiation, and computational results evaluating their potential as photo-switchable fullerene hosts.

Treatment with ancillary reagents (metal ions, acid, or base) can also prompt the guest to be released as a result of structural rearrangement of the host molecule.$^{20,21}$ Using Hg$^{II}$ ions and bispyridyl dianthracene ligands, Kishi et al.$^{22}$ successfully prepared a coordination-driven supramolecular capsule and tube. Only the capsule-like structure can encapsulate fullerenes C$_{60}$ and C$_{70}$. Interestingly, a subsequent capsule-to-tube transformation can release the bound guest fullerenes in response to an external stimulus of Hg$^{II}$ ions. Excitedly, Yoshizawa’s group$^{23}$ developed a new macrocycle, which is composed of four pH-responsive acridinium panels connected alternately by metaphenylene and meta-biphenyl spacers. This polyaromatic macrocycle can provide a pH-responsive open/closed switching function within the framework and a binding capability toward long hydrophilic molecules with lengths longer than that of the cavity. Moreover, it has an ability to release the bound molecules in water at ambient temperature.

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Very recently, a new type of acid-labile acyclic cucurbit[n]uril (CB[n]) molecular container host has been presented by Liu and Ma’s group that can degrade and release the encapsulated guest at accelerated rates under mildly acidic conditions (pH 5.5–6.5). As a typical reduction-responsive group, disulfide bonds have been frequently utilized as reductively degradable linkages and designed for artificial vehicles. Recently, functionalized water-soluble cyclophanes having disulfide moieties within the macrocyclic skeleton as reduction-responsive degradable hosts have been reported, and the entrapped guest molecules by cyclophanes hosts can be successfully released into the bulk phase by treatment with dithiothreitol (DTT). On the other hand, such as fullerene.4,7 host for a given responsive degradable hosts have been reported, and the molecules (so-called carbon nanorings (CNRs)) in which cycloparaphenylenes (π-conjugated molecule with a convex surface, such as fullerene.4,7–9 On these grounds, we became interested in the design of a cleavable and disulfide-linkage-containing CPP host (DSCPP) and exploration of the interaction between the designed host and fullerenes C60 and C70. Figure 1 shows our strategy on the reduction-responsive release of fullerene guest molecules. After the reduction of disulfide bonds of DSCPP, DSCPP becomes a line-shape structure which no long has guest-binding ability because of its unmatching-in-shape with the fullerenes, and accompanies the release of the entrapped fullerene molecules. Generally, the approach for obtaining a synthetic molecule consists of employing computational chemistry methods to design a desired host followed by experimental optimization of its synthesis. It is expected that the systems explored theoretically in this work are useful for future experimental studies and feasible in the laboratory.

2. COMPUTATIONAL METHODS

In this work, the density functional of M06-L and M06-2X, which include medium-range correlation energy and provide accurate descriptions of the noncovalent π–π interactions, are employed for the study of DSCPP-fullerene complexes. The ability of this density functionals to predict and explain the supramolecular chemistry of carbon nanorings at van der Waals distances is very encouraging because density functional theory can be applied economically to predict and analyze large structures and can therefore be used conveniently for supramolecular design.

All the geometric optimizations were performed at the M06-L/MIDI! and M06-2X/6-31G(d,p) levels of theory, and no symmetry constraints were applied during optimizations. Then, harmonic frequency analyses were performed at the same level to confirm whether those structures were local minima or transition states on the potential energy surface. Basis set superposition errors (BSSEs) have been corrected by the counterpoise method when the binding energies (ΔEbind) were calculated. Additionally, we also investigated the ring-opening mechanism of DSCPP under the reduction of the DTT agent at the B3LYP/6-31G(d,p) level of density functional theory. The visualized studies of intermolecular noncovalent interaction regions between host and guest were performed using the Multiwfn program. All other calculations were performed with the Gaussian 09 program.

3. RESULTS AND DISCUSSION

3.1. Geometric Configurations

As mentioned before, we designed a novel nanoring in which a disulfide group linked 10 paraphenylenes units in a cyclic manner. Namely, this novel nanoring host composed of 10 phenyls and one disulfide linkage. For the sake of simplicity and clarity in both text and table headings, the designed nanoring host is abbreviated to DSCPP, and the optimized chemical structure is shown in Figure 2.

![Figure 2. Optimized chemical structures of the DSCPP host: (a) side view and (b) top view (H atoms are omitted for clarity).](https://dx.doi.org/10.1021/acsomega.0c03788)
guest so as to decrease the energies of the host–guest systems, although it will cause energy losses of the host DSCPP energy.

It can be seen from Table 1 that the $d_{cc}$ (the distance between two centers of the host and guest) of DSCPP$\supset$C$_{60}$ is rather small (0.04 and 0.01 Å at M06-2X/6-31G(d,p) and M06-L/MIDI!, respectively), indicating that the centers of the DSCPP host and that of the fullerene C$_{60}$ guest are nearly overlapping. In other words, the fullerene guest can deeply embed into the cavity of the DSCPP and form an inclusion host–guest complex (DSCPP$\supset$C$_{60}$). Obviously, the $d_{cc}$ and π–π interaction regions are closely related, and the shorter $d_{cc}$ means the stronger van der Waals attractive interactions between the host nanoring and the guest fullerene. Although the $d_{cc}$ of the DSCPP$\supset$C$_{70}$ is larger than that in DSCPP$\supset$C$_{60}$ (it is not larger than 0.8 Å (M06-2X/6-31G(d,p)), which is only ~10% of the long axis of C$_{70}$), DSCPP$\supset$C$_{70}$ can also be regarded as an inclusion configuration. The dipole of free DSCPP is about 1.4 Debye. It is well known that the dipole of fullerene C$_{60}$ or C$_{70}$ is zero because of their high symmetry.

Table 1. Geometric Parameters and Dipole Moments of Free Host DSCPP and DSCPP–Fullerene Complexes

| species         | $d_{cc}$ (Å) | long axis (Å) | short axis (Å) | aspect ratio | $R_d$ (%) | $\theta$ (°)$^d$ | dipole (Debye) |
|-----------------|--------------|---------------|----------------|--------------|-----------|----------------|----------------|
| M06-2X/6-31G(d,p) |              |               |                |              |           |                |                |
| free DSCPP      | 17.30        | 12.60         | 1.373          | 32, 33, 34, 35, 36, 37 | 1.38      |
| DSCPP$\supset$C$_{60}$ | 0.04 | 16.70         | 1.253          | 24, 27, 28, 31, 32, 33, 35 | 2.00 |
| DSCPP$\supset$C$_{70}$ | 0.79 | 16.61         | 1.240          | 27, 28, 30, 31, 32, 33 | 1.97 |
| M06-L/MIDI!     |              |               |                |              |           |                |                |
| free DSCPP      | 17.58        | 12.24         | 1.436          | 25, 26, 27, 28, 30 | 1.47 |
| DSCPP$\supset$C$_{60}$ | 0.01 | 16.86         | 1.276          | 20, 21, 23, 24, 25, 26, 27, 31 | 1.90 |
| DSCPP$\supset$C$_{70}$ | 0.29 | 16.52         | 1.220          | 18, 21, 22, 23, 24, 25, 31, 34 | 1.94 |

$^a$d$_{cc}$ is defined as the distance between the two centers of host and guest. $^b$Long axis and short axis are defined in Figure 1. $^c$The ring deformation ratio) = (aspect ratio of free host – aspect ratio of host in complex)/aspect ratio of free host. $^d$θ is defined as the dihedral angles between two paraphenylenes of the host DSCPP.

Figure 3. Space filling models (top view and side view) of (a) the DSCPP$\supset$C$_{60}$ and (b) DSCPP$\supset$C$_{70}$ host–guest complexes (H atoms are omitted for clarity). Carbon and sulfur atoms of the host are shown in gray and light green, respectively.

Figure 4. Interfacial distances ($d_i$) between DSCPP host and guests of (a) DSCPP$\supset$C$_{60}$ and (b) DSCPP$\supset$C$_{70}$.

Energy features and thermodynamic properties of the host–guest interaction are very valuable and important for a deep understanding of the nanoring–fullerene systems. Because M06-2X is better than M06-L for describing the energy of the noncovalent systems including π–π interactions, the BSSE-corrected binding energy ($\Delta E_{*}$), deformation energy of the hosts ($E_{di}$), and the changes of Gibbs free energy ($\Delta G$), enthalpy ($\Delta H$), and entropy ($\Delta S$) at 298.150 K and 1.0 atm of the formation of DSCPP$\supset$C$_{60}$ and DSCPP$\supset$C$_{70}$ obtained at the M06-2X/6-31G(d,p) level of theory are listed in Table 2. The $\Delta E_{\text{CP}}$ in DSCPP$\supset$C$_{70}$ is 118.64 kJ mol$^{-1}$, and that in DSCPP$\supset$C$_{60}$ is not more than 92.4 kJ mol$^{-1}$, which is smaller than that in the [9]-cycloparaphenylene$\supset$C$_{60}$ ([9]CPP $\supset$ C$_{60}$) system$^{31}$ by 42.72 kJ mol$^{-1}$. This indicates that C$_{60}$ should be more strongly bound in the cavity of DSCPP than C$_{60}$, which well coincides with the [6]paraphenyleneacetylene$\supset$fullerene (C$_{60}$ and C$_{70}$) host–guest systems, and well consistent to the result of what the $d_i$ indicates.
The M06-2X/6-31G(d,p) Level of Theory

the two present complexes decrease by 250.48 and 270.17 J

the formation of the host

Because of the number of free molecules decreases by half after

binding processes of C60 and C70 by DSCPP in vacuum are

Enthalpy (ΔH), and Entropy (ΔS) at 298.150 K and 1.000 atm of the Formation of DSCPP⊃C60 and DSCPP⊃C70 Obtained at the M06-2X/6-31G(d,p) Level of Theory

| host–guest | ΔE_{cp} (kJ·mol⁻¹) | ΔG (kJ·mol⁻¹) | ΔH (kJ·mol⁻¹) | ΔS (J·mol⁻¹·K⁻¹) | E_{ij} (kJ·mol⁻¹) |
|------------|-------------------|---------------|---------------|-------------------|-----------------|
| DSCPP⊃C60  | 92.31             | -66.46        | -140.41       | -250.48           | 7.48            |
| DSCPP⊃C70  | 118.64            | -76.38        | -304.12       | -270.17           | 9.50            |

Table 2. BSSE-Corrected Binding Energy (ΔE_{cp}), Deformation Energy of Host (E_{ij}), and Changes of Gibbs Free Energy (ΔG), Enthalpy (ΔH), and Entropy (ΔS) at 298.150 K and 1.000 atm of the Formation of DSCPP⊃C60 and DSCPP⊃C70 Obtained at the M06-2X/6-31G(d,p) Level of Theory

It is noted that the energy losses caused by deformation of the host (E_{ij}) are only 7.48 and 9.50 kJ·mol⁻¹ after the formation of the DSCPP⊃C60 and DSCPP⊃C70, respectively, although significant deformation of DSCPP occurred (see Table 1), suggesting that the designed nanoring DSCPP really has excellent elastic properties. Furthermore, in the case of DSCPP⊃C70, the deformation energy of DSCPP is only larger than that of DSCPP⊃C60 by 2.02 kJ·mol⁻¹. Although the smaller deformation of the host is beneficial to the encapsulation of the guest, the ΔE_{cp} of DSCPP⊃C70 is larger than that of DSCPP⊃C60 by 26.32 kJ·mol⁻¹. Therefore, the designed host DSCPP molecule can selectively encapsulate C70 based on an obvious thermodynamic advantage.

From the thermodynamic properties of the two host–guest systems listed in Table 2, it can be seen that the relative orders of the ΔG and ΔH of the DSCPP⊃C60 and DSCPP⊃C70 complexes are all well consistent with those of ΔE_{cp}. The binding processes of C60 and C70 by DSCPP in vacuum are exergonic and spontaneous, with ΔG values of -66.46 and -76.38 kJ·mol⁻¹ for DSCPP⊃C60 and DSCPP⊃C70, respectively, which means that the deformation of DSCPP⊃C70 is more thermodynamically favorable than that of DSCPP⊃C60. Because of the number of free molecules decreases by half after the formation of the host–guest complexes, the entropies of the two present complexes decrease by 250.48 and 270.17 J·mol⁻¹·K⁻¹. According to the ΔH values, the host–guest binding reactions are found to be exothermic. All the thermodynamic information indicates that the binding of C60 and C70 by the host DSCPP in vacuum is enthalpy-driven and entropy-opposed.

3.3. Frontier Orbital Features and Weak Interaction Regions. Figure 5 shows the compositions and energy levels of the highest occupied molecular orbital (HOMO) of the DSCPP⊃C60 and DSCPP⊃C70 host–guest complexes. It is known that molecular orbitals are not physical observables. However, the properties of the frontier orbitals are often closely related to the electron structures and behaviors. Generally speaking, if the frontier orbitals are extended across the two fragments of the complex, charge transfer (CT) between the host and guest is suggested; otherwise, CT is excluded. As shown in Figure 5, the HOMOs and LUMOs of the complexes are completely localized on the host ring and fullerene guests, respectively. That is, the HOMOs of the complexes are closely related to the host moiety but independent of the guest moiety, and the LUMOs are closely related to the guest moiety but independent of the host moiety, indicating the lack of charge transfer between the host and guest.

Notably, the energies of the HOMOs of the two host–guest complexes are nearly similar to that of the free host DSCPP, but the energies of the LUMOs of the two complexes are obviously lower than those of the free guests C60 and C70. Moreover, the HOMOs of the complexes completely derive from the HOMO of the host DSCPP, and the LUMOs of the two complexes completely derive from the LUMO of the guest fullerene C60 and C70. Namely, the LUMO level of the free C60 and C70 can be raised by noncovalent binding with the nanoring, which may be very important to the fullerene as a promising potential electron-accepting component in high-performance solar cells.

The frontier orbital gaps of the two complexes are much smaller than that of the free host DSCPP; meanwhile, they are also smaller than those of free C60 and C70, suggesting that the electrons on the HOMO of the host–guest complexes are more active than those of the free host or guest. Additionally, although the ΔE_{cp} in DSCPP⊃C70 is larger than that in DSCPP⊃C60 by 26.32 kJ·mol⁻¹, the frontier orbital gap of DSCPP⊃C70 is smaller than that of DSCPP⊃C60 by 0.18 eV, indicating that DSCPP⊃C70 is the more thermodynamically stable host–guest complex, but DSCPP⊃C60 is more chemically stable than DSCPP⊃C70.

Intermolecular weak interaction regions can be detected and visualized in real space based on the electron density ρ and its derivatives, viz., the reduced density gradient (RDG) coming from the electron density (ρ(r)) and its first derivative (RDG(r) = 1/(2(3π)^1/3)∇(ρ(r))) and the second largest eigenvalue (λ_s) of the Hessian matrix of electron density functions. The visualized weak interaction regions in the DSCPP⊃C60 and DSCPP⊃C70 host–guest complexes are shown in Figure 6a,b, respectively. The region marked by green accompanied by light brown around C60 and C70 can be identified as the weak interaction region. In these regions, they mirror the π–π van der Waals interaction between the host and guest, and this also provides evidence for the excellent shape and size matching between the DSCPP nanoring host and C60 or C70 fullerene guests. Additionally, it is easy to see that the weak interaction regions in the present two complexes are not in closed band shapes, which can be attributed to the significant staggered phenyls close to the S–S group.

Figure 5. Compositions and energy levels of frontier orbital of the DSCPP⊃C60 and DSCPP⊃C70 host–guest complexes.
Furthermore, the scatter graphs of the DSCPP$\supset$C$_{60}$ and DSCPP$\supset$C$_{70}$ host–guest complexes are plotted in Figure 6c,d. The spike of the RDG function located in the region where the values of $\lambda_2 \rho$ are very small and fall near zero corresponds to van der Waals interaction, and the spikes corresponding to steric repulsion is located in more positive values of the $\lambda_2 \rho$ function. As shown in Figure 6c,d, the spikes where $\lambda_2 \rho$ falls into $-0.006$ to $0.006$ a.u. are correlated with the $\pi - \pi$ van der Waals interactions between DSCPP and fullerenes, and the spikes where $\lambda_2 \rho$ falls into values near $-0.01$ and $0.01$ a.u. correspond to intramolecular C−H···S weak hydrogen bonds and C−H···H−C interactions of the host DSCPP ring, respectively.

3.4. Ring-Opening Mechanism of the DSCPP. For further illustrating the possibility of the encapsulated fullerene being released, the ring-opening mechanism of the host DSCPP via reduction of the DTT agent is investigated at the B3LYP/6-31G(d,p) level of density functional theory. It is known that DTT is a strong reducing agent, and it is in action only when the pH value is higher than 7 because just the $-S^-$ group rather than $-SH$ has reduction reactivity. Accordingly, $HSCH_2CH(OH)CH(OH)CH_2S^-$ is used as the attacking agent for the ring opening of the substrate (DSCPP).

Figure 7 shows the relative potential energy diagram along the reaction pathway. It is clear that there is a precursor at the beginning of the reaction. Consequently, it then changes via a transition state (TS1) to an intermediate (INT) and then via another transition state (TS2, a pre-TS) to finally arrive at the complete ring-opened structure (P). In addition, the corresponding structures and related bond length involving ring opening are presented in Figure 8. The potential energies of all the transition states and intermediate are smaller than the reactants (DSCPP$ + $DTT$^-$). Moreover, it is noted that the active energies of the whole reaction steps are small, and the potential energy significantly decreases by 244.47 kJ·mol$^{-1}$ after ring opening occurred. Thus, it is very easy to carry out

Figure 6. Visualized weak interaction regions of the (a) DSCPP$\supset$C$_{60}$ (b) DSCPP$\supset$C$_{70}$ host–guest complexes (top view (left) and side view (right)). Scatter graphs of the (c) DSCPP$\supset$C$_{60}$ and (d) DSCPP$\supset$C$_{70}$ host–guest complexes.

Figure 7. Relative potential energy diagram along the reaction pathway.
the ring opening of the free host DSCPP by reduction of \(-S-S\) group either thermodynamically or kinetically.

For the DSCPP\(\supset C_{60}\) or DSCPP\(\supset C_{70}\) host–guest systems, it is believed that it is also easy for the host DSCPP to undergo ring opening under the same reduction conditions because the DSCPP is only noncovalently bound to fullerenes and the reactivity of the \(-S-S\) group would be the same to that of free DSCPP. That is, the guest fullerenes could be facilely released from the cavity of the host DSCPP via the reduction of the \(-S-S\) group.

4. CONCLUSIONS

After the reduction of disulfide bonds of DSCPP, DSCPP becomes a line-shape structure which no long has guest-binding ability because of its unmatching-in-shape with the fullerenes, and accompanies the release of the entrapped fullerene molecules. Generally, theoretical calculation and prediction are very useful and important before experimentally obtaining a desired functional molecule. Based on this consideration, we designed the host DSCPP and explored the host–guest interaction between the designed DSCPP and fullerenes \(C_{60}\) and \(C_{70}\) by means of density functional theoretical methods. It is revealed that the designed host DSCPP has a pear shape with an aspect ratio of \(\sim 1.37\), long axis of 17.30 Å, and short axis of 12.60 Å at the M06-2X/6-31G(d,p) level. Moreover, the DSCPP has excellent elastic deformation properties, which are very important to the strong induced-fit host–guest binding. The high binding energies suggest that both DSCPP\(\supset C_{60}\) and DSCPP\(\supset C_{70}\) are stable host–guest complexes, and the guest \(C_{70}\) is more strongly encapsulated than \(C_{60}\) in the gas phase. The thermodynamic properties indicate that the formation of the two host–guest complexes is thermodynamically spontaneous. Moreover, the ring-opening of the free host DSCPP by reduction of the \(-S-S\) group is very easy to carry out either thermodynamically or kinetically. Namely, the guest fullerenes could be facilely released from the cavity of host DSCPP via the reduction of the \(-S-S\) group. We hope that the synthesis of the investigated disulfide-containing nanoring host and the release of fullerene guests under reducing conditions, such as intracellular environments, are future subjects of interest to be carried out.

Figure 8. Structures of the transition states, intermediate, and product in the ring-opening process.
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Notes
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