

Computational characterization and modeling of buckyball tweezers: density functional study of concave–convex $\pi \cdot \cdot \pi$ interactions†

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The geometries and binding energies of a recent buckyball tweezers ($C_{60}H_{28}$) and its supramolecular complexes are investigated using recently developed density functionals (M06-L and M06-2X) that include an accurate treatment of medium-range correlation energy. The pincer part of the tweezers, corannulene, has a strong attractive interaction with C_{60} . However, due to the entropy penalty, the calculated gas-phase free energy of association of the $C_{60}@$ corannulene supramolecule is positive $3.5 \text{ kcal mol}^{-1}$; and this entropy penalty explains why it is difficult to observe $C_{60}@$ corannulene supramolecule experimentally. By using a π -extended tetrathiafulvalene (TTF), in particular 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (TTFAQ or $C_{20}H_{10}S_4$), as the pincer part, we modeled a new buckyball tweezers. The geometries and binding energies of the new buckyball tweezers and its supramolecular complexes are also calculated. Due to fact that the attractive interaction between TTFAQ and C_{60} is weaker than that between corannulene and C_{60} , the gas-phase binding free energy in the $C_{60}@C_{60}H_{32}S_8$ supramolecular complex is smaller than that in the $C_{60}@C_{60}H_{28}$ supramolecule. We also discuss solvent effects.

1. Introduction

One of the most vigorously developing technological research areas is the field of supramolecular chemistry,^{1–5} which involves the use of noncovalent interactions to assemble molecules into stable, well-defined structures called supramolecules. Most of the experimental studies of supramolecular self-assembly are carried out in the condensed phase since the gas-phase supramolecular experiments are technically too demanding; however, theoretical and computational studies can be more reliably carried out for gas-phase supramolecular systems, and such theoretical studies can shed light on intrinsic supramolecular structures and energetics, thus complementing the experimental investigations.

One of the important noncovalent driving forces for supramolecular assembly is that due to aromatic–aromatic interactions,^{6–22} but electronic structural descriptions of the supramolecular systems governed by aromatic–aromatic interactions are theoretically demanding. On one hand, semiempirical molecular orbital theory (*e.g.*, AM1, PM3, ...) is affordable but is not accurate for this type of noncovalent interaction. On the other hand, coupled cluster theory^{23,24} with single and double excitations and a quasiperturbative treatment of connected triple excitations (CCSD(T)) is usually reliable but is prohibitively expensive for large supramolecular complexes.

One promising intermediate approach is density functional theory (DFT), which has an excellent performance-to-cost ratio. However, the popular B3LYP density functional and most other older functionals are inaccurate for aromatic–aromatic interactions.^{25–28} One can improve the performance of DFT for aromatic–aromatic interactions by including a term specifically designed to model dispersion,^{29–48} typically involving empirical parameters and/or polarizabilities taken from experiment. Examples of such approaches are the DFT-dispersion (DFT-D) method (*e.g.*, TPSS-D,⁴² BLYP-D,³³ B97-D),^{40,46} Johnson and Becke's treatment based on the dipole moment of the exchange hole,^{36,38,48} and the long-range-corrected, Becke-88, one-parameter-progressive correlation plus Anderson–Langreth–Lundqvist correlation (LC-BOP + ALL) functional, which is based on a post-SCF correlation functional with a cutoff criterion and an empirical damping function. Such dispersion-corrected DFT methods have been shown to be very successful^{29–47} in various applications. Since dispersion energy (that part of the attractive van der Waals interaction attributable to correlated single excitations of the interacting particles) can be considered to arise from the correlation hole density,⁴⁹ another way to improve the performance of DFT is to optimize the exchange–correlation functionals for a broad range of properties including rare-gas dimers, aromatic–aromatic interactions, and other data sensitive to medium-range correlation energy, such as barrier heights. The M06-2X functional⁵⁰ developed in our group is based on this approach, and it accounts for dispersion-like interactions as part of the medium-range correlation energy. The M06-2X functional has been validated for $\pi \cdot \cdot \pi$ stacking;^{50,51} it has also been employed to study supramolecular assembly involving a nanoring²² and to study the dimerization of coronene as a model for interacting graphene sheets in multiwalled carbon-based assemblies.⁵¹

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Recently, a double-concave hydrocarbon tweezers-like buckycatcher (Fig. 1) has been synthesized by Sygula *et al.*⁵² This C₆₀H₂₈ tweezers has two corannulene pincers and a tetrabenzocyclooctatetraene tether. The experimental study of Sygula *et al.* has shown that this buckycatcher forms an inclusion complex with buckminsterfullerene C₆₀; the supramolecule is bound by the attractive concave–convex aromatic–aromatic interactions. The present paper presents the first computational study of this important new class of supramolecules.

In the present computational study we also modeled a new buckyball tweezers by using a π -extended tetrathiafulvalene (TTF) as the pincer part. The gas-phase structures, binding energies, and free energy of association will be presented as obtained from full geometry optimizations with DFT. We will also discuss the effect of solvation in the solvent, toluene, used for the experiments.

The paper is organized as follows. Section 2 describes the computational methods used in the present work. Section 3 presents results and discussion, and section 4 has concluding remarks.

2. Theoretical methods and computational details

2.1 Structures and energies

In the present study, two recently developed density functionals, namely M06-L⁵³ and M06-2X,⁵⁰ are employed for the study of supramolecular assembly. M06-L is a local functional for main-group thermochemistry, thermochemical kinetics, noncovalent interactions, and transition metal chemistry, whereas M06-2X is a hybrid one with 54% Hartree–Fock (HF) exchange in the functional. M06-L depends on the local spin density and their gradients and on the local spin kinetic energy densities; M06-2X also involves nonlocal Hartree–Fock exchange. Both functionals may be labeled as “meta” because they include kinetic energy density. M06-2X

is also labeled hybrid because of the dependence on Hartree–Fock exchange.

Two basis sets, namely MIDI! and DIDZ, are employed in the present study. MIDI!⁵⁴ is a well-balanced and economical double- ζ basis set, and DIDZ is a short name for the popular 6-31+G(d,p) basis set.⁵⁵

Since M06-L is a local meta functional, it is much faster than the hybrid M06-2X functional for geometry optimizations. For the prediction of the energetics in π – π interactions, M06-2X is more accurate than M06-L. Therefore the geometries of the hosts, guest, and supramolecules are optimized at the M06-L/MIDI! level of the theory, and the supramolecular binding energies are calculated at the M06-2X/DIDZ level of theory. We corrected basis set superposition error (BSSE) by the counterpoise approach.^{56,57} The BSSEs are listed in Table S1 of the ESI.† The zero-point-exclusive Born–Oppenheimer⁵⁸ gas-phase energy of association (including electronic energy and nuclear repulsion but not vibration or rotation) is called $\Delta E(g)$.

2.2 Free energies

Gas-phase free energies of association were calculated in the harmonic oscillator-rigid rotator approximation.⁵⁹ These calculations employed unscaled vibrational frequencies calculated by M06-L/MIDI!. Since the density functionals have been validated for electronic and zero point energies, the least reliable part of the free energy calculations is the thermal contribution from low-energy vibrational modes. In particular, the harmonic oscillator approximation overestimates the amount of phase space available to low-frequency, wide-amplitude motion. To assess (and, we hope, partially remove) the possible error in treating the low-frequency modes as harmonic oscillators, we repeated the calculations with all vibrational frequencies that are less than 100 cm⁻¹ raised to 100 cm⁻¹; this is called the anharmonic calculation. The harmonic gas-phase free energies of association are labeled $\Delta G_{298}^0(g, \text{harm})$ where the superscript denotes a standard state of 1 bar, and the subscript denotes temperature of 298.15 K. The anharmonic gas-phase association free energies are labeled $\Delta G_{298}^0(g, \text{anh})$.

We also present the free energy of the A + B → AB association reaction for the standard state of 1 M that is used in liquid solutions. This is given by

$$\Delta G_{298}^{1M}(g) = \Delta G_{298}^0(g) + \Delta G_{\text{conc}} \quad (1)$$

where $\Delta G_{\text{conc}} = -1.89 \text{ kcal mol}^{-1}$, which changes the standard state from 1 bar to 1 mole per liter.

2.3 Software

All DFT calculations were carried out using locally modified *Gaussian03*⁶⁰ and *NWChem*⁶¹ computer programs.

3. Results and discussion

3.1 Geometries and binding energies of the C₆₀@C₆₀H₂₈ and C₆₀@C₂₀H₁₀ supramolecules

The geometries of the host, guest, and supramolecules have been optimized at the M06-L/MIDI! level of theory. The

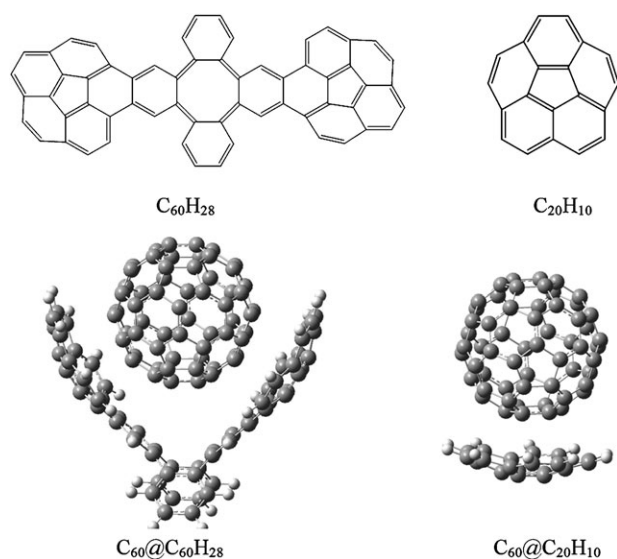


Fig. 1 Host molecules C₆₀H₂₈ and C₂₀H₁₀ and supramolecules C₆₀@C₆₀H₂₈ and C₆₀@C₂₀H₁₀.

optimized C_{60} geometry has 5/6 C–C bond lengths (*i.e.*, between a pentagon and a hexagon) of 1.4575 Å and 6/6 (between two hexagons) C–C bond lengths of 1.3956 Å. Both bond lengths compare very well to the gas-phase electron diffraction⁶² experimental bond lengths, 1.458 and 1.401 Å, respectively.

$C_{20}H_{10}$ is the corannulene molecule, and it is the pincer part of the $C_{60}H_{28}$ tweezers (see Fig. 1). The reported structures are the lowest energy minima from several orientations. In both supramolecular molecules, the 6-membered ring of C_{60} is stacking over the hub ring of corannulene. The ESI† provides additional views of the 3D structures of $C_{60}@C_{60}H_{28}$ to make the relative orientations more clear. The intermolecular distances and Born–Oppenheimer association energies for the $C_{60}@C_{60}H_{28}$ and $C_{60}@C_{20}H_{10}$ supramolecules are listed in Table 1.

Table 1 shows that the $C_{60}@C_{20}H_{10}$ supramolecule has a large equilibrium binding energy of 12.4 kcal mol^{−1}. Even though the gas-phase ionic complex $[C_{60}@C_{20}H_{10}]^+$ has been observed,⁶³ there is no experimental evidence for the supramolecular assembly between corannulene and fullerene. To explain this discordance, we calculated the free energy of association ΔG_{298}^0 of the $C_{60}@C_{20}H_{10}$ supramolecule at the M06-2X/DIDZ//M06-L/MIDI! level, where ΔE is calculated at the M06-2X/DIDZ level and zero-point energies and thermal energetic and entropic contributions are calculated at the M06-L/MIDI! level. We found that the calculated ΔG_{298}^0 is positive 5.4 kcal mol^{−1}, which means that there is a large entropy penalty for the association of C_{60} and $C_{20}H_{10}$ to make the $C_{60}@C_{20}H_{10}$ assembly. These results explain why it is difficult to experimentally detect the $C_{60}@C_{20}H_{10}$ supramolecule.

The calculated equilibrium binding energy of the $C_{60}@C_{60}H_{28}$ molecule is more than twice that in $C_{60}@C_{20}H_{10}$, and this result indicates that the penalty of the deformation of the tweezer is less than the noncovalent attractive interaction between C_{60} and the tether part of the tweezers. The gas-phase free energy of association ΔG_{298}^0 of the $C_{60}@C_{60}H_{28}$ is −6.7 kcal mol^{−1}. These results are in line with the experimental findings of Sygula *et al.*,⁵² who detected the 1 : 1 inclusion supramolecular complex, $C_{60}@C_{60}H_{28}$ (Fig. 1). The calculated nearest neighbor distance for noncovalently bonded carbon atoms in the $C_{60}@C_{60}H_{28}$ supramolecule is 3.1 Å, which is slightly shorter than that in the crystal structure (3.2 Å). The results in Table 1 show that the attractive forces are strong in the concave–convex π – π interactions involving corannulene and C_{60} , but the entropy effects also play important roles in the supramolecular assembly.

Sygula *et al.*⁵² measured the equilibrium constant for association of C_{60} and $C_{60}H_{28}$ in toluene solvent, and this yields a standard-state free energy of association of $\Delta G_{298}^{1M} = -5.4$ kcal mol^{−1}, where the superscript denotes the usual 1 M standard state used in liquid solutions. This is only 3.2 kcal mol^{−1} less negative than our gas-phase value of ΔG_{298}^{1M} in Table 1. The gas-phase value could be converted to solution by

$$\Delta G_{298}^{1M}(\text{toluene}) = \Delta G_{298}^{1M} + \Delta \Delta G_S \quad (2)$$

where

$$\Delta \Delta G_S = \Delta G_S(\text{AB}) - \Delta G_S(\text{A}) - \Delta G_S(\text{B}) \quad (3)$$

where $\Delta G_S(X)$ is the solution free energy of X at fixed concentration. We do not present full calculations of $\Delta \Delta G_S$ here because the best available solvation models are not well validated for fullerene or other large (naphthalene or larger) aromatic solutes, but we expect all three solvation energies in eqn (3) to be large and negative, primarily due to dispersion-like attractive interactions with the solvent. For example, the experimental fixed-concentration solvation free energies of benzene in benzene, toluene in benzene, and toluene in xylene are −4.6, −5.3, and −5.1 kcal mol^{−1}, respectively,⁶⁴ and these values should increase in rough proportion to the solvent-accessible surface area, or at least the portion of it that corresponds to aromatic moieties and that is solvent accessible without an excessive entropic or bending penalty. Using Bondi's values for the van der Waals radius,⁶⁵ augmented by a solvent-offset of 0.4 Å,^{66,67} we calculate the solvent-accessible surface area of 429, 776, and 973 Å² for C_{60} , $C_{60}H_{28}$, and the complex, respectively. (Less than 10% of this comes from the actually inaccessible interior of C_{60} , but it is harder to estimate the possibly inaccessible portion for the other structures.) Explicit-solvent calculations would be useful for balancing the favorable attractive interactions with the entropic cost of arranging large solvent molecules in the first solvation shell and the basket of the tweezers. Nevertheless it is clear that considerable surface area is lost in forming the association complex, and $\Delta \Delta G_S$ is surely positive and probably large enough to fully account for or exceed the deviation of the theoretical ΔG_{298}^{1M} (g) from the experimental ΔG_{298}^{1M} (toluene).

3.2 Bending potential of the $C_{60}H_{28}$ tweezers

The optimum distance between the two most-separated pentagon carbons (R_p , as defined in Fig. 2 and its caption) of the two pincers in the $C_{60}H_{28}$ tweezers is 11.8 Å. After supramolecular assembly, the R_p distance increases to 12.7 Å. In order to understand this deformation effect, we calculated the bending potential at the M06-2X/DIDZ//M06-L/MIDI! level,

Table 1 Intermolecular distances and energetics (kcal mol^{−1}) of $C_{60}@C_{60}H_{28}$ and $C_{60}@C_{20}H_{10}$

Supramolecule	$R_i/(\text{Å})^a$	ΔE (g) ^b	ΔG_{298}^0 (g, harm)	ΔG_{298}^0 (g, anh)	ΔG_{298}^{1M} (g, anh)
$C_{60}@C_{60}H_{28}$	3.10	−26.4	−7.0	−6.7	−8.6
$C_{60}@C_{20}H_{10}$	3.05	−12.4	4.8	5.4	3.5

^a For this table, the intermolecular distance is defined as the smallest distance between two carbon atoms, one in the host and the other one in the guest molecule. ^b Binding energies and free energies of association are calculated at the M06-2X/DIDZ//M06-L/MIDI! level of theory, and the BSSEs have been removed by the counterpoise approach. A negative value indicates that the association is exoergic or exergonic under standard-state conditions.

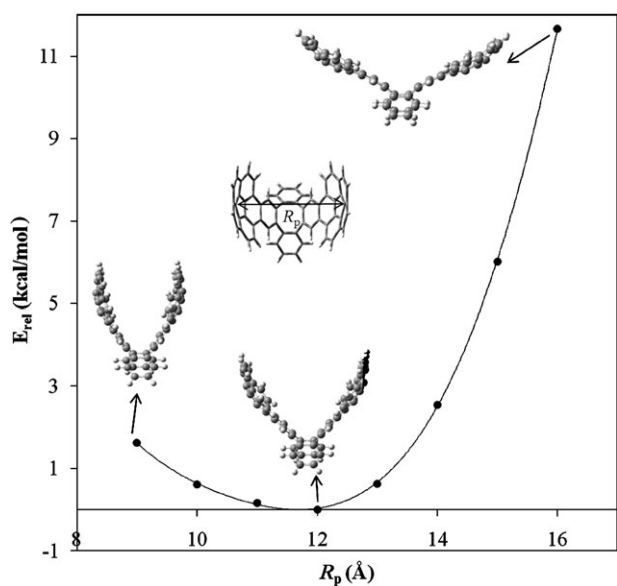


Fig. 2 Bending potential of the $C_{60}H_{28}$ tweezers calculated at the M06-2X/DIDZ//M06-L/MIDI! level of theory. The inter-pincer distance R_p is defined as the distance between two symmetrically related carbon atoms in the 5-membered interior rings of the corannulene moieties of the pincer, in particular carbon-9a¹ and carbon-23a¹. These two carbons are indicated by the double-ended arrow in the figure.

and the results are shown in Fig. 2. As can be seen from Fig. 2, the penalty for the bending deformation in the supramolecular assembly is less than 1 kcal mol⁻¹.

3.3 Modeling of a new tweezers based on π -extended tetrathiafulvalene (TTF)

The tetrathiafulvalene (TTF) derivatives are well known as excellent electron donors, and they can act as electron donors in photoinduced processes when they are coupled with fullerenes in molecular dyads and triads.^{68–71} TTF is a planar molecule, and it cannot form a concave–convex complex with C_{60} . However, when the dithiole moieties are attached to the central benzene rings of an anthracene linker in 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (TTFAQ, $C_{20}H_{10}S_4$), strong steric repulsions, due to carbon-2 of the first dithiole and hydrogen-4 and hydrogen-5 of the anthracene and carbon-2 of the second dithiole and hydrogen-1 and hydrogen-8 of the anthracene, enforce a curved conformation. As shown in Fig. 3, the π -extended TTF, TTFAQ, can form a concave–convex complex with C_{60} .

In Fig. 3, we show a new buckyball tweezers by using TTFAQ as the pincer part and using the tetrabenzocycloocta-

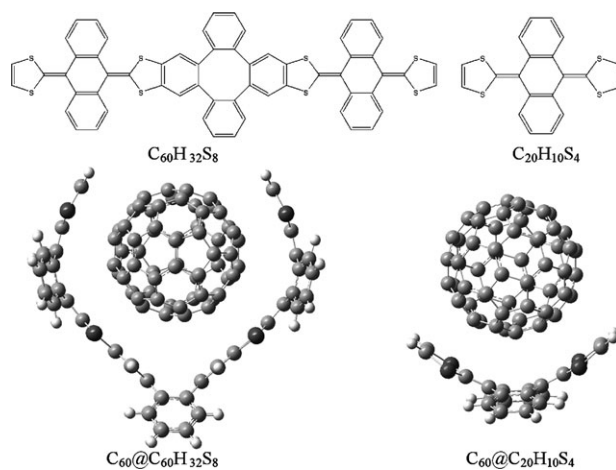


Fig. 3 Host molecules ($C_{60}H_{32}S_8$ and $C_{20}H_{10}S_4$) and supramolecules ($C_{60}@C_{60}H_{32}S_8$ and $C_{60}@C_{20}H_{10}S_4$).

tetraene as the tether, which is the same tether as in the corannulene-based $C_{60}H_{28}$ tweezers of section 3.1. The calculated binding energies and binding free energies are presented in Table 2. Comparing the results in Table 1 to those in Table 2 shows that the binding between TTFAQ and C_{60} is weaker than that between corannulene and C_{60} . Consequently, the binding energy in the $C_{60}@C_{60}H_{32}S_8$ supramolecular complex is smaller than that in the $C_{60}@C_{60}H_{28}$ supramolecule. Both $C_{60}@C_{20}H_{10}S_4$ and $C_{60}@C_{60}H_{32}S_8$ are thermodynamically unfavorable according to their positive value of ΔG_{298}^0 for the association process. As already discussed with respect to Table 1, the solvation-free-energy penalty for association should be positive, so the values of ΔG_{298}^{1M} in toluene are expected to be more positive.

The BSSEs are listed in Table S1 of the ESI,[†] the BSSEs in $C_{60}@C_{60}H_{32}S_8$ is 2.1 kcal mol⁻¹ larger than that in $C_{60}@C_{60}H_{28}$, and this may be due to the nearest neighbor distance being smaller in $C_{60}@C_{60}H_{32}S_8$ (3.04 Å) than in $C_{60}@C_{60}H_{28}$ (3.10 Å).

4. Concluding remarks

In this work, we employed two recently developed density functionals (M06-L and M06-2X) to characterize the geometries and binding energies of a recently synthesized buckyball tweezers ($C_{60}H_{28}$) and its supramolecular complexes. The pincer part of the tweezers, corannulene, has a strong attractive interaction with C_{60} . However, due to the entropy penalty, the calculated standard-state (1 M) gas-phase free energy of association of the $C_{60}@$ corannulene supramolecule is positive 3.5 kcal mol⁻¹; and these results explain why it is difficult to

Table 2 Intermolecular distances and energetics (kcal mol⁻¹) of $C_{60}@C_{60}H_{32}S_8$ and $C_{60}@C_{20}H_{10}S_4$

Supramolecule	$R_i/\text{Å}^a$	$\Delta E(\text{g})^b$	ΔG_{298}^0 (g, harm)	ΔG_{298}^0 (g, anh)	ΔG_{298}^{1M} (g, anh)
$C_{60}@C_{60}H_{32}S_8$	3.04	-13.5	4.4	4.2	2.3
$C_{60}@C_{20}H_{10}S_4$	2.99	-7.6	6.7	8.7	6.8

^a For this table, the intermolecular distance is defined as the smallest distance between two carbon atoms, one in the host and the other one in the guest molecule. ^b Binding energies and free energies of association are calculated at the M06-2X/DIDZ//M06-L/MIDI! level of theory, and the BSSEs have been removed by the counterpoise approach.

observe the C_{60} @corannulene supramolecule experimentally. By using a π -extended tetrathiafulvalene (TTF), 10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (TTFAQ, $C_{20}H_{10}S_4$), as the pincer part, we modeled a new buckyball tweezers. The geometries and binding energies of the buckyball tweezers and its supramolecular complexes have been calculated. Due to the interaction between TTFAQ and C_{60} being weaker than that between corannulene and C_{60} , the binding energy in the C_{60} @ $C_{60}H_{32}S_8$ supramolecular complex is smaller than that in the C_{60} @ $C_{60}H_{28}$ supramolecule.

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