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Intermolecular Interaction-Controlled Tuning of the Two-Photon Absorption of Fullerene Bound in a Buckycatcher

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In this work, we demonstrate for the first time the importance of weak π-stacking interactions in modulating the two-photon absorption (TPA) process of a fullerene−buckycatcher inclusion complex. To unfold the role of weak interactions on the TPA cross-section, we have used the range-separated Coulomb-attenuating method B3LYP functional (CAMB3LYP) for all time-dependent density functional theory calculations. Our calculations suggest that whereas the buckycatcher has very strong TPA active modes at shorter wavelengths, the TPA modes in the fullerene are very weak but have absorption wavelengths that are in the infrared (IR) or near-IR region of the spectrum. Remarkably, the TPA cross-section of the fullerene−buckycatcher (F−C) supramolecule is quite large at desirable near-IR wavelengths. The overall investigation emphasizes the fact that the limitations of buckycatcher and fullerene as promising TPA active materials can be resolved if one uses the weakly coupled F−C supramolecule instead of considering them individually.

In recent years, the two-photon absorption (TPA) process[1] has gained substantial interest due to its potential for applications in several areas, such as optical power limiting,[2] data storage in three dimensions,[3] microfabrication,[4] and photodynamic cancer therapy (PDCT),[5] to mention a few. TPA is a nonlinear optical process that depends on the square of the intensity of the incident radiation and as a consequence it is not observed in daily life. TPA phenomena can only be observed using strong laser light where the density of photons is very high compared to that of a normal monochromatic light source or ordinary sun light. Currently, one of the most important research directions in this field is to find new materials with large TPA cross-sections at desirable wavelengths, materials with a strong TPA at near-IR frequencies are for instance required for use in PDCT.[5] The existing literature on experimental results suggest that the highest TPA cross-section ever attained is of the order of 10^5 Göppert-Mayer (GM) units.[6] With the goal of finding materials with even larger TPA cross-sections, we have recently simulated the TPA cross-section of a 4,6-bis(6-acrid-9-yl)-pyridin-2-yl)pyrimidine tweezer complexed with trinitroflurinone and the value is as high as 2.1×10^6 GM.[7] Instead of searching for TPA active materials in an ad hoc manner, researchers have devoted much effort to designing efficient strategies for making molecules with large TPA cross-sections at suitable wavelengths. In this regard, systematic experimental investigations as well as in-silico simulations have provided us with a wealth of information, which in turn suggests that molecules having long-range charge-transfer interactions, long-chain π-conjugated systems, multibranched dendrimers, porphyrins and metalloporphyrins, alkynylruthenium complexes, semiconducting nanoparticles, quantum dots etc. are good candidates as TPA active materials.[6] It has also been observed that solvents[8] and molecular vibrations[9] might play a crucial role in determining the TPA cross-section of a molecule. Although various physicochemical characteristics associated with the TPA process have been studied quite extensively, the role of weak interactions such as π-stacking interactions in a supramolecular architecture has not yet been explored. Here we demonstrate how one can manipulate both the TPA cross-section and the wavelength just by exploiting the π-stacking interactions in fullerene encapsulated by a corannulene-based tweezer, euphemistically known as a buckycatcher.[10] We have chosen the fullerene−buckycatcher system as our target molecule since earlier investigations suggest that long-range excitation in a three-dimensional architecture might play a significant role in tuning TPA cross-section of a molecule.[6,7]

We have optimized the geometry of all three molecules studied here, namely the fullerene, the buckycatcher, and the fullerene−buckycatcher supramolecule (F−C). The geometry optimizations have been done using the Gaussian 03 suite of programs[11] in a two-step procedure. In the first step, the geometries have been optimized at the semiempirical AM1 level of theory, and the AM1 optimized structures have then been used as a starting guess geometry for a second geometry optimization, carried out using the 6-311G** basis in combination with Truhlar's MPW1B95 functional,[12] whose qualities have already been demonstrated for dispersion-bound van der Waals complexes. We have chosen this functional since π-stacking interactions are the key factor in determining the ground-state geometry of the F−C complex. The final geometry of the F−C complex is shown in Figure 1 and is consistent with earlier theoretical calculations.[13] After geometry optimization, we have calculated transition moments for the one- and two-photon absorption processes from the single residues of linear and

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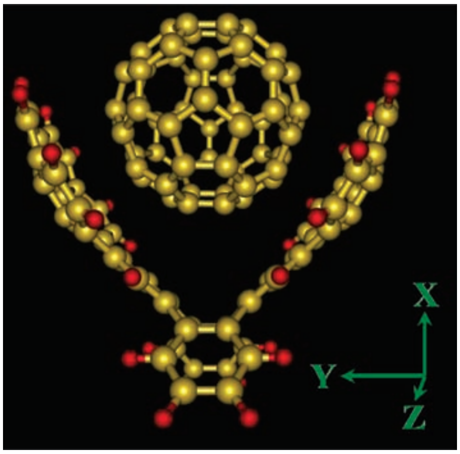

Figure 1. Optimized geometry of fullerene−buckycatcher inclusion complex.

quadratic response functions,[14] respectively, as have been implemented in the framework of time dependent density functional theory (TDDFT)[15] in the DALTON code.[16] For all TDDFT calculations we have adopted the range-separated DFT scheme using the Coulomb-attenuating method B3LYP functional, commonly known as the CAMB3LYP[17] functional, which has already been shown to reproduce experimental TPA cross-sections for a variety of molecules.[18] Within this functional, the B3LYP functional has been modified through an Ewald split, which divides the exchange energy as

$$\frac{1}{r_{12}} = \frac{1 - [\alpha + \beta\,\mathrm{erf}(\mu r_{12})]}{r_{12}} + \frac{\alpha + \beta\,\mathrm{erf}(\mu r_{12})}{r_{12}} \qquad (1)$$

where the first term on the right-hand side corresponds to the short-range interaction and is estimated through DFT. The second term on the right-hand side of eq 1 is linked with long-range interaction and is calculated by Hartree−Fock exchange. The parameters of the CAMB3LYP functional are $\alpha = 0.19$, $\beta = 0.46$, and $\mu = 0.33$ obtained by the optimization of these three parameters to the ionization potential, atomic energies, and atomization energies for a series of reference molecules. At this stage, it is worth commenting that the CAMB3LYP functional is still not designed for excited-state calculation of the van der Waals (vdW) complexes. Although a universal functional with vdW correction would be useful, we do not believe that vdW interaction is important in determining the TPA cross-section directly; instead, the vdW interaction creates an opportunity for long-range excitation and it is well established that CAMB3LYP is the best candidate to treat the long-range character associated with an excitation process at TDDFT level of theory. Due to the size of the F−C molecule, we have limited ourselves to using Dunning's cc-pVDZ for the linear and quadratic response calculations, as larger basis sets would lead to prohibitively CPU intensive calculations. Earlier Poulsen et al.[19] calculated the TPA cross-section of some fairly large molecules using 3-21G and 6-31G* and a few calculations were also carried out with an even larger basis, 6-311G**. They found that inclusion of the extra basis had a very small effect on the TPA cross-section. Therefore we believe that no qualitative changes in the TPA enhancement of the complex molecule relative to the isolated (fullerene and buckycatcher) molecules can be found, although absolute cross-section values may change due to the use of augmented basis functions.

The buckycatcher molecule has only been synthesized very recently through a double Diels−Alder reaction.[10] It has two corannulene pincers tethered by a tetrabenzocyclooctatetraene moiety. The inclusion complex, F−C, has also been synthesized and its structure has been determined through X-ray crystal structure analysis where it was found that the molecular complex has C_s symmetry.[10] Moreover, NMR titration experiments indicate that the π-stacking interaction between fullerene and the bucky catcher is remarkably strong.[10]

TABLE 1: One-Photon Absorption Parameters in A′ Symmetry

molecule	OPA excitation wavelength (nm)	oscillator strength
fullerene	426.0	9.30×10^{-8}
	353.0	1.70×10^{-6}
	337.5	5.50×10^{-6}
buckycatcher	270.0	0.44
	265.5	0.32
	258.5	0.21
fullerene−buckycatcher complex	432.5	3.20×10^{-3}
	359.0	1.09×10^{-3}
	351.0	7.10×10^{-3}

TABLE 2: One-Photon Absorption Parameters in A″ Symmetry

molecule	OPA excitation wavelength (nm)	oscillator strength
fullerene	427.5	1.90×10^{-7}
	352.0	1.14×10^{-5}
	337.5	1.46×10^{-7}
buckycatcher	264.0	9.80×10^{-5}
	261.0	0.53
	248.5	2.04×10^{-4}
fullerene−buckycatcher complex	435.0	8.50×10^{-4}
	359.0	1.40×10^{-3}
	354.0	4.60×10^{-3}

Since the F−C molecule has C_s symmetry, we have calculated one- and two-photon absorption parameters of all the molecules for both irreducible representations (A′, A″). In the C_s point group, the X and Y components of the one-photon transition moments contribute to the oscillator strength in A′ symmetry and the Z component of the transition moment contributes to the oscillator strength in A″ symmetry. This fact is true for all three molecules in the present calculations. One-photon excitation wavelengths and oscillator strengths of the fullerene, buckycatcher, and F−C molecule are presented in Tables 1 and 2. The results in Tables 1 and 2 clearly indicate that one-photon transitions are very weak in both A′ and A″ symmetries for all three excitations of the fullerene and the F−C complex. The oscillator strengths of the buckycatcher molecule in A′ symmetry are quite appreciable for all three excitations, and the corresponding values are again very small in A″ symmetry except for the second excitation. The small transition moment, in particular for the F−C complex, is very promising since the chance of contamination of one-photon absorption (OPA) in the TPA process is rather insignificant. In the present context it is important to notice that coincidence of OPA features with TPA may take place for fairly large molecules;[20] however, such mixing is rather improbable since one-photon oscillator strengths of the F−C molecule are insignificant.

The dominant molecular orbitals associated with the OPA process of F−C complex are shown in Figure 2, and the relevant molecular orbitals of the fullerene and buckycatcher are presented in the Supporting Information. The molecular orbitals suggest that whereas the dominant excitations are local in nature (short-range) for the fullerene and buckycatcher, the excitations are predominantly of long-range character in both irreducible

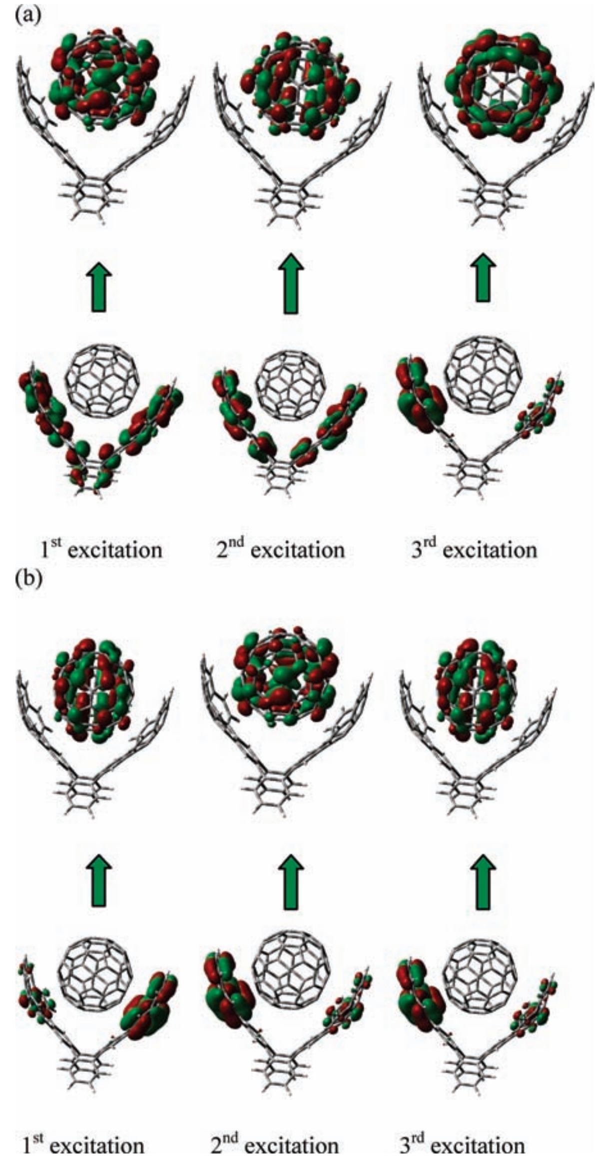

Figure 2. Dominant molecular orbitals associated with OPA process of fullerene−buckycatcher complex in (a) A′ symmetry and (b) A″ symmetry.

representations of the F−C molecule. This in turn justifies our choice of the CAMB3LYP functional. It is also worth mentioning that in contrast to the fullerene and the buckycatcher, excitation wavelengths are significantly red-shifted in the F−C molecule due to π-stacking interactions.

The two-photon transition moment tensor elements S_{ab} between the initial $|0\rangle$ and final $|f\rangle$ states can be evaluated from the following expression

$$S_{ab} = \sum_{n}\left[\frac{\langle 0|\hat{\mu}_a|n\rangle\langle n|\hat{\mu}_b|f\rangle}{\omega_n - \omega_f/2} + \frac{\langle 0|\hat{\mu}_b|n\rangle\langle n|\hat{\mu}_a|f\rangle}{\omega_n - \omega_f/2}\right] \quad (2)$$

where ω_n represents the excitation energy from the ground state $|0\rangle$ to the excited state $|n\rangle$, and $\omega_f/2$ corresponds to half of the excitation energy associated with the transition from the ground to the excited state $|f\rangle$. In this expression, μ_a and μ_b are the Cartesian components of the dipole moment operator.

The TPA cross-section of the molecule for linearly polarized light can in atomic units be calculated as

$$\delta_{au} = 6({S_{xx}}^2 + {S_{yy}}^2 + {S_{zz}}^2) + 8({S_{xy}}^2 + {S_{xz}}^2 + {S_{yz}}^2) + 4(S_{xx}S_{yy} + S_{xx}S_{zz} + S_{yy}S_{zz}) \quad (3)$$

The final expression for the TPA cross-section in GM units, which is directly comparable to experiment, is

$$\delta_{GM} = \frac{(2\pi)^3 \alpha {a_0}^5}{c}\frac{\omega^2}{\pi\Gamma}\delta_{au} \quad (4)$$

where α is the fine structure constant, a_0 is the Bohr radius, c is the speed of light, ω is the frequency of the incoming photons and $\pi\Gamma$ is a normalization factor due to the Lorentzian line-shape broadening of the excited state (Γ = 0.1 eV). The computation of the two-photon transition moment tensor element S_{ab} has been carried out through the use of quadratic response theory. With this theory, the two-photon transition amplitude tensor elements can be extracted as a single residue of the quadratic response function for the dipole moment operators when $\omega_B = \omega_f/2$, and this approach has been described in detail in ref 21. The two-photon parameters in the A′ and A″ representations are depicted in Tables 3 and 4, respectively. The results in these tables suggest that the TPA cross-sections of the buckycatcher (10^5-10^6 GM) in both irreducible representations are significantly larger than those of the fullerene (0.12−2.3 GM), but unfortunately the TPA wavelengths of the buckycatcher molecule are very short (497−540 nm), which makes the molecule unsuitable for many applications, in particular for PDCT.[5] The situation is, however, quite promising if we look at the TPA results for the F−C molecule.

In this case, the TPA process takes place in the near-IR wavelength region (702−870 nm), with appreciable cross-section (10^3-10^4 GM) in both irreducible representations. The results in the tables also reveal that the TPA cross-sections of the F−C molecule in both symmetries are about 10^3-10^5 times larger than the TPA cross-section of a bare fullerene molecule, which clearly indicates that one can modulate the TPA

TABLE 3: Two-Photon Absorption Parameters in A′ Symmetry

molecule	TPA excitation wavelength (nm)	TPA cross-section (δ_{GM})
fullerene	852	2.30
	706	0.12
	675	0.85
buckycatcher	540	6.50×10^5
	531	3.80×10^6
	517	5.70×10^5
fullerene−buckycatcher complex	865	2.80×10^3
	718	8.90×10^3
	702	6.20×10^4

TABLE 4: Two-Photon Absorption Parameters in A″ Symmetry

molecule	TPA excitation wavelength (nm)	TPA cross-section (δ_{GM})
fullerene	855	2.31
	704	1.02
	675	1.90
buckycatcher	528	1.90×10^5
	522	1.50×10^5
	497	2.10×10^5
fullerene−buckycatcher complex	870	1.50×10^3
	718	1.40×10^3
	708	1.40×10^3

parameters by utilizing weak π-stacking interactions. Previously, a number of theoretical as well as experimental works were carried out on various fullerenes, e.g., C_{60}, C_{70}, etc., and their derivatives.[22−25] The results of ZINDO calculations in combination with the sum-over-all-states approach for fullerene (C_{60}) suggested that, in the wavelength range 400−1000 nm, it has only one TPA active mode with cross-section 1000 GM at 518 nm wavelength, and that the other TPA modes are very weak.[24] In this work, we found that all the TPA modes of fullerene are very weak in the wavelength range studied, 675−855 nm. Thus, the result of the present investigation is consistent with these earlier findings.

We have also examined the two-photon transition tensor elements and note that in the A′ symmetry, the S_{yy} (3.1, 4.2, and 16.4, respectively) and S_{zz} (1.8, 1.6, and 2.4, respectively) components of F−C are much stronger than other diagonal and off-diagonal elements. On the other hand, all diagonal elements are zero in the A″ representation of F−C, and the TPA contribution comes mainly from the S_{yz} (3.0, 2.4, and 2.3, respectively) component. The analysis of the tensor elements of the two-photon transition moment clearly indicates that TPA is active in the y- and z-directions of the F−C molecule. The dominant molecular orbitals associated with the excitation processes of the F−C molecule qualitatively suggest that excitations are of the long-range type and that the transitions take place from the buckycatcher to the fullerene. The long-range excitations being from the buckycatcher to the fullerene, the overlap between the orbitals of the ground and excited states that dominates the one-photon transition is virtually negligible, and this in turn indicates that the TPA collects its intensity from virtual excited states of a more delocalized character. This result is in agreement with our recent findings[7] where the TPA cross-section of the 4,6-bis(6-acrid-9-yl)pyridin-2-yl)pyrimidine tweezer complexed with trinitrofluorinone were shown to display a huge TPA cross-section of the complex molecule, which was attributed mainly to long-range charge-transfer interactions in a three-dimensional network.

To conclude, we have explored the two-photon absorption properties of the fullerene, buckycatcher, and fullerene−buckycatcher (F−C) supramolecule to show the importance of π-stacking interactions in controlling TPA parameters. Our investigations suggest that whereas the buckycatcher has a number of very strong TPA active modes at shorter wavelengths, the TPA modes in the fullerene are very weak even though the absorption wavelengths are suitably long. Our calculations further reveal that F−C has strong TPA modes at desirable near-IR wavelengths. Thus, the limitations of the buckycatcher and fullerene as promising TPA active material can be conquered if we use the weakly coupled F−C molecule instead of considering them individually. We strongly believe that our calculations will encourage experimentalists to consider the potential of the F−C as a TPA active material at near IR wavelengths.

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Supporting Information Available: Figures of the F−C molecule and its constituents, i.e., fullerene and buckycatcher, the optimized Cartesian coordinates of the F−C molecule, the dominant molecular orbitals involved in the excitation process at both irreducible representations (A′ and A″) for fullerene and buckycatcher. This material is available free of charge via Internet at http://pubs.acs.org.

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