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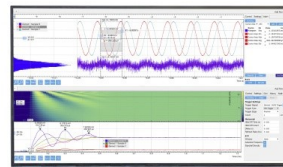
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The effect of structural changes on charge transfer states in a light-harvesting carotenoid-diaryl-porphyrin-C₆₀ molecular triad

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We present a detailed study of charge transfer (CT) excited states for a large number of configurations in a light-harvesting Carotenoid-diaryl-Porphyrin-C₆₀ (CPC₆₀) molecular triad. The chain-like molecular triad undergoes photoinduced charge transfer process exhibiting a large excited state dipole moment, making it suitable for application to molecular-scale opto-electronic devices. An important consideration is that the structural flexibility of the CPC₆₀ triad impacts its dynamics in solvents. Since experimentally measured dipole moments for the triad of ~ 110 D and ~ 160 D strongly indicate a range in structural variability in the excited state, studying the effect of structural changes on the CT excited state energetics furthers the understanding of its charge transfer states. We have calculated the variation in the lowest CT excited state energies by performing a scan of possible variation in the structure of the triad. Some of these configurations were generated by incrementally scanning a 360° torsional (dihedral) twist at the C₆₀-porphyrin linkage and the porphyrin-carotenoid linkage. Additionally, five different CPC₆₀ conformations were studied to determine the effect of pi-conjugation and particle-hole Coulombic attraction on the CT excitation energies. Our calculations show that configurational changes in the triad induces a variation of ~ 0.6 eV in CT excited state energies in the gas-phase. The corresponding calculated excited state dipoles show a range of 47 D–188 D. The absorption spectra and density of states of these structures show little variation except for the structures where the porphyrin and aryl conjugation is changed.
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INTRODUCTION

The elaborate and efficient photochemical energy conversion processes exhibited by photosynthetic reaction centers has stimulated much research into the design and synthesis of supramolecular artificial reaction centers which can mimic most of the major aspects of photosynthetic solar energy conversion.^{1–11} Natural photosynthetic reaction centers utilize incident photons to initiate a complex series of electronic transitions to achieve a high-energy charge separated state.^{5,7} The understanding of the fundamental photosynthetic electronic transition pathways, which include singlet-singlet energy transfer, triplet-triplet energy transfer, and photo-initiated electron transfer, has provided a firm platform for the development of chemical systems which duplicate such efficient energy conversion processes.^{3,7,12–33} The molecular building blocks employed in many artificial reaction centers for the successful mimicry of photosynthetic energy conversion usually consist of organic/inorganic pigments covalently linked to electron donor and/or acceptor moieties.^{17,18,21,22,24,25,34–43}

To emulate the light-absorbing property of chlorophylls, many artificial reaction centers feature porphyrins, chlorophyll derivatives, and related cyclic tetrapyrrolic molecules as the primary chromophore and excited-state electron

donor.^{3,12,16–18,20,31,34,36,37,40,42,44–49} Modeling natural photosynthesis led to the inclusion of quinones as the electron acceptor among some of the earliest synthesized photosynthetic mimics.^{19,26,27,29,50–52} Subsequently, fullerenes were found to possess ideal electron acceptor qualities in artificial photosynthetic systems due to their large electron affinity, large charge accumulation capacity, and a small reorganization energy upon electron transfer.^{53–60} These considerations led to the synthesis of a CPC₆₀ molecular triad consisting of a diarylporphyrin (P) covalently linked to a carotenoid polyene (C) and a C₆₀ fullerene³³ (Fig. 1). The main charge-transfer transition pathway between the ground-state and the final ⁺CPC₆₀[−] charge-separated state involves a local excitation on the porphyrin moiety, followed by electron transfer to the adjacent C₆₀ component. Next, the carotenoid transfers an electron to the positively charged porphyrin to yield the final charge-separated state. Since many dyad-based artificial reaction centers suffer from rapid charge recombination, the triad succeeded in retarding charge recombination by the addition of a secondary donor (carotenoid) molecule which allowed for an increased separation between the particle and hole states.^{14,33}

The synthesis and photochemistry of the CPC₆₀ molecular triad established that fullerenes can act as effective primary electron acceptors in multi-component systems larger than porphyrin-fullerene dyads.³³ The molecular triad generated long-lived charge-separated states with high quantum yields even at low temperature. A salient photochemical

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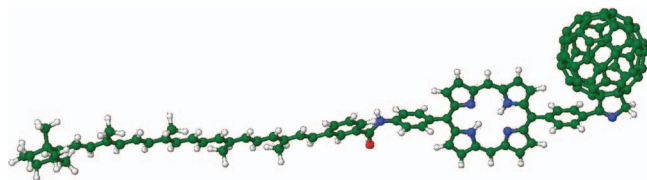


FIG. 1. The ground state structure of the carotenoid-porphyrin-fullerene triad has a linear structure.

feature observed in the CPC₆₀ triad is that the $^+C^{\bullet}-P-C_{60}^{\bullet-}$ charge-separated state recombines to yield a carotenoid triplet state rather than the molecular ground state, similar to photosynthetic reaction centers.¹⁴ For the CPC₆₀ triad, the charge transfer $^+C^{\bullet}-P-C_{60}^{\bullet-}$ transition yields a singlet radical pair state which recombines to yield a $^3C-P-C_{60}$ triplet carotenoid state.¹⁴

A recent study suggests that the photoinduced charge separation process of the triad is driven by correlated motion of electrons and nuclei.⁶¹ The experimentally determined lifetime for the $^+CPC_{60}^-$ charge separated state is ~ 170 ns in a 2-methyltetrahydrofuran solution.³³ In 2003, Smirnov *et al.* employed a transient dc photocurrent technique to study transient dipoles formed upon excitation of the porphyrin chromophore in the CPC₆₀ triad.⁶² The large magnitude (>150 D) of the experimentally determined dipole of the triad conforms to the particle-hole picture of the charge separated excited state, in which the hole state resides on the carotenoid component and the particle state is localized on the C₆₀ fullerene at a large particle-hole separation (>30 Å).

A previous Density Functional Theory (DFT) study by our group on the ground state properties of the triad compared DFT-optimized structures of a linear triad and an elbow-shaped triad.⁶³ It was determined that the linear triad is energetically more stable than its elbow-shaped conformer counterpart.⁶³ The ground-state CPC₆₀ structure consists of a pyrrole-C₆₀ linked to a diaryl-porphyrin, where the porphyrin moiety is perpendicular to the aryl rings. The aryl rings, in turn, are coplanar with the carotenoid component. The porphyrin is connected to the carotenoid by an amide linkage. A comparison of the total density of states (DOS) for the triad with the DOS projected onto three subunits (pyrrole-C₆₀, carotenoid with amide linkage, and diaryl-porphyrin) revealed that the hybridization of the molecular orbitals belonging to different components is negligible such that the orbitals involved in charge-transfer excited state transitions are mostly localized on the parent components.⁶³ Moreover, the triad absorption spectrum represents a nearly linear combination of the spectra of the components. In a separate study, the optical absorption spectrum of the triad was calculated using a time-dependent DFT (TDDFT) formalism.⁶⁴ Again, the decomposition of the spectrum into optical densities corresponding to the isolated components clearly demonstrated that the total spectrum is very well approximated by the sum of the component spectra. The main features and shape of the TDDFT spectrum were in good agreement with experiment, where a small shift of approximately 0.3–0.4 eV between the calculated and observed peaks

was attributed to solvent polarization in the experimental measurements.⁶⁴

In another study, the perturbative delta-self consistent field (P-ΔSCF) method was applied to the study of charge transfer excitations in the CPC₆₀ molecular triad.⁶⁵ The large particle-hole distance in the final $^+CPC_{60}^-$ charge separated state allows for an accurate estimate of the charge transfer excitation energy within the separated fragment limit, where the CT energy is determined from the carotenoid ionization energy (IP), the fullerene electron affinity (EA), and the fullerene-carotenoid Coulomb interaction ($1/R$) according to Mulliken's equation ($IP-EA-1/R$). The P-ΔSCF excited state method gives an excitation energy of 2.46 eV for the $^+CPC_{60}^-$ charge separated state in gas-phase, which is in good agreement with the point-charge estimate ($IP-EA-1/R$) of 2.5 eV.⁶⁵ The P-ΔSCF study of CPC₆₀ also showed that the polarization of a solvent, represented as a discrete lattice, may influence the charge transfer process by stabilizing the large dipole moment of the particle-hole state.⁶⁵ The importance of solvent polarization is also brought out by the experimental study of Gust *et al.*³³ in which charge separation was observed in benzonitrile and (2-methyl)-tetrahydrofuran but not observed in toluene. The effect of polar solvent is significant as the experimental estimate of the CT energy of the $^+CPC_{60}^-$ state is significantly smaller than the gas-phase calculated value.^{25,65}

The magnitude of the excited state dipole moment for the triad was estimated to be 153 D from the measurement of transient DC photocurrent of the triad in tetra-hydrofuran and in 2-methyl tetrahydrofuran.⁶² In determining the dipole moment from the DC photocurrent the following approximations were used in Ref. 62. The solvent reaction effect was modeled within the Onsager model approximating the solute as a point dipole in an elliptical cavity in the dielectric. The effective dipole of a solute in solvent is higher than in gas-phase due to the polarization of the solvents. The dipole estimated from the photo-voltage was further corrected for different quantum yields under different conditions achieved by varying the solvent and excitation laser frequency.⁶² The approximations in this estimate entail a simplification of the molecular shape (ellipsoid), underestimation of the Coulomb attraction between the polarizable chromophores as well as the oppositely charged carotenoid-fullerene components, and conformational changes for the charge separated state in solution. The shape approximation is important since a spherical shape approximation of the cavity lowers the dipole to 110 D. An alternative evaluation consisting of a decomposition of the total dipole moment into solute and solvent polarization contributions gave an experimental estimate of 156 D, close to a value of 163 D estimated from ground state structure where the particle-hole separation is ~ 34 Å.⁶² The polarization interaction between the carotenoid and porphyrin chromophores will have the effect of shortening the particle-hole distance, which may reduce the dipole magnitude but not necessarily induce structural changes. On the other hand, a Coulombic interaction between the negatively charged C₆₀ fullerene and the positively charged carotenoid tail in the excited state may induce significant structural changes which can move the carotenoid chain into a closer distance to the

fullerene component. Experimental evidence for such a folded conformer comes from a study of the triad in micelle nanoreactors suspended in water, where contractions in the molecular volume of the triad were attributed to entropy changes arising from solvent movements and possible conformational changes upon photoinduced electron transfer in generating a dipole of ~ 110 D.⁶⁶ The conformational changes of the triad in water were studied by Cheung *et al.*⁶⁷ using classical molecular dynamics simulations. This study has brought out that the linear structure favored in the gas phase is one of the least populated conformational states, which shows that the triad may undergo significant structural changes in solution. On the other hand, recent force field calculations by Balamurugan *et al.*⁶⁸ demonstrate that the charge transfer state in presence of polar solvent prefers a linear structure. The presence of solvents may also lead to softening of the vibrational modes. The complete description of solvents should include the electronic polarization effects, thermal fluctuations, and greater conformational variability. This can only be done using *ab initio* molecular dynamics simulation similar to Ref. 69. Such calculations are prohibitively expensive particularly for systems like the triad.

In the present investigation, we extend our two previous DFT studies of the CPC₆₀ triad with a combined ground- and excited-state electronic structure study of various configurations of the linear-shaped triad. The presence of the solvents induces configurational variations⁷⁰ as well as electronic polarization. Since our calculations are on the gas-phase triad, this study brings out the changes in the CT energy due to the structural changes only, separate from the electronic polarization effects due to the polar solvents. In order to gain insight into the large differences in structural configurations (linear vs folded) and excited state dipole moment magnitude (~ 160 D vs ~ 110 D) observed for the triad, we have calculated CT energies for a set of 21 distinct triad configurations. In order to study changes in the CT energy due strictly to configurational variations, single-point calculations were performed for the structures reported in the present study. For each structure, the calculated lowest excited state transition corresponds to the lowest CT state. To the best of our knowledge, rigorous all-electron calculations have not been carried out for a series of triad structures, mainly due to the large computational expense involved in the ground- and excited-state calculations of systems as large as the CPC₆₀ triad (207 atoms).

COMPUTATIONAL METHOD

The calculations reported here were carried out using DFT as implemented in the NRLMOL code.^{71–73} We employed the Perdew, Burke, and Ernzerhof (PBE) exchange-correlation energy functional within the generalized gradient approximation for all calculations reported here.^{74,75} The calculations were performed at the all-electron level using a large Gaussian basis set specially optimized for the PBE functional used in this work.⁷³ The basis set for a given atom is contracted from the same set of primitive gaussians. The numbers of the primitive gaussians, s-type, p-type, and d-type contracted functions, along with the range

TABLE I. The numbers of s-, p-, and d-type contracted functions, number of primitive gaussians and the range of the gaussian exponents used for each atom.

Atom	s-type	p-type	d-type	Primitives	Exponent range
C	5	4	3	12	2.22×10^4 –0.077
H	4	3	1	6	7.78×10 –0.075
N	5	4	3	13	5.18×10^4 –0.25
O	5	4	3	13	6.12×10^4 –0.10

of the exponents are given in Table I. This basis set resulted in a total of 6170 basis functions for the triad conformers studied here. All ground-state and excited-state calculations were performed using spin-polarized wavefunctions. The P- Δ SCF excited state method^{65,76,77} is used here to determine the energies of the charge transfer excited state transitions. The P- Δ SCF method provides accurate estimates of the experimentally obtained charge transfer excited state energies for a set of 12 supramolecular Tetracyanoethylene (TCNE)-hydrocarbon dyads and model pentacene fullerene OPV complex.⁷⁶ Previously calculated CT excitation energies for porphyrin-C₆₀ co-facial dyads are in excellent agreement with the range of experimental values reported in the literature for similar porphyrin-fullerene systems.⁷⁸ The method has also been applied to the study of charge transfer energetics in relation to varying geometrical orientation of the tetraphenyl-porphyrin/C₆₀ (TPP/C₆₀) and (zinc)tetraphenylporphyrin/C₆₀ (ZnTPP/C₆₀) supramolecular dyads.⁷⁹

To obtain the excitation energy, for example, the HOMO to LUMO transition, an electron from the HOMO is placed in the LUMO and the self-consistent problem is solved using the perturbative Δ SCF method. The energy of the triplet state is obtained if the two unpaired electrons in the HOMO and LUMO orbitals are of the same spin. However, if two unpaired electrons in the HOMO and LUMO orbitals have opposite spin, then such a state is a mixed state (a 50–50 mixture of pure singlet and triplet states) with an energy that is an average of the singlet and triplet set. The energy of the singlet state is calculated using the Ziegler-Rauk method.⁸⁰

RESULTS AND DISCUSSION

The importance of studying various structures of the CPC₆₀ molecular triad is more pronounced for the excited state than the ground state. For the ground state, X-ray and NMR data show the all-trans configuration for the amide/carotenoid backbone to be the most stable.^{50,81} However, for the excited state the formation of a radical cation on the carotenoid component in the charge separated state may facilitate rotation about the carbon-nitrogen amide bond to generate various cis-conformations in the carotenoid backbone.^{82,83} Since the one-electron oxidation of a carotenoid may lead to bond length equalization between single and double bonds in the conjugated amide/carotenoid backbone, a reduction in the rotational barrier for bonds that are formally double bonds in the ground state allows for more conformational flexibility in the cationic carotenoid component.^{82,83}

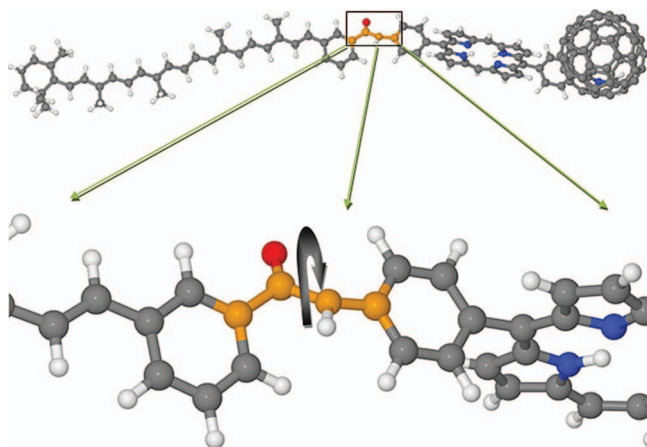


FIG. 2. The 4-atom dihedral segment (orange) was used to generate a full 360° torsion scan consisting of 7 steps of 45° increments. The lowest CT excitation energies were calculated at each torsion-scan step.

In the present study, we undertook a systematic scan of configurations resulting from torsions. This is based on the assumption that the triad molecule is likely to have several low energy torsional modes which will be populated at low temperature. The structural modifications of the triad are likely to occur at the linkage connecting different units. To examine such possible configurations, two different dihedral segments from the CPC₆₀ molecular structure were selected, denoted as PF and CP, through which various structures were generated by dihedral-angle rotations about each of the chosen 4-atom dihedral segments (shown in Figures 1 and 3). The PF (porphyrin/fullerene) designation corresponds to triad configuration variations where the structural modifications originate from torsions about the “(C₆₀-pyrrole)-porphyrin” linkage. Similarly, the CP (carotenoid/porphyrin) designation describes structural changes effectuated through

TABLE II. Charge transfer excitation energies (in eV), ground- and excited-state dipole values (Debye) for the 7 triad conformations generated by torsions about the carotenoid/porphyrin linkage. CP denotes carotenoid/porphyrin.

Triad conformer	CT excitation energy	Ground state dipole	Excited state dipole
CP 45°	2.46	7.9	165.6
CP 90°	2.50	9.2	168.0
CP 135°	2.49	9.0	169.4
CP 180°	2.47	8.0	171.1
CP 225°	2.48	8.4	173.7
CP 270°	2.50	9.3	174.6
CP 315°	2.48	8.6	171.7

torsions about the “porphyrin-carotene” amide linkage. These configurations are not necessarily minima of the potential energy surface of the triad in gas-phase but can possibly occur in solution phase. Our goal here is to examine how much of change in CT energies occur due to the configurational changes only.

In Fig. 2 we show a dihedral segment of the CPC₆₀ triad at the linkage between the carotenoid and porphyrin subunits. The dihedral segment was scanned for full 360° torsion in increments of 45° which generated 7 configurations. At each of the 7 dihedral steps, the excited state energies for the lowest CT state (HOMO to LUMO transition) was calculated to determine the effect of varying conformational degrees of freedom for the amide/carotenoid backbone on the CT excitation energy (shown in Figure 3). Since our purpose is to understand the effect of torsional distortion on the CT energy, the resulting configurations are not optimized. The calculated CT excitation energies for the lowest lying CT state of the 7 triad conformations (denoted as CP for carotenoid/porphyrin linkage) are given in Table II. For each CP conformation, we also

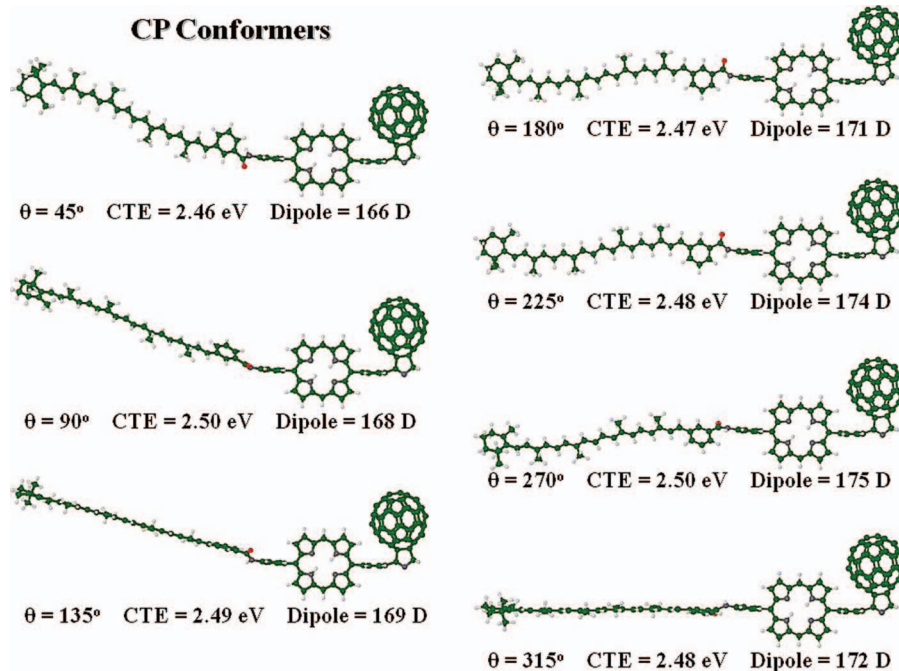


FIG. 3. The angle (θ), charge transfer energy, and excited state dipole magnitude values are shown for each of the 7 distinct CP conformers.

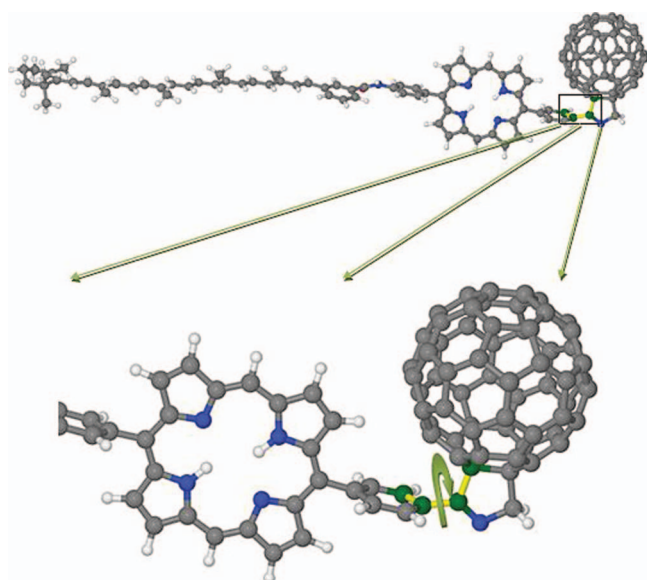


FIG. 4. The 4-atom dihedral segment (green) was used to generate a full 360° torsion scan consisting of 7 steps of 45° increments. The lowest CT excitation energies were calculated at each torsion-scan step.

report the calculated ground- and excited-state dipole moment magnitudes. The calculated CT energies lie within a range of 2.44 eV–2.50 eV. The calculated excited state dipoles, corresponding to the particle state localized on the fullerene and the hole state localized on the carotenoid, are large and lie close to experimentally reported dipole values.

For the torsion displayed in Figure 4, we have evaluated the CT energy at 7 dihedral steps in increments of 45° for several low-lying CT states to determine the effect of varying conformational degrees of freedom for the porphyrin/ C_{60} -pyrrole linkage on the CT excitation energy. The calculated

TABLE III. Charge transfer excitation energies (in eV) and ground- and excited-state dipole values (Debye) for the 7 triad conformations generated by torsions about the porphyrin/fullerene linkage. PF denotes porphyrin/fullerene.

Triad conformer	CT excitation energy	Ground state dipole	Excited state dipole
PF 45°	2.55	8.8	174.9
PF 90°	2.58	10.6	185.4
PF 135°	2.57	10.5	188.7
PF 180°	2.57	9.7	187.2
PF 225°	2.56	9.4	181.8
PF 270°	2.58	10.6	182.1
PF 315°	2.51	9.5	176.5

CT excitation energies for the lowest lying CT state of the 7 triad conformations (denoted as PF for porphyrin/fullerene linkage) are given in Figure 5 and Table III. For each PF conformation, we also report the calculated ground- and excited-state dipole moment magnitudes. The calculated CT energies lie within a range of 2.50 eV–2.58 eV, which are slightly larger than the CT energies of the CP conformers. The calculated excited state dipoles for the PF conformers are larger than the CP conformers, where the values lie within the range of 170 D–189 D.

To determine the existence of new isomers that can result from these torsions, the set of 14 triad conformers described as CP and PF above, was also optimized at the AM1, PM3, and PM6 semi-empirical levels of theory using the MOPAC2009^{84,85} quantum chemistry software package. Similar energy ordering was obtained across the different semi-empirical methods for this set of isomers. From the semi-empirical calculations of the 14 conformers and the linear triad, a set of 5 conformers with energies within a ~ 0.5 eV

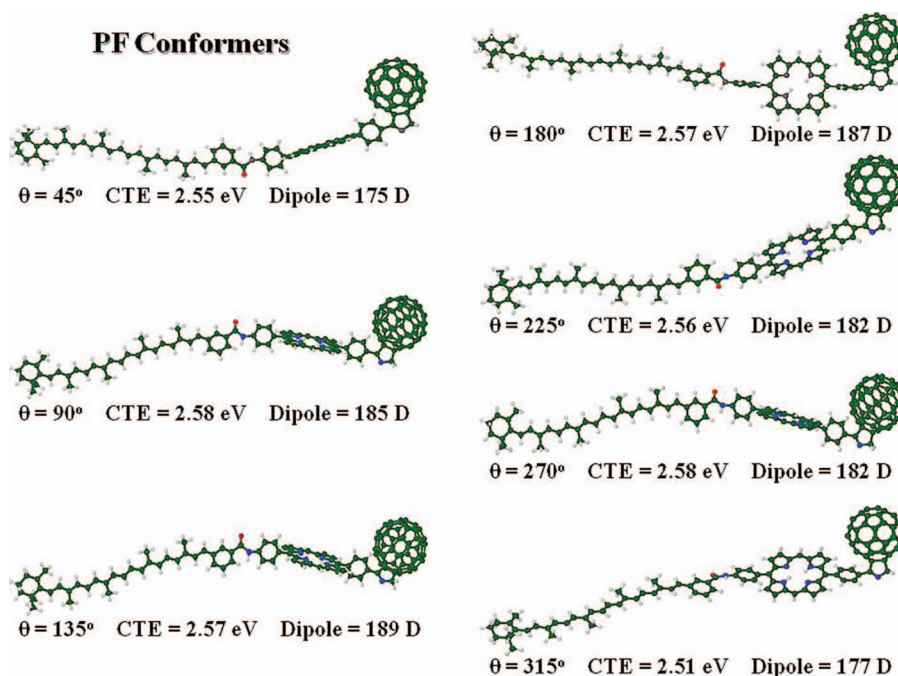


FIG. 5. The angle (θ), charge transfer energy, and excited state dipole magnitude values are shown for each of the 7 distinct conformers generated through torsion of the porphyrin-fullerene (PF) linkage.

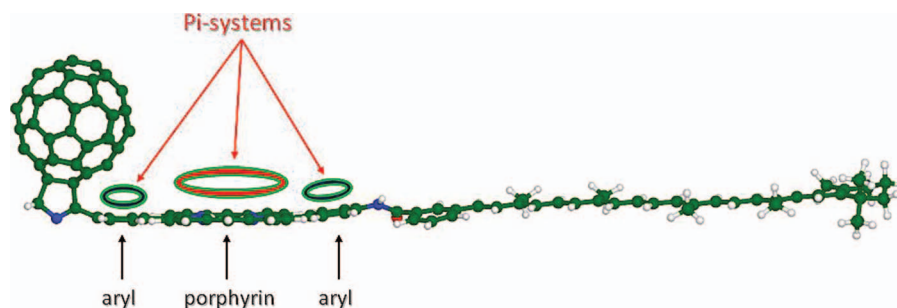


FIG. 6. Simple Hückel type representations of the cyclic pi-conjugation exhibited by porphyrin and aryl systems.

range of the linear-triad energy was selected for further geometry optimization using density functional theory with the NRLMOL code. The all-electron DFT optimization (6170 basis functions) of the five competing triad conformer structures exhibited a structural tendency toward the linear-shaped geometry of the triad. The only distinct structural feature shared by the five competing DFT-optimized conformers is a propensity toward the torsion of the porphyrin macrocycle plane with respect to a fixed C₆₀ and carotenoid. This is the same torsion examined in Table III. Thus, these torsions do not result in any significant change in the CT excitation energy or in a significantly different structure.

In the CPC₆₀ molecular triad, electron transfer is mediated by the covalent linkage joining the donor and acceptor components. The porphyrin component of the triad contains aryl rings as linkage groups at the meso-positions of the pi-conjugated macrocycle. The aryl linkage rings exhibit angles of $45^\circ < \Theta < 90^\circ$ with the porphyrin plane. Resonance stabilization serves as a major driving force for conformations which exhibit extended conjugation between the meso-aryl groups and the porphyrin moiety and a rotational motion about the single bond joining the aryl ring to the macrocycle may populate conformations with significant pi-pi overlap (as shown in Figure 6). Consequently, extended conjugation between the pi-system of the aryl ring and the pi-system of the porphyrin macrocycle may influence the donor-acceptor electronic interaction, which in turn affects the electron-transfer rate.¹³ Studies have addressed this issue by attempting to disrupt extended conjugative interactions by placing alkyl substituents at beta-

pyrrolic positions.^{86,87} The aim is to force strict orthogonality between the aryl molecular plane and the porphyrin macrocycle plane through steric repulsion effects of the alkyl substituents on the aryl ring. Several factors compete against an induced strict perpendicular aryl-porphyrin plane alignment, where the porphyrin macrocycle may undergo significant distortions due to the increased steric repulsion. In addition, conformations in solution will most likely sample a rotational motion about the single bond joining the aryl ring to the porphyrin macrocycle.^{13,25}

In the present study, we examine the effect of extended conjugation between the pi-system of the aryl rings and the pi-system of the porphyrin macrocycle on the donor-acceptor CT excitation energies. We have defined a pseudo-dihedral parameter in Figure 7. The dihedral parameter is evaluated, with respect to the ground-state dihedral, in 4 increments of 45° for a total torsional scan of 180° . At one end of the pseudo-dihedral scan, the pi overlap between the porphyrin macrocycle and its two aryl linkage groups at the meso-positions is maximal, whereas at the other end of the dihedral scan the extended pi-conjugation is completely disrupted by a relative perpendicular structural orientation between the porphyrin and aryl molecular planes. By calculating charge transfer excitation energies at each dihedral increment, we can gain understanding into the effect of pi-conjugation coupling interactions on the CT excited-state energies. The calculated CT excitation energies for the lowest lying CT state of the 4 triad conformations are given in Table IV. For each pseudo-dihedral conformation, we also report the calculated ground- and excited-state dipole moment magnitudes. The calculated CT energies lie within a range of 2.48 eV–2.53 eV and the calculated excited state dipoles lie within the range of 165 D–176 D.

Since the excited state dipole moments of all the conformers show large dipole moments, we constructed a

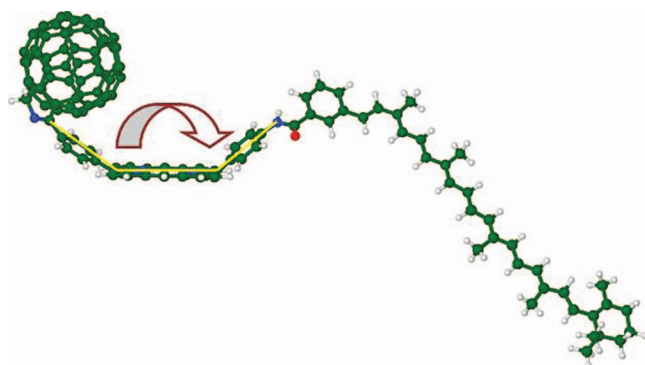
FIG. 7. The pseudo-dihedral scan of 180° explores a varying degree of extended pi-conjugation between the porphyrin macrocycle and its two meso-aryl linkage groups.

TABLE IV. Charge transfer excitation energies (in eV), ground- and excited-state dipole values (Debye) for the 4 triad conformations generated by torsions about the pseudo-dihedral.

Triad conformer	CT excitation energy	Ground state dipole	Excited state dipole
Dihedral 45°	2.48	8.4	167.5
Dihedral 90°	2.50	8.8	165.4
Dihedral 135°	2.53	9.4	166.6
Dihedral 180°	2.50	9.2	176.0

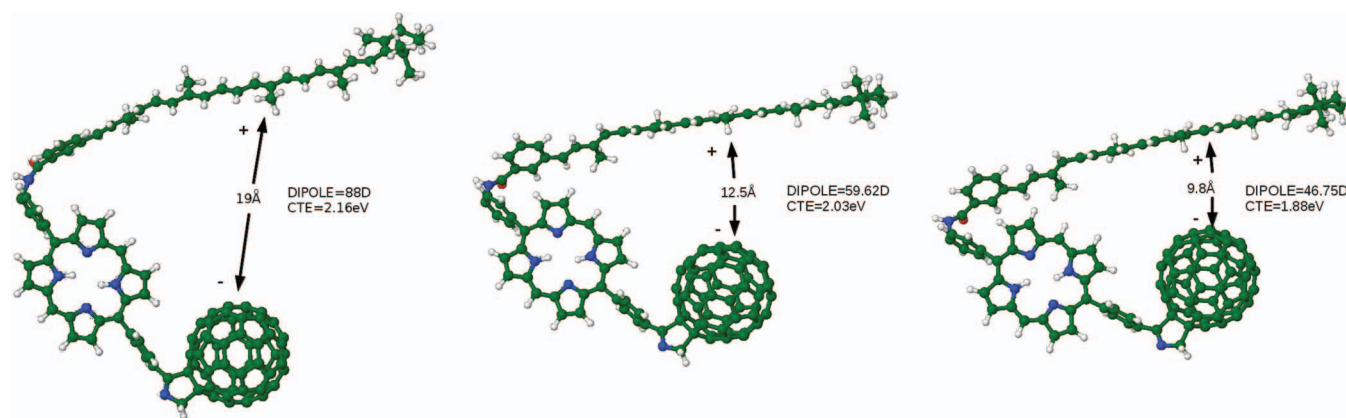


FIG. 8. Folded triad conformations exhibiting a close interaction between the particle and hole states in the excited state.

folded geometry which is likely to possess a significantly lower excited state dipole moment as shown by experiment (~ 110 D).⁶⁶ Based on this experimental observation, we have generated a folded configuration in which the porphyrin-carotene extension wraps closely around the fullerene component where the C_{60} -carotene particle-hole distance is ~ 19 Å (shown in Figure 8). We would like to point out that similar structures were observed in classical molecular dynamics simulations of the ground state structure. Our calculated value for the CT excitation energy of the folded conformation yields a value of 2.16 eV, which is ~ 0.3 eV lower than the average CT energy of the CP and PF conformers. The excited-state dipole moment is reduced by half for the folded conformation (88 D) in comparison to the average dipole value for the CP and PF conformers. This is due to the reduced distance between the particle and hole in this structure. The difference in CT energy between the linear and the folded structure is similar to that can be obtained from Mulliken's formula which indicates low electronic interaction between the carotene and the fullerene. In the same spirit, we obtained two other distorted folded structures in which the carotenoid-fullerene distances were further reduced such that in the excited state the dipole moment reduced to 60 and 46 D. The energy of the charge transfer state reduced to 2.03 and 1.88 eV. In these highly distorted structures the distance of the carotenoid and fullerene reduced to nearly 12 (10) Å. The decrease in the CT energy in the folded conformer primarily occurs because of the increased Coulomb interaction between the particle and hole. The exciton binding energy in the conformer with the excited state dipole of 88 D is 0.3 eV compared to vanishing small value for the linear triad structure. In the maximum folded conformer the exciton binding energy increases to 0.7 eV. The exciton binding energy was computed by subtracting the CTE from the quasi-particle gap. The quasiparticle gap was obtained from the self-consistent total energy differences of the total energies of the triad in neutral, singly positively and negatively charged states. The closer proximity of the donor and acceptor units increases the exciton binding energy. The changes in CTE and the exciton binding energies are not exactly linear possibly due to increase in steric repulsion in the folded conformers. The reduced magnitude of the excited state dipole in the folded structures will likely

decrease the solvent-polarization induced stabilization of the CT state.

The energy of the $C^+PC_{60}^-$ charge transfer excited state is reported to be 1.20 eV by Gust and co-workers,²⁵ which is significantly different from the gas-phase calculated value of 2.46 eV for the linear conformer. From the above results we find that the structural changes can reduce the energy of the CT state in the gas-phase by a few tenths of an electron-volt up to 0.6 eV even for conformers where the excited state dipole is significantly smaller. The average change can only be determined from a statistically weighted average of the structures. However, it is unlikely that the average change in CTE due to the structural changes will be as high as 0.6 eV. The remaining difference is likely to be due to the electronic polarization effect produced by the polar solvent molecules.

The small change in energy of the charge transfer excited states is likely due to the small interaction between the spatially separated components. To examine the change in the electronic structure due to the structural variations, we have plotted the total density of states of the ground state for all the conformers studied here (Fig. 9). Since the position of the Fermi level changes by about 0.2 eV depending on the structure, the Fermi level is displayed in the figure as a thick line. The density of states are shown in five sections. Section A shows the DOS of all the structures generated from torsion of carotenoid-porphyrin linkage (CP), B includes the structures from torsion of porphyrin-fullerene linkage (PF), section C shows the DOS of the optimized structures from the set B, D shows the structures derived from pseudo-dihedral angle scan, and the folded structures are shown in section E. The peak positions near Fermi level corresponding to the HOMO and LUMO remain same. The HOMO of the triad is on the carotenoid and the lowest three LUMOs are located on the fullerene. The peaks just below the HOMO correspond to the porphyrin orbitals and a carotenoid occupied level. The DOS of the folded conformers and the ones derived from pseudo-dihedral scan show deviations in the DOS of the levels below HOMO. We point out that the structural changes in these conformers are significant.

We further examined the effect of such conformational change on the optical properties such as absorption spectra calculated from the dipole transition between one-electron states as $\sigma(E) = \int |\langle \psi_i | \vec{p} | \psi_j \rangle|^2 f_i (1 - f_j) \delta(\epsilon_i - \epsilon_j - E)$,

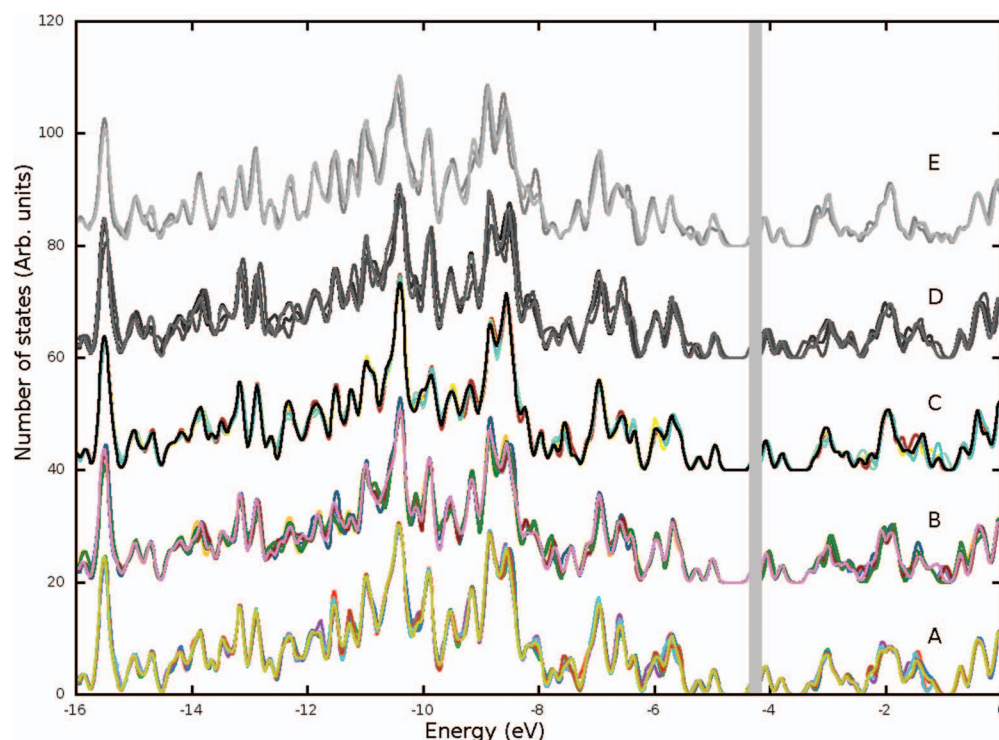


FIG. 9. The density of states for the conformers generated through (A) the torsion of the carotenoid-porphyrin linkage, (B) torsion of the porphyrin-fullerene linkage (C) optimized structures of the set B, (D) the set obtained through scan of the pseudo-dihedral angle and (E) the folded conformers.

where p is the dipole operator, ϵ is the single particle energy, f is the occupancy, and E is the photon energy. Our earlier calculation of the absorption spectra of the ground state triad using the above formulation showed qualitative agreement with TDDFT calculations.^{63,64} In the linear ground

state structure, the absorption spectra of the triad becomes a combination of the spectra of the isolated components. The first peak arises from the transitions in carotenoid states, the second due to porphyrin transitions while the later three are dominated by transitions between fullerene states. The

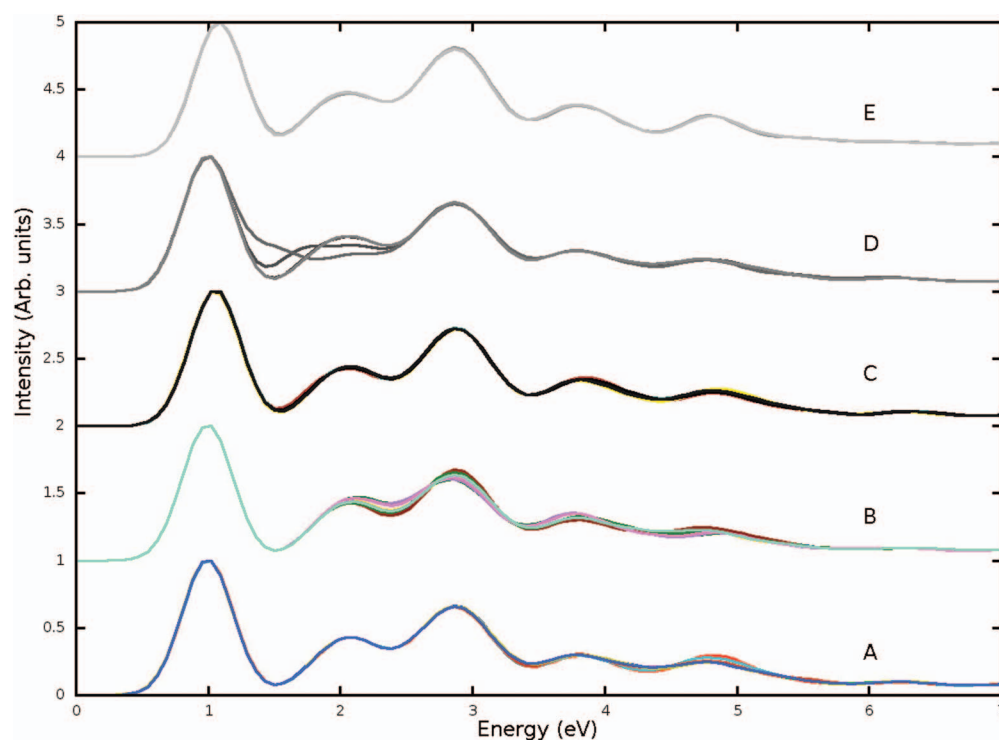


FIG. 10. The absorption spectra for the conformers generated through (A) the torsion of the carotenoid-porphyrin linkage, (B) torsion of the porphyrin-fullerene linkage (C) optimized structures of the set B, (D) the set obtained through scan of the pseudo-dihedral angle and (E) the folded conformers.

absorption spectra of the conformers (Fig. 10) show that dipole transition probabilities change very little for the conformers corresponding to a torsion of carotene-porphyrin linkage and porphyrin-fullerene linkage. That is due to the fact that the structures of the components vary little whereas the structures of the linkers change. For example, the torsion of the amide linker does not change the carotene structure. A recent study of thermal effects on the optical properties of cyanine dye indicated that the intramolecular thermal fluctuations can influence the overall absorption spectra.⁶⁹ This can also happen for the triad molecule as interactions with solvent can result in excitations of modes associated with individual carotene or fullerene or porphyrin components. While such excitations can influence the overall absorption spectra, they are unlikely to result in appreciable change in the CT energy as our calculations indicate. This can be indirectly inferred from the little variations in the CT energy upon the structural changes that results from optimizations at various levels of theories from the DFT to PM6, AM1 methods. The pseudo-dihedral conformers however show larger change in dipole transition probabilities which arises due to change in conjugation between the porphyrin and the aryls as the pseudo-dihedral angle changes. The increase in conjugation changes the DOS mostly for the porphyrin component. The transition probability between the carotene and fullerene still remains zero. The changed transition probabilities indicate the possibility of alternate charge transition pathways in such conformers. Both the density of states and the absorption spectra show that only in the pseudo-dihedral conformers the electronic structure changes noticeably. However, the CT energy changes noticeably for the folded conformers which occurs mostly due to the increased particle-hole interaction compared to the linear structure.

CONCLUSIONS

We have examined the effect of structural changes on the gas-phase CT excited states of the CPC₆₀ molecular triad. In this work, we de-coupled the effect of structural changes on the CT excitation energy from the electronic polarization effects due to polar solvents. Experimental evidence indicates that the triad undergoes conformational changes in solution, where the measured excited state dipole moments of 160 D and 110 D indicate a significant conformational variation in going from a linear structure to a folded conformation, respectively. To study the conformational flexibility of the triad, we generated a series of 14 distinct configurations through torsional scans about the carotene-porphyrin linkage and the porphyrin/fullerene linkage. In addition, we studied a few folded configuration is exhibiting a shorter donor-acceptor (carotene-fullerene) distance than the set of CP and PF triad conformers. Our calculations show that the CT excited state energy and the excited state dipole moment of the molecular CPC₆₀ triad varies slightly across the CP and PF triad conformers, where the calculated CT energy values for the triad lie close to 2.5 eV and the dipole values range from 165 D–188 D. In comparison to the CP and PF conformers, the CT excited state energy of the folded conformations varies by ~0.4–0.6 eV with a value of 2.16–1.88 eV and the excited

state dipole magnitude is significantly reduced. Due to the structural flexibility of the CPC₆₀ triad, we also examined a configurational scan in which, at one end, the porphyrin macrocycle and its two meso-aryl groups lie nearly co-planar and at the other end, the molecular planes are perpendicular to each other. This particular conformational scan was designed to study the effect of extended pi-conjugation on the CT excited state energy of the triad. Although experimental studies show that such extended conjugation may affect the electronic coupling, which in turn impacts the CT rates, our calculations show that extended pi-conjugation exhibited by the porphyrin/aryl co-planar configuration does not produce a significant change in the CT excitation energy value. Optimization of the distorted structures generated from torsion of the porphyrin-fullerene and carotene-porphyrin linkages led to a linear structure. The results on the effect of structural torsion on the gas-phase CT energy suggest that the solvent induced polarization plays a more important role in stabilization of the CT state compared to solvent induced structural distortions. We are currently pursuing a combined QM/MM approach to determine the shift in CT excitation due to the solvents.

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