Organic Photovoltaics: A Charge Transfer Perspective In The Study Of Donor-Acceptor Systems

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ORGANIC PHOTOVOLTAICS: A CHARGE TRANSFER PERSPECTIVE IN THE STUDY OF DONOR-ACCEPTOR SYSTEMS

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Dedication

To My Family
ORGANIC PHOTOVOLTAICS: A CHARGE TRANSFER PERSPECTIVE IN
THE STUDY OF DONOR-ACCEPTOR SYSTEMS

by

MARCO AUGUSTO OLGUIN, BSc, MSc

DISSEPTION

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Abstract

The present research involves the study of donor-acceptor (D/A) dyad complexes from a charge transfer energy perspective. The aim is to provide insight and predictive understanding into the charge transfer processes of the molecular-level components in donor-acceptor based organic solar cells using computational methods to describe photochemical processes at the quantum mechanical level within the Density Functional Theory (DFT) approximation. Predictive understanding is anchored in reproducing experimental results, wherein the present work a perturbative excited-state DFT method is described in detail and shown to give Charge Transfer (CT) energies in excellent agreement with benchmark experimental data. With an accurate excited state method for calculating CT excitation energies at hand, the present research applies the method to the study of D/A pairs employed in photovoltaic devices. An examination is made of the effect on the CT energetics of varying the donor and acceptor component in the dyad and the changes in the frontier orbital energy levels and CT energies with respect to a varying D/A distance and D/A relative orientation. The results of the perturbative excited state DFT calculations provide direct insight into photovoltaic device efficiency since the CT energy determines the achievable open circuit voltage of a donor-acceptor based organic solar cell device.
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Chapter 1: Introduction

The elaborate and efficient photochemical energy conversion processes exhibited by photosynthetic reaction centers has stimulated much research into the design and synthesis of supermolecular based artificial reaction centers which mimic most of the major aspects of photosynthetic solar energy conversion.\textsuperscript{1-4} Natural photosynthetic reaction centers constitute remarkable molecular-level photovoltaic devices which utilize essentially every incident photon to initiate a complex series of electronic transitions to achieve a high-energy charge separated state. The generation of this long-lived charge separated state is at the heart of photosynthetic energy conversion. The understanding of the fundamental photosynthetic electronic transition pathways, which include singlet-singlet energy transfer, triplet-triplet energy transfer, and photoinitiated electron transfer, has provided a firm platform for the development of chemical systems which duplicate such efficient energy conversion processes.\textsuperscript{1-4} 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; although, a myriad of non-covalent supramolecular dyads demonstrate light harvesting properties as well.\textsuperscript{5}

To emulate the light-absorbing property of chlorophylls, many artificial reaction centers feature porphyrins as the primary chromophore and electron donor. Modeling natural photosynthesis led to the inclusion of quinones as the electron acceptor among the earliest synthesized photosynthetic mimics.\textsuperscript{6} 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.\textsuperscript{4} Certain supermolecular triads incorporate a carotenoid moiety as a secondary electron donor in order to retard the charge recombination rate and thereby increase the lifetime of the charge-separated state.\textsuperscript{7} The above-mentioned considerations for the design of photosynthetic mimics led to the synthesis of a seminal CPC\textsubscript{60} molecular triad consisting of a diarylporphyrin (P) covalently linked to a carotenoid polyene (C) and a C\textsubscript{60} fullerene, which stands as an elegant demonstration of energy conversion with design and tuning precision achieved at the molecular level.\textsuperscript{7}
The development of efficient photovoltaic devices derived from small-molecule organic semiconductors is driven, in part, by an extensive tunability of molecular properties afforded by the wide chemical functionality characteristic of substituted organic molecules. The broad and diversified group functionalization possible for organic molecules has lead to a search for new materials designed at the molecular level where improvements in efficiency may be realized by modifying chemical functional groups to alter the solubility, optical, electrical, and morphological properties of solar cells.\textsuperscript{5} The tuning of these properties in OSCs through chemical functionalization contributed to significant improvements in power conversion efficiency achieved within a decade with an increase from 1\% to above 11\%.\textsuperscript{8, 9} Other advantages in developing OSCs as an efficient light-harvesting application for meeting increasing energy demands are a relatively simple synthesis, with great advances achieved in synthetic organic chemistry for pi-conjugated systems displaying attractive optoelectronic properties, and easy processability in manufacture.\textsuperscript{10} Additionally, pi-conjugated systems are excellent sensitizers with good absorption coefficients in the visible part of the solar spectrum.\textsuperscript{11, 12}

The two most common deposition processes for organic molecular semiconductors are thermal deposition methods and solution processing techniques.\textsuperscript{5, 8-10} Thermal vapor deposition processes allow for a highly reproducible thin film growth and for complete planar-heterojunction (PHJ) and bulk heterojunction (BHJ) solar cell device fabrication.\textsuperscript{5, 8-10} The main photomechanism of PHJ and BHJ organic solar cells originates at the donor-acceptor (D/A) interface, where photoinduced charge transfer may yield a sought-after charge-separated state.\textsuperscript{8, 10, 13-15} Whether this charge separated state contributes to the photocurrent of the OSC by becoming mobile charge carriers is a complex multi-parameter problem which depends on several interrelated factors such as favorable HOMO/LUMO D/A energy differences needed to drive the charge separation process, the exciton diffusion length, and the morphology and phase separation of the active donor-acceptor layer.\textsuperscript{9, 13, 14} The morphology impacts the overall solar cell performance in regard to charge transport properties, where the morphology of the active layer greatly influences the dissociation of Coulombic-bound excitons into charge carriers in the active bulk layer.\textsuperscript{5, 10, 13} Within any D/A morphology, improved interfacial charge separation is achieved
if molecular components are chosen such that an optimal energy offset between the LUMO of the donor and the LUMO of the acceptor is met.\textsuperscript{15}

As for solution-processed solar cell devices, a major challenge encountered is the synthesis of highly soluble donor and acceptor molecules that exhibit semiconductor properties, where many of the well-established molecular photo-sensitizers, such as phthalocyanines (Pc) and porphyrin molecules, exhibit a relatively low solubility and require environmentally inconvenient chlorinated solvents for solution processing.\textsuperscript{5} The use of water as a solvent in solution-processed solar cells presents the advantage of simplifying the device fabrication process. Recently, Jones and co-workers employed water-soluble tetrasulfonated copper Pc (CuPc-S4) donor molecules in the production of solar cell devices where the active area was prepared from aqueous CuPc-S4 solutions and the corresponding acceptor layer consisted of C\textsubscript{60} fullerenes.\textsuperscript{16} The devices showed a light-to-energy conversion of 0.32\% under standard conditions, with no contribution to device photocurrent from the CuPc-S4 donor. Subsequently, Torres and co-workers set out to overcome the low photocurrent contribution of water-soluble sulfonated Pc donor systems by varying the number of sulfonate substituents at the periphery of the zinc-Pc macrocycle with the aim of shifting the donor-acceptor frontier orbital energies.\textsuperscript{17}

Organic photovoltaics are close to becoming a largely deployed low cost alternative to inorganic photovoltaics. The idea of harvesting energy from a source that is abundant, inexpensive, and environment-friendly such as sunlight has led to the synthesis of a large number of molecular photovoltaics (dyads, triads, tetrads, hexads, etc.) and organic bulk heterojunctions.\textsuperscript{8, 10} Such systems typically consist of a donor, which generally absorbs light and creates an exciton. The photoexcited electron in the donor is subsequently transferred to the acceptor to form a charge transfer (CT) state. One of the crucial quantities that plays a role in the efficiency of organic solar cells is the open circuit voltage, which depends on the difference of energies of the frontier orbitals of donor and acceptor and the exciton binding energy.\textsuperscript{15} Increasing the open circuit voltage by choosing appropriate donor and acceptor components is an active area of research. Theoretical calculations, particularly based on the first principles, can play an important role in the selection of appropriate donors and acceptors to
enhance the open circuit voltage and/or in understanding and designing the photovoltaics with higher efficiency.

Many different light-harvesting organic chemical systems have been designed and studied in recent years with the aim of use in organic photovoltaic devices. One such class of systems is the supramolecular donor-acceptor dyad, which has been synthesized in various compositions and tested for efficient photovoltaic properties. Early studies on polymer-fullerene blends led to the development of bulk heterojunction solar cells using highly-conjugated donor and acceptor systems. The natural light-harvesting systems, in turn, inspired the use of porphyrins and metalloporphyrins as donors. The porphyrin or metalloporphyrin system acts as a chromophore. The combination of porphyrins and fullerenes is one of the most extensively studied organic donor-acceptor pairs and parallels the potential in efficiency of the other widely studied photovoltaic systems such as polymer/fullerene blends. Various factors which contribute to the electron-transfer efficiency and the lifetime of the charge separated state are the donor-acceptor distance and relative orientation, electronic coupling, solvent polarity, nature and type of linker, and the nature of the bonding interaction between the fullerene and porphyrin systems. In a majority of the porphyrin-fullerene (PF) complexes, the fullerene is linked to the porphyrin through a variety of linker molecules but the final structure often shows a pi-pi stacking between the flat porphyrin surface and the curved fullerene surface. The center-to-center distance in these systems is from 6.5 Å to 7.0 Å. Some dyad conformers are predicted to be conformally mobile with the porphyrin moiety swinging back and forth from one side of the fullerene to the other.

The present research involves the study of donor-acceptor dyad and triad complexes from a charge transfer energy perspective. The aim of the present research is to provide insight and predictive understanding into the charge transfer processes of the molecular-level components in donor-acceptor based organic solar cells using computational methods to describe photochemical processes at the quantum mechanical level within the Density Functional Theory (DFT) approximation. Predictive understanding is anchored in reproducing experimental results, wherein the present study a perturbative excited-state DFT method is described in detail and shown to give CT energies in excellent agreement with benchmark experimental data. With an accurate excited state method for calculating CT excitation
energies at hand, the present research applies the method to the study of D/A pairs employed in photovoltaic devices. The current study examines the effect on the CT energetics of varying the donor and acceptor component in the dyad and the changes in the frontier orbital energy levels and CT energies with respect to a varying D/A distance and D/A relative orientation. The results of the perturbative excited state DFT calculations provide direct insight into photovoltaic device efficiency since the CT energy determines the achievable open circuit voltage of a device.

The remainder of the work will be divided into six different major chapters. A background chapter describes the concept of a charge-transfer complex and certain challenges faced in the computational study of CT transitions. For example, several traditional theoretical methods account for an accurate description of excited states by constructing a wavefunction that spans several electronic configurations, but such methods are not practical for the study of many of the large molecular systems currently employed in photovoltaic devices. As an alternative excited state method, the time-dependent formalism of Density Functional Theory (DFT) has become a widely used approach in the study of excited states but is limited to small and medium sized molecules when range-correction schemes, necessary to achieve good accuracy for CT excitations, are employed.

In the third major chapter, a method is outlined that offers a practical way to obtain excitation energies from a self-consistent ground state Hamiltonian and Kohn-Sham DFT orbitals. This perturbative approach is used to compute the lowest charge transfer excitation energies for a set of tetracyanoethylene (TCNE)-hydrocarbon complexes, \( \text{C}_2\text{H}_4\text{-C}_2\text{F}_4 \), \( \text{NH}_3\text{-F}_2 \), pentacene-\( \text{C}_{60} \), and (tetraphenyl)porphyrin-\( \text{C}_{60} \) complexes. The results show that the method can provide a reliable description of charge transfer excitation energies, which are comparable to that obtained by time-dependent density functional theory (TDDFT) using specially optimized range-corrected functionals. By examining the performance of this method in obtaining charge transfer excitation energies for a benchmark set of donor-acceptor complexes, it is shown that the perturbative-\( \Delta \text{SCF} \) (P\( \Delta \)SCF) method can provide a good description of charge transfer excitation energies for DA complexes and has potential to be used in the computational screening of suitable donor-acceptor complexes with target charge transfer excitation energies.
The fourth major chapter applies the perturbative-ΔSCF (PΔSCF) excited state method developed in the previous chapter to porphyrin-fullerene donor-acceptor pairs in a detailed study of charge transfer energetics in large molecular systems of interest in current photovoltaic applications. Porphyrin and fullerene donor-acceptor complexes have been extensively studied for their photoinduced charge transfer characteristics. This chapter details a study of the electronic structure of ground states and a few charge transfer excited states for four co-facial porphyrin-fullerene molecular constructs using density functional theory at the all-electron level with large polarized gaussian basis sets. The donors are base- and Zn-tetraphenyl porphyrin and the acceptor molecules are C_{60} and C_{70}. The complexes reported here are non-bonded with a face-to-face distance between the porphyrin and the fullerene of 2.7 Å to 3.0 Å. The energies of the low lying excited states including charge transfer states were calculated using the perturbative excited state method and are in good agreement with available experimental values.

The fifth major chapter examines the effect of geometrical orientation on the charge transfer energetics of supramolecular (tetraphenyl)-porphyrin/C_{60} dyads. The charge transfer (CT) excited state energies of donor-acceptor (D/A) pairs determine the achievable open-circuit voltage of D/A-based organic solar cell devices. Changes in the relative orientation of donor-acceptor pairs at the interface influence the frontier orbital energy levels, which impacts the dissociation of bound excitons at the D/A-interface. This chapter entails a study of the effect of relative orientation on CT excited state energies of porphyrin-fullerene dyads, where the donors studied are base- and Zn-tetraphenyl porphyrin coupled to C_{60} as the acceptor molecule in an end-on configuration. A comparison is made between the energetics of a few low-lying CT states for the end-on geometry to the previously calculated CT energetics of the co-facial orientation. The calculated CT excitation energies are larger for the end-on orientation in comparison to the co-facial structure by 0.6 eV – 0.75 eV.

The sixth major chapter entails a study of the effect of varying the number and position of sulfonate substituent groups attached to the ZnPc molecule on the frontier orbital energies of the donor and the CT excitation energy of the corresponding donor-acceptor complex. Several low-lying Charge Transfer (CT) excited-state energies were calculated for four non-covalently bound dyads composed of a
sulfonated-ZnPc coupled to C₆₀. The results show that the di- and tri-sulfonated systems yield a CT state as the lowest-energy excited state in the system. In contrast, an energy re-ordering for the tetra-sulfonated ZnPc system leads to local excitations lying lower in energy than the CT state, displaying a possible deactivation pathway obstructing charge separation. Since several different donor-acceptor relative orientations may co-exist at an organic heterojunction, we compare the energetics of a few low-lying CT states for the end-on geometry of a di-sulfonated system to its co-facial orientation counterpart. The calculated CT excitation energies are larger for the end-on orientation in comparison to the co-facial structure by ~1.5 eV, which results principally from a substantial decrease in exciton binding energy in going from the co-facial to the end-on orientation. Furthermore, changes in relative donor-acceptor orientation have a larger impact on the CT energies than changes in donor-acceptor distance. TDDFT calculations on the various sulfonated ZnPc donor molecules show a significant splitting of the Q-band for only one of the four donor systems. The excited state calculations, in line with previous experimental studies, show that the systematic variation of chemical functional groups is a promising avenue for the substituent-level tuning of various physical properties of organic semiconductors.

The final chapter presents a detailed study of charge transfer (CT) excited states for a large number of structural conformations in a light-harvesting Carotenoid-diaryl-Porphyrin-C₆₀ (CPC₆₀) molecular triad. The molecular triad undergoes a 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 conformational flexibility of the CPC₆₀ triad impacts its dynamics in solvents. Since experimentally measured dipole moments for the triad of ~110 Debye (D) and ~160 Debye strongly indicate a range in conformational variability for the triad in the excited state, studying the effect of conformational changes on the CT excited state energetics furthers the understanding of its charge transfer states. The lowest CT excited state energies for a series of 14 triad conformers were calculated using the perturbative-∆SCF method, where the structural conformations were generated by incrementally scanning a 360 degree 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. The calculations show that structural conformational changes in the triad produce a variation of ~0.4 eV in CT excited state energies in the gas-phase. The corresponding calculated excited state dipoles show a range of 88 D – 188 D.
Chapter 2: Background

The formulation of a charge transfer complex in terms of stabilizing donor-acceptor molecular interactions was first introduced by Mulliken\textsuperscript{46} in resonance language, where the supramolecular chemical interaction was represented using the following resonance structures:

\[ D\cdots A \leftrightarrow D^+\cdots A^- ; \text{D=donor, A=acceptor} \]

This donor-acceptor resonance hybrid features a contribution from ionic (D\textsuperscript{+}/A\textsuperscript{−}) character, which accounts for the molecular association in the absence of a net charge and net dipole moment in each of the isolated monomers. In resonance terms, the energy to drive charge transfer complexation is derived from resonance stabilization. Such charge transfer (CT) interactions yield signature spectroscopic features upon photon absorption that are not present in the spectral bands of the isolated donor and acceptor system, which reflects the presence of associated D/A species.\textsuperscript{46} In many D/A systems, a relatively large intensity for the CT band allows for microstructural characterization of D/A aggregates in solution.\textsuperscript{18, 25, 35, 47} Among the earliest excited state spectroscopic studies of charge transfer complexes consisting of bound arene-halogen dimolecular systems revealed an intense spectral CT band near 3000\textsuperscript{A} characteristic of benzene and similar pi-conjugated systems.\textsuperscript{46} Understanding chemical properties related to the photoinduced D\textsuperscript{+}/A\textsuperscript{−} state is a major component in the development of efficient donor-acceptor based organic solar cells.

In studying photochemical properties central to photovoltaic device efficiency, such as photoinitiated charge transfer, the correct description of excited states is of paramount importance. Quantum chemical methods have developed a high level mathematical modeling sophistication and an accompanying efficient implementation in robust computational software which permits fast and reliable calculations of molecular properties to be run routinely on modest resource laptop and desktop computing architectures with results yielding remarkable accuracy (in comparison to experiment) for systems in the ground state. The reliable description of excited states, on the other hand, has posed a greater challenge to computational chemistry. The variational method, which may be considered the power underlying the accurate predictive power of quantum chemical methods for ground-state molecular properties, cannot be applied to excited state calculations in a straightforward manner.\textsuperscript{48}
Since such variational calculations bias the ground-state, representations of excited states derived from a favored ground state configuration tend to systematically overestimate excitation energies. Many semiempirical methods developed for the study of excited states incorporate the scaling of certain parameters to match the experimentally determined longest wavelength transition of a suitable reference system. For ab-initio methods, a reasonable description of excited states requires a relatively large and flexible basis set suitable for a simultaneous description of ground-state and excited-state configurations.

For theory to play an important role in the computational design of donor-acceptor complexes, a method is needed that can provide a reasonable description of excited states, particularly the charge transfer excited states, of these complexes. Accurate traditional quantum chemical methods such as Configuration Interaction (CI) or Multireference CI are impractical due to the size of the donor-acceptor complexes employed in currently developed photovoltaic cells, which typically contain about 100–200 or more atoms. The density functional theory (DFT) based calculations have played a central role in understanding various material properties and in the computational design of novel materials.\textsuperscript{49} The excited state description of systems containing about a hundred atoms is now routinely obtained using the time dependent density functional theory (TDDFT), particularly the linear response formulation of the DFT.\textsuperscript{50-55} Indeed, the time dependent density functional theory has become the workhorse for the calculations of excited states and optical spectra for a wide range of systems. This is due to the success of TDDFT in predicting vertical excited states with sufficient accuracy as well as its favorable scaling with system size compared to other accurate methods. Despite the favorable scaling, the TDDFT calculations using large or moderately large basis sets are rare on systems containing about 200 or more atoms.

The TDDFT method (employing popular exchange-correlation approximations) is of limited use in determining the excited states of donor-acceptor complexes. It is now well established that the TDDFT using standard exchange-correlation functionals significantly underestimates the charge-transfer excitation energies.\textsuperscript{56} This occurs due to a negligible overlap of donor-acceptor orbitals participating in the charge transfer excitations.\textsuperscript{56} Peach and co-workers have examined the correlation between the extent of overlap between the orbitals’ participation in the excitation and the error in the excitation
The development of suitable exchange-correlation functionals to correct for this deficiency is currently an active area of research. A few improvements such as the use of range separated hybrid functionals wherein the Kohn-Sham exchange functional is split into short-range and long-range components have been proposed. The range-splitting parameter is obtained either empirically by fitting to a large set of excitation energies of related systems, or non-empirically by minimizing the deviation of the negative of the highest occupied molecular orbital (HOMO) eigenvalue from the ionization energy. The desirable nonempirical attribute of the latter approach unfortunately results in a system dependent range splitting parameter. These range-split functionals can provide a good description of charge transfer energies for small donor-acceptor complexes. Their application to larger donor-acceptor complexes of practical interest are, however, limited. A constrained formalism of DFT is recently gaining popularity where a constraint is used to achieve a good description of the lowest charge transfer excitation.

The lowest charge transfer excitation energy for a donor-acceptor complex with infinite donor-acceptor separation is given by the energy

$$E_{CT} = \text{IP}^D - \text{EA}^A$$

where the IP$^D$ is the ionization energy of the donor molecule and EA$^A$ is the electron affinity of the acceptor molecule. For finite systems, the above equation gives the quasi-particle gap. To obtain the $E_{CT}$ for donor-acceptor complexes separated by a finite distance R, the Coulomb energy ($1/R$) corresponding to the electrostatic interaction between the charged donor-acceptor complexes must be added to the right hand side of equation 1. Both the ionization energy and the electron affinity can be accurately obtained by the difference of the self-consistent energies of neutral and charged complexes using standard DFT functionals. The Coulomb term needed to estimate $E_{CT}$ is usually obtained using the partial charges on the donor and acceptor in the Coulomb energy expression. As partial charges often show a strong dependence on the method used to obtain them, the excitation energies obtained by this approach can be error-prone.
Chapter 3: Perturbative \( \Delta \)-Self-Consistent-Field Excited State Method

To obtain the excitation energy, we first solve the ground state Kohn-Sham problem. A single Slater-determinant can be constructed from the single particle self-consistent lowest \( N \) Kohn-Sham orbitals \( \phi \) to describe the ground state wavefunction as

\[
\Psi \left( \left\{ r_n \right\} \right) = (-1)^p P(\phi_1 \phi_2 \cdots \phi_N)
\]

where \( N \) is the number of particles. The wavefunctions for single excitations can be constructed from occupied orbitals \( \phi_i \) and the unoccupied orbitals \( \chi_i \) as

\[
\Phi_{\text{ex}} = (-1)^p P(\phi_1 \phi_2 \cdots \phi_h \cdots \phi_N, \cdots, \chi_p)
\]

where subscripts \( h \) and \( p \) refer to the hole and particle states. The ground state density \( \rho_g \) is determined by the Kohn-Sham orbitals with occupancy \( f \) as \( \rho_g = \sum_i N_i |\phi_i|^2 \). Rigid occupancy shift yields a trial density of an excited state \( \rho_{\text{ex}} = \rho_g - \rho_h + \rho_p \), where \( \rho_h = |\phi_h|^2 \) and \( \rho_p = |\phi_p|^2 \). The self-consistent ground state single-particle Hamiltonian is \( H_g = H(\rho_g) \). The excited state Hamiltonian similarly can be expressed as \( H_{\text{ex}} = H(\rho_{\text{ex}}) \). However, \( H_{\text{ex}} \) thus calculated is not self-consistent. Varying the density as in a self-consistent procedure can lead to a collapse of the second set of orbitals to the first.\(^{65}\) Gill and co-workers have described a maximum overlap method to circumvent the variational collapse and have applied it to study core excitations in a set of small molecules.\(^{66}\) The present approach is an alternative to the the maximum overlap method. In our approach, we impose an orthogonality condition, which is a natural constraint in many-body theories or in equiensemble DFT. The ground state wavefunction will be orthogonal to the excited state wavefunction constructed from the Kohn-Sham orbitals if \( \langle \phi_h | \phi_j \rangle \) for \( j \neq h \). In practice, we adopt a perturbative approach to relax the active and passive occupied orbitals. The perturbation Hamiltonian is expressed as the difference between the ground state Hamiltonian \( H_g \) and the excited state Hamiltonian \( H_{\text{ex}} \) as follows:

\[
H = \alpha(H_{\text{ex}} - H_g)
\]
Here, $\alpha$ is a variational parameter such that $dE/d\alpha=0$, where $E$ is the total energy of the system. $\phi_h$ and $\chi_p$ are the active hole and particle orbitals. If these orbitals are held rigidly then they are automatically orthogonal to the perturbed orbitals. This is, however, unphysical as these orbitals will rearrange due to the change in Coulomb repulsion. The perturbed occupied passive orbitals are changed as

$$
\left| \phi'_k \right> = \left| \phi_k \right> + \sum_{j>N}^{\text{unoccupied}} \frac{\alpha \left< \chi_j \left| \Delta H \right| \phi_i \right> \chi_j}{\epsilon_j - \epsilon_i}
$$

The $\phi$ orbitals thus calculated are non-orthogonal and need to be orthogonalized.

Instead of holding the active orbitals rigid, which will be an unphysical constraint on the orbitals, it is possible to refine the method further by relaxing the particle orbital in the space of the unoccupied orbitals. This approach is intuitively more correct since it is unreasonable to expect the particle orbital to be an eigenfunction of the ground state Hamiltonian. For example, in the cases where the excitation involves charge transfer from one part of the system to another, this constraint cannot be a valid assumption. The energy minimization with respect to $\alpha$ allows orbital relaxation effects to be taken into account and is necessary for the accurate estimation of the excitation energy. The excited states can then be expressed as

$$
\Phi_{ex} = (-1)^p P\left( \phi'_1 \phi'_2 \ldots \phi'_h \ldots \phi'_N ; \chi'_p \right)
$$

where

$$
\left| \chi'_p \right> = \left| \chi_p \right> + \sum_{j \neq p} \frac{\alpha \left< \chi_j \left| H \right| \chi_p \right>}{\epsilon_j - \epsilon_p} \left| \chi_j \right>
$$

Here, $j$ goes over all the unoccupied orbitals. Similarly, the hole orbital is also expanded as

$$
\left| \phi'_h \right> = \left| \phi_h \right> + \sum_{j \neq h} \frac{\alpha \left< \phi_j \left| H \right| \phi_h \right>}{\epsilon_j - \epsilon_h} \left| \phi_j \right>
$$
Here, \( j \) goes over all the occupied orbitals. The updated active and passive orbitals are orthogonalized using Lowdin’s orthogonalization scheme.\(^{67}\) The orthogonality between the ground state and the individual excited states is maintained since \( \langle \phi_h | \phi_i \rangle = 0 \) for \( i \neq h \) and \( \langle \phi_h | \chi_j \rangle = 0 \) for all \( j \).

The density is then calculated from the occupied passive and active orbitals as

\[
\rho' = \sum_j \left| \phi'_j \right|^2 + \left| \chi'_p \right|^2
\]

The energy is then calculated from the \( H(\rho') \) non-self-consistently. The same procedure is repeated with different values of \( \alpha \). From a set of \( \alpha \) and the corresponding total energies, the \( \alpha \) for lowest energy is determined. In this method, the excited state density is varied by varying the parameter \( \alpha \) using the Newton-Raphson method. As the diagonalization step is not required, the method is relatively inexpensive. The \( \alpha_{\text{lowest}} \) can be extracted from at least a set of three \( \alpha \) parameters. Application of the method to a large number of CT states of various DA complexes shows that the variational procedure in practice requires about 6–12 iterations with different values of \( \alpha \). In essence, an excited state wavefunction orthogonal to the ground state wavefunction is constructed and the total energy of the excited state is obtained variationally by optimizing the parameter \( \alpha \). As mentioned above, variation of the \( \alpha \) parameter allows relaxation of the occupied orbitals. Once the self-consistent energy is obtained, the excitation energy can be computed by subtracting the total energy of the excited state from the ground state energy. The method is thus based on the \( \Delta \)SCF method but unlike the standard \( \Delta \)SCF approaches, it avoids the variational collapse of the excited state. The method is subject to the same criticism as the standard \( \Delta \)SCF method and lacks a formal justification, in general, since many wavefunctions in principle can correspond to the ground state density, which is the starting point. The application of \( \Delta \)SCF approaches can be justified for the excitations to the lowest state of a given symmetry.\(^{68}\) Very recently, Cullen and co-workers described the relation between the adiabatic TDDFT and \( \Delta \)SCF method.\(^{48}\) In another recent study, Kowalczyk et al. noted comparable performance of the TDDFT and \( \Delta \)SCF methods in predicting vertical excitation energies of 16 organic dye molecules and demonstrated the \( \Delta \)SCF densities to be stationary densities of TDDFT within the adiabatic approximation.\(^{69}\) The \( \Delta \)SCF method,\(^{68, 70-72}\) which was the routine DFT method for obtaining excitation
energies\textsuperscript{73, 74} prior to the availability of TDDFT, is still being widely used.\textsuperscript{66, 69, 75-81} Very recently, the ΔSCF method was extended to solids and was shown to give accurate estimates of band gaps for solids.\textsuperscript{82} There are variants of ΔSCF schemes known as constrained DFT in the literature. The present method, which uses an orthogonality constraint to prevent variational collapse, is one among these. An alternative route to obtain CT energies (CTE), known as constrained DFT (CDFT), uses a bias potential, which is varied until certain constraints on electrons are satisfied.\textsuperscript{64} Typically, in this approach the potential in the desired part of the system is lowered until expected charge transfer occurs. In Sec. III, we show that the present approach allows the calculation of CT energies without the use of any additional constraints except for the orthogonality constraint.

3.1 RESULTS AND DISCUSSION

The above method is implemented in the NRLMOL (Naval Research Laboratory Molecular Orbital Library) suite of codes.\textsuperscript{83-85} The cost of obtaining a variational solution for the excited state is about the same as that for the ground state. The difference with respect to the ground state calculation is that the diagonalization step is replaced by the energy minimization step. Typically, as mentioned above, the solution is obtained in 6–12 steps. The memory demand for the excited state calculation is much larger than the ground state calculation as the ground state Hamiltonian matrix needs to be stored. The virtual states also need to be stored in memory unlike the ground state calculation. In our several calculations using this method, we have noticed that the memory requirement becomes an issue only when the total number of basis functions exceeds 10,000 – 11,000. To assess the accuracy of the present method in predicting the charge transfer excitation energies, we have calculated the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) charge transfer excitation energies for a set of TCNE-hydrocarbon based donor-acceptor complexes, C\textsubscript{2}H\textsubscript{4}-C\textsubscript{2}F\textsubscript{4}, NH\textsubscript{3}-F\textsubscript{2}, pentacene-C\textsubscript{60}, and tetraphenylporphyrin-C\textsubscript{60} complexes. The TCNE-hydrocarbons have been used in the literature as a benchmark set to assess the success of various approaches proposed for the CT excited state calculations.\textsuperscript{62} In our calculations, we used the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation\textsuperscript{86} (GGA) to describe exchange-correlation effects and employed a large
The structures of the TCNE-hydrocarbon complexes were obtained from a previous study. To obtain the excitation energy, an electron from the HOMO is placed in the LUMO orbital and the self consistent problem is solved using the method described above. 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
TABLE I. The HOMO to LUMO charge transfer excitation energies in TCNE hydrocarbon complexes, the C\textsubscript{5}H\textsubscript{4}C\textsubscript{2}F\textsubscript{4}, NH\textsubscript{3}-F\textsubscript{2}, pentacene-C\textsubscript{60}, and the tetrphenyl porphyrin (TPP)-C\textsubscript{60} complexes. The numbers in the round bracket in the first column correspond to the distance between donor and acceptor unit. The asterisk and (S) indicate that the values are in gas-phase and in solution for TCNE-hydrocarbons. All energies are in eV. See text for experimental values and more details.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Mixed</th>
<th>Triplet</th>
<th>2M-T</th>
<th>2M-T-0.3</th>
<th>Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCNE-benzene**</td>
<td>3.61</td>
<td>3.59</td>
<td>3.63</td>
<td>3.8</td>
<td>3.59</td>
</tr>
<tr>
<td>TCNE-napthalene**</td>
<td>2.53</td>
<td>2.34</td>
<td>2.72</td>
<td>2.7</td>
<td>2.6</td>
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<tr>
<td>TCNE-toluene**</td>
<td>3.24</td>
<td>3.06</td>
<td>3.42</td>
<td>3.4</td>
<td>3.36</td>
</tr>
<tr>
<td>TCNE-xylene**</td>
<td>2.99</td>
<td>2.93</td>
<td>3.05</td>
<td>3</td>
<td>3.15</td>
</tr>
<tr>
<td>TCNE-anthracene(S)</td>
<td>1.81</td>
<td>1.67</td>
<td>1.95</td>
<td>1.82</td>
<td>1.73</td>
</tr>
<tr>
<td>TCNE-9-10-dimeth-anth(S)</td>
<td>1.56</td>
<td>1.48</td>
<td>1.64</td>
<td>1.77</td>
<td>1.44</td>
</tr>
<tr>
<td>TCNE-9-cmo-anth(S)</td>
<td>1.95</td>
<td>1.71</td>
<td>2.19</td>
<td>1.84</td>
<td>1.84</td>
</tr>
<tr>
<td>TCNE-9-10ch-anth(S)</td>
<td>2.13</td>
<td>1.93</td>
<td>2.33</td>
<td>1.96</td>
<td>1.96</td>
</tr>
<tr>
<td>TCNE-9-form-anth(S)</td>
<td>2.09</td>
<td>1.88</td>
<td>2.3</td>
<td>1.95</td>
<td>1.9</td>
</tr>
<tr>
<td>TCNE-9-meth-anth(S)</td>
<td>1.69</td>
<td>1.54</td>
<td>1.84</td>
<td>1.71</td>
<td>1.55</td>
</tr>
<tr>
<td>TCNE-9-chloro-anth(S)</td>
<td>1.87</td>
<td>1.68</td>
<td>2.06</td>
<td>1.82</td>
<td>1.74</td>
</tr>
<tr>
<td>TCNE-9-cyano-anth(S)</td>
<td>1.91</td>
<td>1.80</td>
<td>2.02</td>
<td>2.03</td>
<td>2.01</td>
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<td>C\textsubscript{5}H\textsubscript{4}C\textsubscript{2}F\textsubscript{4} (8 Å)</td>
<td>10.5</td>
<td></td>
<td>12.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{5}H\textsubscript{4}C\textsubscript{2}F\textsubscript{4} (25 Å)</td>
<td>11.78</td>
<td>11.92</td>
<td>.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{5}H\textsubscript{4}C\textsubscript{2}F\textsubscript{4} (100 Å)</td>
<td>12.2</td>
<td>12.36</td>
<td>.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH\textsubscript{3}-F\textsubscript{2} (8 Å)</td>
<td>9.22</td>
<td>9.19</td>
<td>9.25</td>
<td>9.49</td>
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</tr>
<tr>
<td>Pentacene-C\textsubscript{60} (20 Å)</td>
<td>3.10</td>
<td>3.19</td>
<td>.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pentacene-C\textsubscript{60} (100 Å)</td>
<td>3.47</td>
<td>3.77</td>
<td>.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPP-C\textsubscript{60} (20 Å)</td>
<td>3.27</td>
<td>3.30</td>
<td>.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The energy of the singlet state can be obtained using the Ziegler-Rauk method\textsuperscript{71} by subtracting the triplet energy from two times the energy of the mixed state. The calculated energies of the mixed, singlet, and triplet states for a few donor-acceptor complexes are given in Table I. The gas phase experimental values are available for the TCNE-benzene, TCNE-napthalene, TCNE-toluene, and TCNE-xylene complexes (marked by double asterisk in Table I).\textsuperscript{88} The calculated excitation energies of these complexes are in excellent agreement with experimental values.\textsuperscript{88} For the other TCNE-complexes for which experimental excitation energies are in solvent, we included an average solvent shift of 0.3 eV as estimated by Baer and co-workers.\textsuperscript{62} The calculated excitation energies, when corrected for solvent effects, are again in excellent agreement with experimental values. We have also included the TDDFT results with range corrected functionals reported by Baer and co-workers. Present values of excitation energies agree well with the TDDFT results. The method thus provides an alternative to
computationally more demanding approaches such as TDDFT with specially optimized range-corrected functionals.

The CT excitation energy of the C$_2$H$_4$-C$_2$F$_4$ dimer is another difficult case for theories.$^{55, 63}$ Tawada and co-workers found that the CT energy of the C$_2$H$_4$-C$_2$F$_4$ dimer using a range-corrected functional agrees well with the experimental estimate of 12.5 eV at infinite separation.$^{63}$ This experimental value (12.5 eV) is estimated using the the experimental IP of C$_2$H$_4$ (10.7 eV) and the experimental EA of C$_2$F$_4$ (−1.8 eV) and using the relation IP$^D$ − EA$^A$ − 1/R, where R is the distance between donor and acceptor. We have calculated the CT energies of the C$_2$H$_4$-C$_2$H$_4$ complex keeping the separation between the two units at 8 Å and 25 Å. The calculated excitation energies at these distances are 10.49 eV and 11.78 eV, which are in excellent agreement with the experimental estimates of 10.7 eV and 11.9 eV, respectively. The complex NH$_3$-F$_2$ was included by Zhao and Truhlar as a test case for the prediction of CT energy.$^{55}$ Our calculated CT excitation energy for this complex is 9.25 eV, which is in very good agreement with 9.49 eV calculated at the the SAC-CI/6-31+G(d,p) level of theory by Zhao and Truhlar.$^{55}$ They have calculated the CT energy of NH$_3$-F$_2$ at various levels of approximation that includes TDDFT/PBE0, TDDFT/B3LYP, M06-HF, etc. and have found the M06-HF functional to be the most accurate among those tested. The errors for the B3LYP and PBE0 functional are about 5–6 eV. Thus, it is gratifying that the present method can provide a fairly accurate estimate of the CT energy.

Finally, we applied the present approach to the systems that have been used experimentally as possible material for the active layer in organic photovoltaic cells. We selected two donor acceptor complexes: pentacene-C$_{60}$ and a larger tetraphenylporphyrin (TPP)-C$_{60}$ complex (cf. figure2). One of the criteria for the selection of these complexes was the availability of gas-phase experimental ionization energies of pentacene and TPP and the electron affinity of the C$_{60}$ fullerene from which an experimental estimate of the CT excitation energy can be obtained. Porphyrin and phthalocyanine derivatives are often used as electron donors in organic photovoltaic (OPV) cells while the pentacene-C$_{60}$ is a simple prototype system of OPV that has been extensively studied. The ionization energy (gas phase) of pentacene is 6.59 eV and the C$_{60}$ electron affinity is 2.68 eV.$^{89}$ Thus, at infinite intramolecular
Figure 2. The pentacene-C$_{60}$ and tetraphenyl porphyrin-C$_{60}$ complexes in end-on orientation. The electron densities of the HOMO (blue) and the LUMO (red) orbitals are shown.

separation of donor and acceptor in the pentacene-C$_{60}$ complex, the CT energy is 3.91 eV. At finite separation R, this CT energy estimate will decrease due to the Coulomb interaction term $-1/R$. We calculated the CT energy of the pentacene-C$_{60}$ complex at three intramolecular separations in the DA complex. In this DA complex, the C$_{60}$ and pentacene are placed in an end-on form. The HOMO is on pentacene and the LUMO is on the C$_{60}$ fullerene, the lowest HOMO-LUMO transition is therefore a CT excitation. In general, the active layer in an OPV solar cell is deposited using spin coating and will have a mixture of several different orientations of the donor and acceptor molecule. Here, we chose an end-to-end orientation as the polarization effects are reduced in this orientation. The polarization effects will
change the HOMO and LUMO levels of the molecules and are difficult to include in the experimental estimate. We computed the CT excitation energy of the pentacene-C$_{60}$ complex at 20 Å and 100 Å. The calculated CT energies are 3.10 eV and 3.47 eV, respectively. The excitation energy increases with distance due to a reduction in the attractive Coulomb energy between the hole and particle. The calculated CT energies are in very good agreement with experimental estimates of 3.19 eV and 3.77 eV.

Likewise, we have calculated the CT energy of a TPP-C$_{60}$ complex. The experimental gas-phase ionization energy of TPP is 6.7 eV. Using the experimental EA of C$_{60}$ (2.68 eV), the CTE for the infinitely separated TPP-C$_{60}$ complex is 4.02 eV. Like in the pentacene-C$_{60}$ complex, the TPP and C$_{60}$ were placed in the end-on manner and the CTE was calculated at a distance of 20 Å. The lowest CT excitation here corresponds to the transition from the HOMO, which is localized on TPP, to the LUMO that sits on the C$_{60}$ fullerene. Our calculated CTE value of 3.27 eV is in excellent agreement with the experimental estimate of 3.30 eV. Thus, the present method provides fairly accurate estimates of CT energy for this complex. It is evident from Table I that overall, the performance of the present method in predicting CT energies is quite good. For the gas phase TCNE-hydrocarbon complexes, the maximum error is on the order of 0.1 eV. In case of TCNE-hydrocarbon complexes in the solvent, the maximum error is about the same as in gas phase except for TCNE-9-cyano-anth complex for which it is about 0.3 eV. It is interesting to note that the structure for the TCNE-9-cyano-anthracene system is the only complex which does not exhibit the general structural motif consisting of the TCNE component centered above the geometric center of the anthracene (cf. Fig. 1(l)). We have also noted that the forces are high for this structure at the PBE-GGA level. For that structure, the discrepancy between our calculated energy and both experiment and TDDFT was quite high (∼0.65 eV). We have therefore further optimized the structure and obtained a more symmetric structure. The calculated HOMO-LUMO CT energy for this complex is 2.02 eV. Inclusion of the average solvent shift of 0.3 eV reduces the CT energy to 1.72 eV. The discrepancy between the experimental value and our calculated value reduced from 0.65 eV to 0.29 eV. Thus, for the set of molecules studied here, the error is at most 0.3 eV, which is far less than that in TDDFT calculations using standard functionals. Particularly encouraging is the good agreement between experimental estimates of excitation energies with the predicted values for
the pentacene-C\textsubscript{60} and TPP-C\textsubscript{60} systems as they are representative models of an active organic layer used in OPVs. This agreement may improve as experimental estimates do not include the polarization effects that would alter the HOMO and LUMO levels upon complex formation. In a recent work, the $\Delta$SCF method was shown to provide good estimates of vertical excitations in dye molecules.\textsuperscript{69} This work shows that the present method, which is a variant of the $\Delta$SCF scheme that prevents variational collapse, can provide good estimates of the CT excitation energies, which are particularly challenging to obtain for systems containing a few hundred atoms. The success of the present approach over TDDFT is probably related to the recent observation by Ziegler and co-workers that the $\Delta$SCF schemes include the higher order self-interaction terms that are missing in TDDFT for a qualitatively correct description of the charge transfer excitations.\textsuperscript{48}

To summarize, we have illustrated our recent perturbative approach to obtain the CT excitation energies. The method has a strong constraint imposed by orthonormality that must hold for wavefunction-based methods or the equiensemble DFT formalism. The performance assessment of this method in predicting charge-transfer excitation energies has been carried out on a set of molecules that are used in the literature as a benchmark for this purpose and also on the models of an active layer in OPV cells. The method offers a practical way to obtain fairly accurate estimates of a large number of CT excited states of realistic donor-acceptor complexes (about 200–300 atoms) using modern petascale computers due to its embarrassingly parallel nature (calculation of one excited state is independent of others). As the open circuit voltage of the organic photovoltaic is proportional to the energy offset between the donor HOMO and acceptor LUMO, the method has a potential to play an important role in identifying suitable combinations of donor and acceptors. We are using this approach in our laboratory to study several large donor acceptor complexes.
Chapter 4: Charge Transfer Excitation Energies in Porphyrin-Fullerene Dyads

The photoinduced charge transfer process in a donor-acceptor conjugate involves two key steps. A local excitation takes place on the donor component of the dyad, which acts as the chromophore, followed by a transfer of the excited electron to the acceptor molecule. The electron transfer process can however involve more than two steps. In the absence of any hole-conducting layer, the hole state remains localized on the donor system. In order to provide insight into the CT process, it is necessary to employ a computational method which accurately calculates the energetics of the final charge separated excited state. The energy of a charge transfer state can be roughly estimated from
\[ E = IP - EA - 1/R \]
where IP and EA are, respectively, the ionization potential of the donor and the electron affinity of the acceptor. Here, R is the particle to hole separation. The density functional theory (DFT) is a computationally efficient and accurate method suitable for the study of donor-acceptor systems which are typically too large for quantum chemical approaches. However, the standard Kohn-Sham formulation of DFT is limited to the ground state. The linear response formulation of the time-dependent extension of DFT (TDDFT) is currently the method of choice to obtain excitation energies for systems containing a few tens of atoms. Though quite successful, in general, in describing the valence excitations it fails to correctly describe CT interactions with the currently available exchange-correlation functionals. The description of charge transfer excitations with sufficient accuracy is a challenge for the density functional based methods and is currently a topic of intense research. Range-corrected density functionals within TDDFT have shown to improve the poor description of charge transfer excitations by appropriately tuning the range splitting parameter. Although the use of range-corrected functionals, which incorporate a percentage of Hartree-Fock exchange, in TDDFT for CT excited-state calculations improves the accuracy, the method becomes quite expensive for large systems such as the porphyrin-fullerene (PF) supramolecular dyad. A recent study applied the constrained-DFT (C-DFT) method to calculate the HOMO-LUMO CT excitation energy in C_{70}/ZnTPP. The C-DFT approach imposes a constraining potential to enforce the localization of electron density.
The delta-self-consistent field (ΔSCF) method has been used by a number of authors for the calculation of various types of local excitations.\textsuperscript{66, 69, 73, 74, 78-80} We have developed and employed another ΔSCF type DFT based approach which enforces the constraint of orthogonality between the ground-state and excited-state Slater determinants constructed from Kohn-Sham orbitals.\textsuperscript{96} The orthogonality-constrained DFT method gave CT excited state energies for a carotenoid-porphyrin-C\textsubscript{60} molecular triad which are in good agreement with the estimate made from equation (1). An application of our method to a small database of molecules recently used in the calibration of a range-split functional shows excellent agreement with experimental values.\textsuperscript{97} In this study, we apply the perturbative ΔSCF (PΔSCF) method in the calculation of CT excited-state energies for a set of four porphyrin-fullerene supramolecular dyads.

4.1 Computational Method

The calculations reported here were carried out using density functional theory as implemented in the NRLMOL code.\textsuperscript{83, 87, 98, 99} We employed the Perdew-Burke-Ernzerhof (PBE)\textsuperscript{86, 100} exchange-correlation energy functional within the generalized gradient approximation for all sets of calculations. 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.\textsuperscript{87}

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 functions along with the range of the exponents are given in Table II. This basis set resulted in a total of 4300–4700 basis functions for four different complexes studied here. We have used our recently developed DFT based method to determine the energies of the excited states.\textsuperscript{96} The notable feature of this method is that it maintains the orthogonality constraint between the ground state and excited state Slater determinantal wavefunctions. This method uses a perturbative approach to determine the excited state orbitals and density and does not contain any empirical or system dependent parameters.
TABLE II. The numbers of s-, p-, d-type contracted functions, number of primitive gaussians, and the range of the gaussian exponents used for each atom.

<table>
<thead>
<tr>
<th>Atom</th>
<th>s-type</th>
<th>p-type</th>
<th>d-type</th>
<th>Primitives</th>
<th>Exponent Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>12</td>
<td>(2.22 \times 10^4 - 0.077)</td>
</tr>
<tr>
<td>H</td>
<td>4</td>
<td>3</td>
<td>1</td>
<td>6</td>
<td>(7.78 \times 10^{-10} - 0.075)</td>
</tr>
<tr>
<td>N</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>13</td>
<td>(5.18 \times 10^4 - 0.25)</td>
</tr>
<tr>
<td>Zn</td>
<td>7</td>
<td>5</td>
<td>4</td>
<td>20</td>
<td>(5.00 \times 10^6 - 0.055)</td>
</tr>
</tbody>
</table>

4.2 RESULTS AND DISCUSSION

Several experimental studies have shown that in the majority of porphyrin-fullerene supramolecular dyads the closest donor-acceptor interaction occurs between one of the electron-rich 6:6 fullerene bonds and the geometric center of the porphyrin/metalloporphyrin system.\(^{45}\) The corresponding distances are on the order of 2.7 Å – 3.0 Å. The porphyrin-fullerene structures employed for the study of CT excited states were taken from the Wang and Lin study where the PF dyads were optimized at the all-electron level using the PBE functional and double zeta polarization basis containing more than 1500 Slater type orbitals for each dyad.\(^{101}\) The fullerene-porphyrin dyad structure optimization requires use of van der Waals interaction potentials apart from the DFT description of the effective potential. Although most standard density functionals do not correctly describe van der Waals interactions, the relaxed geometries obtained by Wang et al. show that the porphyrin-fullerene relative orientations and distances are in agreement with experiment.\(^{45}\) From our DFT calculations we find that the forces on the geometries provided by Wang et al. are small (~0.2 eV/Å). Additionally, we performed a geometry optimization using NRLMOL on the C\(_{70}\)/ZnTPP dyad using the PBE exchange-correlation functional with the incorporation of Grimme’s general dispersion correction scheme.\(^{102}\) The resulting relaxed geometry did not differ significantly from the structures in Wang’s paper with no significant alteration of the porphyrin-fullerene center-to-center distances. Therefore, we performed only single point calculations on the rest of the structures. Figure 3 displays the ground state density of states (DOS) projected on the components for the supramolecular complexes. The density of the fullerene states does not vary appreciably in changing the donor from base tetraphenyl-porphyrin to Zn-
tetraphenyl-porphyrin. We, therefore, present the fullerene DOS only for the TPP complexes. The C\textsubscript{60} DOS shows very mild symmetry breaking in which the levels are split by a few meV. The reduced symmetry of the C\textsubscript{70} and a larger number of valence electrons results in a larger number of high lying occupied and low lying unoccupied states. Although the Zn states are found to be deeper in energy (not shown), the presence of the Zn in the porphyrin results in more valence states about 1 eV below the Fermi level. Experiments have shown that replacing C\textsubscript{60} by C\textsubscript{70} leads to better absorption due to the reduced symmetry of the fullerene.\textsuperscript{103-105}

Figure 3. The total density of states of the C\textsubscript{60}/TPP and C\textsubscript{60}/ZnTPP and projected DOS on the TPP, ZnTPP, and C\textsubscript{60} are shown in the left panels. The counterparts of C\textsubscript{70}/TPP and C\textsubscript{70}/ZnTPP are shown in the right panels.

In all of the dyads, the HOMO is localized on the porphyrin and the LUMO is localized on the fullerene component. The highest two occupied and lowest two unoccupied states of porphyrin are the Gouterman orbitals responsible for the characteristic absorption bands of the porphyrin.\textsuperscript{12} In all four
complexes the HOMO and HOMO-1 orbitals are the porphyrin occupied Gouterman orbitals. The isolated C\textsubscript{60} and C\textsubscript{70} fullerenes have five-fold degenerate HOMO orbitals. These orbitals form the HOMO-2 to HOMO-6 orbitals in the complexes with TPP and HOMO-3 to HOMO-7 in the complexes with ZnTPP. The HOMO-2 orbital of the ZnTPP complexes is localized on the porphyrin. In the complexes with TPP, several of these fullerene HOMOs are seen to spread over the porphyrin while the degree of hybridization is relatively less for the complexes with ZnTPP. The HOMO-LUMO gaps obtained from the Kohn-Sham DFT scheme lie between 0.83 eV and 1.02 eV. The dyads containing ZnTPP have smaller gaps compared to those with TPP. This result is in agreement with earlier published DFT calculations.\textsuperscript{106} The LUMO of isolated C\textsubscript{60} has t\textsubscript{1u} symmetry which is broken in these complexes. The isolated C\textsubscript{70} has doubly degenerate LUMO with e\textsubscript{1} symmetry and a closely lying LUMO+1 with a\textsubscript{1} symmetry. These orbitals form the lowest three LUMOs of the four complexes studied here. The HOMO to LUMO transition in all of the complexes is a charge transfer excitation. The HOMO-LUMO gaps do not reflect the correct energies for the charge transfer excitation partly as DFT underestimates the gap and partly because they do not incorporate the particle-hole interaction and the polarization of the passive orbitals. We have used our recently developed method to calculate the energies of several lowest excited states. A characteristic feature of these donor-acceptor systems is that the states associated with the electron transfer are spatially well separated with vanishing overlap. Consequently, the transition dipole matrix between the particle and hole states vanishes. In the following we concentrate on a few lowest charge transfer states spanning the hole orbitals from HOMO to HOMO-2 and the particle orbitals from LUMO to LUMO+3. In these complexes, the LUMO to LUMO+2 originate from the three-fold degenerate or nearly degenerate fullerene LUMO. Figure 4 shows a schematic representation of the C\textsubscript{60}/ZnTPP CT states for which the excited state energies were calculated. The left side of the figure shows the HOMO, HOMO-1, and HOMO-2 orbitals of the C\textsubscript{60}/ZnTPP complex localized on the donor ZnTPP component. The right side of the figure displays the LUMO, LUMO+1, and LUMO+2 orbitals localized on the acceptor C\textsubscript{60} component of the dyad. Since these orbitals are localized on their respective donor/acceptor component, the transitions (shown as arrows) correspond to CT excited states. The three lowest LUMOs studied here are nearly degenerate
Figure 4. The lowest few charge transfer excitation states and their energies in the C$_{60}$/ZnTPP dyad.

since they originate from the $t_{1u}$ LUMO of isolated C$_{60}$, which is also reflected in the excitation energies from a given occupied porphyrin orbital. The LUMO+3 orbital is located on the porphyrin and therefore the HOMO or HOMO-1 to LUMO+3 does not constitute a CT state. The porphyrin to porphyrin lowest singlet excitation (involving the Gouterman orbitals HOMO and LUMO+3) occurs at 1.97 eV and the lowest ZnTPP to C$_{60}$ charge transfer excitation state has energy 1.68 eV. There are only a few experimental studies on non-bonded porphyrin-fullerene dyads. The bulk of the experiments are performed on covalently linked systems. The experimentally derived energies of the charge transfer state of covalently linked C$_{60}$/ZnTPP vary from 1.24 eV to 1.38 eV depending on the linker, structure, and center-to-center distance between the C$_{60}$ and the porphyrin.$^{26, 38, 107}$ Since extended porphyrins often show changes in its electronic structure discerned from absorption spectra, the values of the charge
transfer states of a linked system cannot be compared directly with our calculated values.\textsuperscript{108, 109} Moreover, the calculated gas-phase values do not include the reorganization of the components and the effects of the solvents on the charge transfer excited state. A few low-lying CT excitations of \( C_{70}/\text{ZnTPP}, C_{70}/\text{TPP}, \) and \( C_{60}/\text{TPP} \) dyads are shown in figures 5, 6, and 7.

![Figure 5. The lowest few charge transfer excitation energies in the \( C_{70}\text{ZnTPP} \) dyad.](image)

The doubly degenerate \( e_1 \) and \( a_1 \) LUMOs of isolated \( C_{70} \) form the lowest unoccupied orbitals of the dyads containing \( C_{70} \). The lowest excitation in the \( C_{70}/\text{ZnTPP} \) occurs at 1.95 eV, which is higher than the lowest excitation of \( C_{60}/\text{ZnTPP} \) by 0.27 eV. Replacing the ZnTPP by base TPP increases the lowest excitation further roughly by another 0.1 eV for \( C_{70}/\text{TPP} \). Similarly, replacing the ZnTPP by
TPP in dyads containing C₆₀ increases the lowest CT energy by 0.1 eV. Replacing C₆₀ by C₇₀ increases the CT energy or the open circuit voltage by 0.27 eV. From these values it appears that changing the fullerene component produces a more significant change in the CT excitations compared to the change in porphyrin component. Our calculations indicate that the open circuit voltage of the C₇₀/TPP dyad is the largest among the four dyads studied here. It is known that C₇₀ containing donor-acceptor conjugates are more efficient since C₇₀ is also a better absorber than C₆₀. Our calculations show that energy loss in exciton separation is also reduced in C₇₀ containing PF conjugates. The energies of the excited states studied here are tabulated in Table III. In the table, the non-CT excited states are indicated by an asterix. We present energies for both singlet and triplet states of single particle excitations. The singlet energies are calculated from the values of the mixed and triplet states using the Ziegler-Rauk approach. In Table IV we show the DFT calculated ionization potentials of the donor and electron.
TABLE III. A few excited state energies for the four supramolecular dyads. The energies of the triplet states are given in parentheses. All energies are in eV.

<table>
<thead>
<tr>
<th>Transition</th>
<th>C60/ZnTPP</th>
<th>C70/ZnTPP</th>
<th>C60/TPP</th>
<th>C70/TPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO-2 → LUMO+3</td>
<td>2.88(2.86)</td>
<td>2.76(2.76)</td>
<td>3.15(3.11)</td>
<td>2.25(2.19)</td>
</tr>
<tr>
<td>HOMO-2 → LUMO+2</td>
<td>2.12(2.04)</td>
<td>2.31(2.31)</td>
<td>1.74(1.66)</td>
<td>1.86(1.76)</td>
</tr>
<tr>
<td>HOMO-2 → LUMO+1</td>
<td>2.13(2.07)</td>
<td>2.38(2.38)</td>
<td>1.73(1.61)</td>
<td>1.79(1.69)</td>
</tr>
<tr>
<td>HOMO-2 → LUMO</td>
<td>2.11(2.05)</td>
<td>2.45(2.39)</td>
<td>1.77(1.67)</td>
<td>1.78(1.72)</td>
</tr>
<tr>
<td>HOMO-1 → LUMO+3</td>
<td>2.26(2.06)</td>
<td>2.63(2.63)</td>
<td>2.27(2.07)</td>
<td>2.62(2.56)</td>
</tr>
<tr>
<td>HOMO-1 → LUMO+2</td>
<td>2.12(2.12)</td>
<td>2.23(2.23)</td>
<td>2.04(1.98)</td>
<td>2.39(2.37)</td>
</tr>
<tr>
<td>HOMO-1 → LUMO+1</td>
<td>2.12(2.12)</td>
<td>2.24(2.24)</td>
<td>2.04(2.00)</td>
<td>2.39(2.39)</td>
</tr>
<tr>
<td>HOMO-1 → LUMO</td>
<td>2.12(2.12)</td>
<td>2.28(2.28)</td>
<td>1.99(1.95)</td>
<td>2.46(2.46)</td>
</tr>
<tr>
<td>HOMO → LUMO+3</td>
<td>1.97(1.71)</td>
<td>2.36(2.36)</td>
<td>1.97(1.67)</td>
<td>2.29(2.23)</td>
</tr>
<tr>
<td>HOMO → LUMO+2</td>
<td>1.70(1.68)</td>
<td>1.98(1.98)</td>
<td>1.77(1.73)</td>
<td>2.09(2.07)</td>
</tr>
<tr>
<td>HOMO → LUMO+1</td>
<td>1.68(1.68)</td>
<td>1.95(1.96)</td>
<td>1.78(1.74)</td>
<td>2.05(2.05)</td>
</tr>
<tr>
<td>HOMO → LUMO</td>
<td>1.70(1.68)</td>
<td>2.00(2.00)</td>
<td>1.77(1.73)</td>
<td>2.13(2.13)</td>
</tr>
</tbody>
</table>

TABLE IV. The ionization potentials (IP) of the donor and electron affinities (EA) of the acceptor in isolation and in the four dyads studied here. All energies are in eV.

<table>
<thead>
<tr>
<th></th>
<th>TPP</th>
<th>ZnTPP</th>
<th>C60</th>
<th>C70</th>
<th>C60/TPP</th>
<th>C70/TPP</th>
<th>C60/ZnTPP</th>
<th>C70/ZnTPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>EA</td>
<td>2.69</td>
<td>2.67</td>
<td>2.65</td>
<td>2.65</td>
<td>2.56</td>
<td>2.61</td>
<td>2.56</td>
<td>2.61</td>
</tr>
<tr>
<td>IP-EA</td>
<td>3.47</td>
<td>3.56</td>
<td>3.59</td>
<td>3.59</td>
<td>3.56</td>
<td>3.56</td>
<td>3.59</td>
<td>3.56</td>
</tr>
</tbody>
</table>

affinity of the acceptor in isolation and in complexes. The results show that the fullerene LUMO is raised only marginally except for the C60/TPP complex, where it changes by 0.13 eV. On the other hand, the Zn-porphyrin HOMO is raised by as much as 0.22 eV in the C60/ZnTPP dyad but the change in the TPP HOMO is marginal and is lowered in C70/TPP. The upward shift of the Zn-porphyrin HOMO results in a reduction of the open circuit voltages in these dyads as the fullerene LUMO changes only marginally upon complexation. Overall, the IP-EA, which is the charge transfer energy at infinite separation, is largest for the C70/TPP complex. Experiments carried out by Mukherjee et al. report that
the CT excitations from the octadecyloxyphenyl-porphyrin to C$_{70}$ and to C$_{60}$, respectively, occur at 1.70 eV and 1.79 eV in toluene.$^{111}$ They also observed that replacing toluene by chloroform, which is a more polar solvent, increases the CT excitation energies by only 5–7 meV. This is in contrast to the solvent effects observed for covalently linked C$_{60}$ and Zn-porphyrin.$^{47}$ While our calculated C$_{60}$/TPP CT excitation energies are in excellent agreement with experiment and earlier TDDFT calculations with B3LYP, those of C$_{70}$/TPP are higher than experiment by 0.3 eV. The experimental charge transfer energies for covalently linked C$_{60}$/TPP range from 1.48 eV to 1.75 eV in various polar and non-polar solvents.$^{26, 35}$ For covalently linked ZnP-C$_{60}$ dyads with face-to-face topology, this energy can vary between 1.27 eV – 1.86 eV depending on solvent polarity, topology, and linker.$^{11, 23, 25, 37, 112}$ We

Figure 7. The lowest few charge transfer excitation energies in the C$_{60}$TPP dyad.
emphasize that our calculations are done on gas-phase dyad molecules, ignore ionic relaxations upon excitation and all effects of solvents. The polarization effect of the solvents, particularly in polar solvents, will be crucial since the solvents will produce a reaction field which will stabilize the CT excited states. The ground state dipole moments of the dyads are from 1.8 Debye for ZnTPP-containing dyads to 2.8 Debye for the TPP-containing ones. The excited state dipole moments for the HOMO to LUMO excitation are between 19.9 Debye for C$_{60}$-containing dyads to 21.4 Debye for C$_{70}$-containing dyads. Since the excitation energies calculated in this work are vertical without any ionic relaxation, the dipole moments only show the rearrangement in electronic density. The discrepancy between the calculated values and experimental values for the C$_{70}$/TPP dyad requires more investigation incorporating solvents which is being pursued in our laboratory.

Another property of interest for exciton splitting in such donor-acceptor systems is the interfacial dipole moment. The calculation of an interfacial bilayer as will be present in an OPV is beyond the scope of the present work. However, we have calculated the ground state interfacial dipole moments as a function of the distance between the porphyrin-fullerene components. The ground state dipole moment near equilibrium separation indicates the formation of interfacial dipoles which can help align the orbitals and thus facilitate exciton dissociation. The ground state dipole moments of the four dyads are plotted as a function of porphyrin-fullerene separation in the lowest panel in figure 8. The direction of the dipoles is from the fullerene to the porphyrin. The dipole can originate from charge transfer from porphyrin to fullerene and due to polarization. Ground state charge transfer in covalently linked porphyrin-fullerene face-to-face complexes was also proposed by Armaroli et al. to explain the broadening of the dyad absorption spectrum toward the low energy region. Wang et al. also estimated a small ground state charge transfer from porphyrin to fullerene. The ground state charge transfer will decrease with increasing separation between the components and at large distances the polarization is mostly responsible for the dipole formation. In figure 9 we show an isosurface of difference of ground state electron density of the dyad at equilibrium separation from the densities of the isolated components. The blue (pink) surface shows the regions where density difference is negative (positive). From the figure it is seen that substantial charge redistribution takes place on the fullerene
Figure 8. The ground state dipole moments and charge transfer excitation energies as a function of donor-acceptor separation.

We have also calculated the lowest HOMO to LUMO excitation energies for these four systems as a function of the porphyrin-fullerene separation. The top panel of figure 8 shows the charge transfer excited state energies for the four dyads studied here. The asymptotic behavior of the curves shows the 1/R behavior of the particle-hole interaction. Due to the ground state dipole formation, the CT excited state energy curve does not exactly fit the equation IP-EA-1/R in the near region. The interfacial dipoles shift the vacuum levels of the donor and the acceptor molecules leading to shifts in the values of the IP and EA. In summary, we have studied the electronic structure of the ground and several charge transfer excited states of a set of four donor-acceptor dyads where the donors are base-tetraphenylporphyrin and Zn-tetraphenylporphyrin and the acceptor choices are C_{60} and C_{70}. Our DFT calculations on these non-
covalently bonded dyads show that the acceptor choice has a more significant impact on the charge transfer energy and therefore on the open-circuit voltage than the donor component among the choices studied here. The lowest CT excitations in C$_{70}$-containing complexes are higher by 0.27 eV compared to their C$_{60}$-containing counterparts. The C$_{70}$/TPP dyad has the highest open-circuit voltage among the four dyads. We also find that the Zn-porphyrin ionization potential shows large changes when paired with a fullerene. The HOMO of ZnTPP is raised up to 0.22 eV upon complex formation. Such an effect can lower the open-circuit voltage since the electron affinities of both C$_{60}$ and C$_{70}$ show marginal change upon complex formation. A small interfacial dipole pointing from the fullerene to the porphyrin exists in the dyads. The dipole moment decreases with increased separation between the two components. At large separation, the chief contribution to the dipole formation is from polarization whereas at closer range small charge transfer from porphyrin to fullerene also takes place. Our calculated excited state energies show 1/R behavior in the asymptotic region.

Figure 9. The difference in ground state density of the C$_{60}$/TPP dyad and its isolated components
Chapter 5: Effect of Geometrical Orientation on Charge Transfer Energetics

Organic systems are promising candidate materials for achieving efficient functionality in energy-generating applications such as photovoltaic devices. One such class of photovoltaics makes use of supramolecular chemical interactions, such as pi-pi stacking, dispersion forces, interface-polarization, and charge-transfer for the fabrication of ordered and layered molecular architectures capable of orienting various donor-acceptor complexes into structural configurations which facilitate charge transfer excitations. The fundamental photo-conversion process in donor-acceptor based photovoltaic devices is generating mobile charge carriers by separating the photo-excited particle-hole states through a conduction band. One realization of this idea takes form in the fabrication of multi-component assemblies of donor-acceptor pairs adsorbed on metal surfaces. In a “bottom-up” approach, a 2-D binary molecular layer composed of donor-acceptor pairs may be synthesized beginning with the chemical deposition of a layer of donor-chromophoric molecules or acceptor molecules onto a metal surface. Recently, Bonifazi and co-workers synthesized various supramolecular assemblies formed from chromophore-substrate interactions involving porphyrin molecules adsorbed on the Ag (110) and Ag (111) metal surfaces. In this study, non-covalent attractive interactions between the C\textsubscript{60} and porphyrin moieties were exploited in the construction of selectively engineered periodic binary supramolecular assemblies on silver surfaces. Structural characterization performed by scanning probe methods, such as STM, revealed that 2D porphyrin supramolecular porous networks adsorbed on Ag (111) at a low surface coverage were capable of complexing C\textsubscript{60} molecules in a periodic array of hosting cavities. The underlying non-covalent character of the supramolecular porphyrin-C\textsubscript{60} interaction may allow for a greater control in the construction of ordered, large assemblies in comparison to similar covalently linked porphyrin-fullerene dyads. The reason being that the deposition method enables the self-assembly of predetermined molecular modules through stabilizing non-covalent interactions as exhibited by the STM analysis of the binary molecular layer of porphyrin and C\textsubscript{60} adsorbed on silver surfaces. Further, post-assembly covalent functionalization of the donor-acceptor pairs may translate into a significant increase in durability and functionality required for the extreme conditions present in operating practical devices. This bottom-up approach exploits non-covalent

The central electronic process in organic photovoltaics is the formation of a photo-induced charge-transfer excited state. The energy of the charge transfer state is important from the perspective of organic photovoltaic device efficiency since experimental evidence shows that the charge transfer energy determines the achievable open-circuit voltage of such devices.15 Charge transfer states contribute to the photocurrent if the dissociation of the particle-hole state into charge-separated states is achieved.129 Conversely, the charge-transfer potential may be lost through a radiative recombination of the excited particle-hole state to the ground state or through non-radiative decay to the ground-state or non-emissive exciton states.1, 4, 26 A complete description of the charge dissociation process in the porphyrin-fullerene donor-acceptor complex requires an understanding of the behavior and characteristics of various electronic processes and energy levels with respect to changes in donor-acceptor distance and relative orientation, electronic coupling, strength of the non-covalent interaction, and polarization effects arising from the donor-acceptor interface. Most notably, the relative orientation plays many important roles in determining photophysical properties of charge transfer complexes.9 For example, the different possible orientations at the interface of porphyrin-fullerene supramolecular dyads generate varied associated local electric fields which influence the charge transfer energetics. Also, the strength of the stabilizing non-covalent pi-pi interaction between a porphyrin-C$_{60}$ dyad is expected to be maximal for the co-facial configuration shown in the left part of Figure 10, where the donor-acceptor surface-to-surface interaction is largest, and minimal for the end-on orientation depicted on the right side of Figure 10. Similarly, the dispersive-related polarization effects originating from the interaction between the porphyrin and fullerene charge distributions will decrease in going from the co-facial orientation to the end-on configuration. Therefore, calculating the charge transfer excitation energies for both the co-facial and end-on porphyrin-C$_{60}$ supramolecular dyad may provide a reliable estimate for a
range of achievable open-circuit voltage in a photovoltaic cell composed of the corresponding repeating donor-acceptor binary monolayers.

Figure 10. The left side shows the co-facial orientation of the non-bonded porphyrin-C$_{60}$ dyad. The right-side displays two different views of the end-on orientation.

To provide predictive understanding of charge transfer processes in complement to experimental work focused on the design of efficient donor-acceptor based organic photovoltaic cells through chemical deposition, an excited state quantum chemical method may be employed for the calculation of charge transfer excited state energies for various dyad orientations. Although current experimental deposition methods, such as sublimation under Ultra High Vacuum (UHV) conditions, ad-layer formation by immersion of a surface in a liquid or deposition of a solution, allow for the selective control in patterning donor-acceptor pairs on metal substrates, the complex interplay between metal-adsorbate and adsorbate-adsorbate interactions may give rise to varying donor-acceptor distances and relative orientations in the supramolecular binary monolayer. Therefore, several possible configurations may co-exist in a single binary monolayer of porphyrin-C$_{60}$ donor-acceptor pairs. By calculating the charge transfer excitation energies for various porphyrin-C$_{60}$ orientations, we can gain understanding into the effect of geometrical orientation on the CT energetics. The results of such calculations may further guide experimental chemical deposition work by determining the donor-acceptor coating configuration which yields the largest CT excitation energies. In the case of self-assembly constructs of porphyrin-C$_{60}$ pairs, two competing configuration distributions are drawn from experimental studies which show that fullerenes, upon co-deposition onto the porphyrin-metal nanotemplate, tend to form long chains and/or a 2-D network. The long-chain

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fullerene adsorption mode gives rise to co-facial porphyrin-fullerene supramolecular configurations whereas the 2D-array configuration displays end-on type interactions between the porphyrin and fullerene components. The molecular simulation configuration given by the elaborate molecular dynamics (MD) calculations of Barone and co-workers reproduces experimental observations of both periodicity and adsorbate-adsorbate interactions where both the end-on and co-facial porphyrin-fullerene geometrical orientations are present.  

In the present work, we use the recently developed perturbative-$\Delta$SCF (P-$\Delta$SCF) density functional method for the calculation of charge transfer excitation energies in the end-on orientation of the non-covalent porphyrin-$C_{60}$ dyad. The P-$\Delta$SCF excited state method avoids a major problem encountered in excited state electronic structure methodologies denoted as the “variational collapse” of the excited state manifold into the ground state manifold (which occurs when a variational energy minimization is applied to an excited state orbital configuration) by maintaining orthogonality between the excited-state and ground-state Slater determinantal wavefunctions. This method uses a perturbative approach to determine the excited state orbitals and density and does not contain any empirical or system dependent parameters. The occupied orbital manifold is allowed to relax in the presence of a particle-hole pair. The details of the method may be found in references 97 and 98. This method has been shown to give an accurate value for the charge transfer excitation energy of a carotenoid—$C_{60}$ particle-hole state observed in a 207-atom molecular triad. In addition, the P-$\Delta$SCF method reproduces the experimentally obtained charge transfer excited state energies for a set of 12 supramolecular TCNE-hydrocarbon dyads. Our previously calculated CT excitation energies for the porphyrin-$C_{60}$ co-facial orientation are in excellent agreement with the range of experimental values reported in the literature for similar porphyrin-fullerene dyads. Importantly, the P-$\Delta$SCF method reproduces the ($-1/R$) behavior of the CT particle-hole state potential with respect to increasing distance between the donor and acceptor components. We apply it here to the study of charge transfer energetics in relation to geometrical orientation of the porphyrin-$C_{60}$ and (zinc)porphyrin-$C_{60}$ supramolecular dyads.
5.1 **Computational Method**

The calculations reported here were carried out using density functional theory (DFT) as implemented in the NRLMOL code.\textsuperscript{83, 87, 98} We employed the PBE exchange-correlation energy functional within the generalized gradient approximation for all calculations reported here.\textsuperscript{86, 137} 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.\textsuperscript{87} 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 functions, along with the range of the exponents are given in Table V. This basis set resulted in a total of 4300–4600 basis functions for the two complexes studied here (C\textsubscript{60}/TPP and C\textsubscript{60}/ZnTPP). We have used our recently developed DFT based excited state method to determine the energies of the charge transfer excited state transitions.

<table>
<thead>
<tr>
<th>Atom</th>
<th>s-type</th>
<th>p-type</th>
<th>d-type</th>
<th>Primitives</th>
<th>Exponent Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>12</td>
<td>$2.22 \times 10^4 - 0.077$</td>
</tr>
<tr>
<td>H</td>
<td>4</td>
<td>3</td>
<td>1</td>
<td>6</td>
<td>$7.78 \times 10 - 0.075$</td>
</tr>
<tr>
<td>N</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>13</td>
<td>$5.18 \times 10^4 - 0.25$</td>
</tr>
<tr>
<td>Zn</td>
<td>7</td>
<td>5</td>
<td>4</td>
<td>20</td>
<td>$5.00 \times 10^6 - 0.055$</td>
</tr>
</tbody>
</table>

5.2 **Results and Discussion**

The structural characterization of binary monolayers composed of C\textsubscript{60} and porphyrin-derived molecules adsorbed on a Ag (111) metal surface revealed that C\textsubscript{60} molecules complex the interstitial sites of the porphyrin-metal substrate.\textsuperscript{116, 120, 126} Furthermore, an MD study simulating the adsorption of porphyrins on the metal surface followed by the deposition of C\textsubscript{60} fullerenes over the porphyrin layer yielded 20-nanosecond snapshots with similar coating configurations as described by the STM analysis.\textsuperscript{133} These porphyrin-C\textsubscript{60} configurations, which differ from other supramolecular porphyrin-fullerene dyads exhibiting a co-facial geometry, adopt an end-on orientation. The excited-state charge
transfer dynamics is expected to change in going from a co-facial alignment (Figure 10-left) to an end-on porphyrin-C$_{60}$ orientation (Figure 10-right) in large part due to reduced interfacial polarization effects and a smaller pi-pi stacking contribution. The charge transfer excitation energies are also expected to be dependent upon the relative porphyrin-C$_{60}$ orientation. Since the open circuit voltage depends on the charge transfer excitation energy, it becomes important to study the charge-transfer excited states of various dyad configurations which may be encountered by chemical deposition methods of fabrication of supramolecular binary monolayers. We have recently calculated a series of orbital-level CT excited state energies for the co-facial C$_{60}$-porphyrin supramolecular dyad by employing the perturbative-$\Delta$SCF (P-$\Delta$SCF) density functional excited state method.$^{136}$ The porphyrin-fullerene co-facial geometry consists of a center-to-center distance of ~3.5 Å with an electron-rich 6:6 fullerene bond centered over the planar porphyrin macrocycle (Figure 10). In the present study, we undertake a similar computational task for the end-on configuration of the porphyrin-fullerene supramolecular dyad, where the term end-on denotes a planar porphyrin macrocycle adjacent to a C$_{60}$ fullerene as shown in Figure 10. The porphyrin plane is co-planar with an equatorial plane of C$_{60}$ with a center-to-center distance of 11.2 Å and an edge-to-edge distance of ~3.5 Å. This particular porphyrin-C$_{60}$ distance for the end-on orientation was chosen as a simple estimate based on various experimentally reported values of unit cell parameters describing the size, shape, and periodicity of porous porphyrin clusters adsorbed on metal surfaces.$^{116, 120, 123, 126}$

A characteristic feature of the charge transfer process in donor-acceptor pairs is that the states associated with electron transfer are spatially well separated with vanishing overlap, where the transition dipole matrix elements coupling the particle-hole states are zero or vanishingly small. The highest two occupied and lowest two unoccupied states of porphyrin are the Gouterman orbitals responsible for the characteristic absorption bands of the porphyrin macrocycle in isolation.$^{12}$ The larger interaction in the co-facial arrangement pushes up one of the HOMO of C$_{60}$ just below the Gouterman orbitals of the TPP in C$_{60}$/TPP. For both of the end-on structures (C$_{60}$/TPP and C$_{60}$/ZnTPP), the HOMO is localized on the porphyrin and the LUMO is localized on the fullerene component. Upon forming a complex with the C$_{60}$ fullerene, the porphyrin Gouterman orbitals become the HOMO and HOMO-1 orbitals of the porphyrin-fullerene dyad. The five-fold degenerate HOMO orbitals for the isolated C$_{60}$ fullerene form
the HOMO-3 to HOMO-7 orbitals in the complexes with TPP and ZnTPP. However, the energy difference between the porphyrin HOMO-2 and the C$_{60}$ 5-fold degenerate h$_{u}$ HOMOs in the complex is less than 0.1 eV and therefore a reordering of these orbitals can take place in the complex. The t$_{1u}$ LUMO of isolated C$_{60}$ form the lowest three LUMOs of the two supramolecular dyads studied here. The splitting of the three LUMOs is very small, on the order of a few meV, due to the reduced interaction between the fullerene and the porphyrin as compared to a co-facial orientation. One of the porphyrin unoccupied Gouterman orbitals hybridizes with the higher fullerene LUMOs resulting in delocalized orbitals in C$_{60}$/TPP. The HOMO-LUMO gaps obtained from the Kohn-Sham DFT scheme give a value of 0.67 eV (C$_{60}$/TPP) and 0.73 eV (C$_{60}$/ZnTPP). The HOMO-LUMO gaps do not reflect the correct energies for the charge transfer excitation due in part to DFT underestimating the gap and partly because they do not incorporate the particle-hole interaction and the polarization of the passive orbitals.

Figures 11 and 12 depict the lowest few CT excited state transitions from the porphyrin Gouterman orbitals to the C$_{60}$ LUMOs for C$_{60}$/TPP and C$_{60}$/ZnTPP, respectively, by arrows originating from the porphyrin donor states shown on the left side to the corresponding C$_{60}$ acceptor states displayed on the right side of the figure. Table VI displays the calculated singlet excitation energies for the CT excited state transitions between the porphyrin-localized donor states and the C$_{60}$-localized acceptor states. The singlet excitation energies are calculated following the prescription given by Ziegler et al., that is, by subtracting the triplet energy from twice the energy of the mixed state.$^{110}$ A comparison between the co-facial and end-on singlet excitation energies is made side by side in Table VI for both the C$_{60}$/TPP and C$_{60}$/ZnTPP dyads. The local excitations or the excitations where the particle orbital is spread over both the components are distinguished by superscript a. Since the LUMO+3 state is delocalized over both the porphyrin and fullerene components for the C$_{60}$/TPP end-on orientation, the HOMO-1 to LUMO+3 (2.15 eV) and HOMO to LUMO+3 (2.30 eV) excited states do not correspond to CT transitions or local porphyrin excitations. Interestingly, the energy of the mixed excited state is larger than the triplet excitation energy for the HOMO to LUMO+3 transition, whereas the HOMO-1 to
Figure 11. CT excited state transitions (in eV) for C₆₀/TPP. Transitions are depicted by arrows originating from the porphyrin donor states shown on the left (blue) to the corresponding C₆₀ acceptor states (red) displayed on the right.

LUMO+3 transition exhibits a triplet excitation energy larger than the mixed excited state energy. Although a direct comparison between the excitations cannot be made, the table shows that for each of the C₆₀/TPP and C₆₀/ZnTPP dyads, the end-on geometry yields significantly larger excitation energies for the charge-transfer transitions. The lowest CT energy for the C₆₀/TPP dyad is about 0.6 eV larger for the end-on orientation as compared to its co-facial counterpart. This difference increases to about 0.75 eV for the C₆₀/ZnTPP system. In turn, a comparison of the excitation energies between the end-on geometries of C₆₀/TPP and C₆₀/ZnTPP shows that the excitation energies vary at a maximum of 0.05 eV. Thus the presence of the zinc atom hardly affects the CT energies.

In Table VII we show the DFT calculated ionization potential of the donor and electron affinity of the acceptor in isolation and in complexes. Our calculated value of the ionization energy for the
isolated base tetraphenyl porphyrin is in good agreement with the gas-phase UPS experimental value of 6.39 eV.\textsuperscript{90} Similarly, the DFT calculated electron affinity value of the isolated fullerene is in excellent agreement with the experimental value of 2.68 eV.\textsuperscript{89} The table shows that the base tetraphenyl-porphyrin and (Zn)tetraphenyl-porphyrin HOMO in the end-on orientation shifts minimally compared to the co-facial complexes. The results show that the fullerene LUMO is shifted marginally except for the co-facial C\textsubscript{60}/TPP complex, where it changes by 0.13 eV. The fullerene LUMO is shifted in opposite directions for the end-on and co-facial orientations in both C\textsubscript{60}/TPP and C\textsubscript{60}/ZnTPP. The change in IP-EA in C\textsubscript{60}/TPP is on the order of 0.1 eV, whereas in C\textsubscript{60}/ZnTPP it is \textasciitilde0.06 eV. In both the C\textsubscript{60}/TPP and C\textsubscript{60}/ZnTPP systems, the large change in CT excitation energy in going from the co-facial to the end-on
geometry occurs primarily due to a reduced exciton binding energy (EBE). Interestingly, a difference in EBE of ~0.6 eV in going from the co-facial geometry to the end-on configuration is seen for both C$_{60}$/TPP and C$_{60}$/ZnTPP systems. The EBE values given in Table VII are calculated as the difference between the quasi-particle gap and the CT pair energy, where the values are nearly identical for both end-on structures (C$_{60}$/TPP and C$_{60}$/ZnTPP). We have also calculated the difference in ionization energy of C$_{60}$/TPP for the HOMO and the HOMO-1 levels using a fixed occupancy ∆SCF approach. We find that the IP for the HOMO-1 state is larger by 0.25 eV than the IP of the HOMO state. This same energy difference is reflected in the CT energies for transitions to the lowest three LUMOs, indicating that the exciton binding energy is similar in these excitations.

TABLE VI. Calculated energies (in eV) for the charge transfer excited state transitions between the porphyrin-localized donor states and the C$_{60}$-localized acceptor states. The HOMO, HOMO-1, and HOMO-2 states are localized on the porphyrin component. The LUMO to LUMO+4 states are localized on the C$_{60}$ fullerene. *States that are not purely CT states with non-zero transition matrix element between the hole and particle orbitals.

<table>
<thead>
<tr>
<th>Transition</th>
<th>C$_{60}$/TPP(E)</th>
<th>C$_{60}$/TPP(Co)</th>
<th>C$_{60}$/ZnTPP(E)</th>
<th>C$_{60}$/ZnTPP(Co)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO-1 → LUMO+4</td>
<td>3.54</td>
<td>------</td>
<td>2.52$^a$</td>
<td>------</td>
</tr>
<tr>
<td>HOMO-1 → LUMO+3</td>
<td>2.15$^a$</td>
<td>2.27$^a$</td>
<td>3.19</td>
<td>2.26$^a$</td>
</tr>
<tr>
<td>HOMO-1 → LUMO+2</td>
<td>2.69</td>
<td>2.04</td>
<td>2.65</td>
<td>2.12</td>
</tr>
<tr>
<td>HOMO-1 → LUMO+1</td>
<td>2.67</td>
<td>2.04</td>
<td>2.64</td>
<td>2.12</td>
</tr>
<tr>
<td>HOMO-1 → LUMO</td>
<td>2.63</td>
<td>1.99</td>
<td>2.62</td>
<td>2.12</td>
</tr>
<tr>
<td>HOMO → LUMO+4</td>
<td>3.30</td>
<td>------</td>
<td>2.33$^a$</td>
<td>------</td>
</tr>
<tr>
<td>HOMO → LUMO+3</td>
<td>2.30$^a$</td>
<td>1.97$^a$</td>
<td>3.01</td>
<td>1.97$^a$</td>
</tr>
<tr>
<td>HOMO → LUMO+2</td>
<td>2.42</td>
<td>1.77</td>
<td>2.45</td>
<td>1.70</td>
</tr>
<tr>
<td>HOMO → LUMO+1</td>
<td>2.40</td>
<td>1.78</td>
<td>2.43</td>
<td>1.68</td>
</tr>
<tr>
<td>HOMO → LUMO</td>
<td>2.37</td>
<td>1.77</td>
<td>2.42</td>
<td>1.70</td>
</tr>
</tbody>
</table>

The ground state dipole moments of the end-on dyads are weak with values of 0.29 Debye for C$_{60}$/TPP and 0.40 Debye for C$_{60}$/ZnTPP. A comparison of the charge density in the C$_{60}$/TPP dyad and
that of isolated C₆₀ shows negligible polarization of the charge in the C₆₀ molecule due to the porphyrin. The charge transfer excited state dipole moments range from 41 – 47 Debye for the two complexes studied here. Since the excitation energies calculated in this work are vertical without any ionic relaxation, the dipole moments only show the rearrangement in electronic density. Experiments carried out by Mukherjee et al. report CT excitation values for the octadecyloxyphenyl-porphyrin to C₆₀ transition at 1.79 eV in toluene.¹³⁸ Our calculated co-facial C₆₀/TPP CT excitation energies are in excellent agreement with experiment and earlier C-DFT/TDDFT calculations.²² The experimental charge transfer energies for covalently linked co-facial type C₆₀-TPP dyads range from 1.48 eV to 1.75 eV in various polar and non-polar solvents.²⁶,³⁵ For covalently linked ZnPorphyrin-C₆₀ dyads with face to face topology, this energy can vary between 1.27 eV and 1.86 eV depending on solvent polarity, topology, and linker.¹¹,¹⁸,²³,²⁵,³⁷ Our calculations are done on gas-phase dyads, ignore ionic relaxations upon excitation, and all effects of solvents. The polarization effect of the solvent, particularly in polar solvents, will be crucial since the solvent produces a reaction field which stabilizes the CT excited states. This effect would be higher for the end-on configurations since the dipoles resulting from charge transfer transitions are larger compared to the co-facial configurations. The stabilization of the excited states therefore will be larger for end-on geometries.

**TABLE VII.** Calculated ionization potentials (IP) of the donor and electron affinity (EA) of the acceptor in isolation and in complexes (DFT). The exciton binding energy (EBE) is calculated as the difference between the quasi-particle gap and the CT pair energy.

<table>
<thead>
<tr>
<th></th>
<th>TPP</th>
<th>ZnTPP</th>
<th>C₆₀</th>
<th>C₆₀/TPP (E)</th>
<th>C₆₀/TPP (Co)</th>
<th>C₆₀/ZnTPP (E)</th>
<th>C₆₀/ZnTPP (Co)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EA</td>
<td>2.69</td>
<td>2.76</td>
<td>2.56</td>
<td>2.72</td>
<td>2.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IP-EA</td>
<td>3.46</td>
<td>3.59</td>
<td>3.51</td>
<td>3.47</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EBE</td>
<td>1.09</td>
<td>1.72</td>
<td>1.09</td>
<td>1.72</td>
<td></td>
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</tbody>
</table>
Electric fields arising from interfacial dipoles and other polarization effects play a key role in the electronic and optical processes of opto-electronic devices.\textsuperscript{13,139} A recently published review addresses how interfacial effects can affect the efficiency of the charge-separation and charge-recombination processes occurring in OPVs.\textsuperscript{139} A comprehensive description of the electronic structure at the heterojunction between the donor and acceptor materials is beyond the scope of the present work. A ground state dipole moment near equilibrium separation indicates the formation of interfacial dipoles which can help align the orbitals in such a manner to facilitate exciton dissociation.\textsuperscript{139} The ground state dipole moment for these end-on geometries are quite small and nearly vanishes as the separation between the two components increases. The magnitude of the dipole moment at the nearest center-to-center distance is four times smaller for the end-on orientation as compared to the co-facial structure. This is mainly due to the negligible polarization and charge transfer in the ground state for the end-on orientation in comparison to its co-facial counterpart.

We further studied the effect on the CT energy of varying the porphyrin-fullerene center-to-center distance for the end-on orientation of C\textsubscript{60}/TPP. In order to examine the behavior of the CT energy as a function of distance, we have calculated the lowest HOMO to LUMO CT excitation energies for the porphyrin-C\textsubscript{60} end-on orientation as a function of the porphyrin-fullerene center-to-center separation in increments of 0.5 Å. The variation in CT energy for the distance range of increasing particle-hole separation is significant, where the excited state results reveal that the porphyrin-fullerene CT energy changes by ~0.3 eV in spanning a donor-acceptor distance of 2.5 Å. Thus, a change in the donor-acceptor distance for the end-on dyads studied here has a larger impact on the CT energy than varying the donor component of the dyad in going from base tetraphenyl-porphyrin to Zn-tetraphenylporphyrin. Still, the geometrical orientation has the largest effect on the CT energy as shown in the present comparison of the end-on orientation to the co-facial orientation. At large donor-acceptor distances, where the interfacial polarization effects are negligible, the CT excitation energy may be calculated from the simple estimate based on the following equation\textsuperscript{46}:

\begin{equation}
E_{\text{CT}} = IP_{\text{donor}} - EA_{\text{acceptor}} - 1/R \quad (1)
\end{equation}
where $\text{IP}_{\text{donor}}$ and $\text{EA}_{\text{acceptor}}$ are, respectively, the ionization potential of the donor and the electron affinity of the acceptor. Here $R$ is the particle to hole separation. Importantly, the CT excited state energies given by the P-$\Delta$SCF method with respect to increasing porphyrin-fullerene end-on distance reproduce the expected $(-1/R)$ asymptotic tapering of the CT energy as plotted according to equation (1).

5.3 CONCLUSIONS

The end-on orientation of the non-covalent supramolecular porphyrin-$C_{60}$ dyad gives larger CT excitation energies in comparison to its co-facial analogue by 0.6 eV to 0.75 eV. This difference in CT energies is significant considering the scale in which CT excited state energies take place for similar co-facial porphyrin-fullerene non-covalent dyads, where experimentally determined CT energies lie in the range of 1.27 eV to 1.86 eV. Since the open-circuit voltage ($V_{\text{OC}}$), which represents the maximum voltage measured in a solar cell, depends mainly on the charge transfer energetics, the results of the present study become important from the perspective of evaluating the performance efficiency of OSCs, where current-voltage properties play a central role in the characterization of OSC devices. The dependence of $V_{\text{OC}}$ on the energy ordering of the donor-acceptor frontier orbitals allows for the tuning of $V_{\text{OC}}$ by combining various donor and acceptor molecules with HOMO-LUMO energy differences within a targeted range. Another way of tuning the energy levels of the frontier orbitals is by controlling the relative orientation between the donor and acceptor molecule. In the case of supramolecular porphyrin-fullerene pairs deposited on metal surfaces, the CT interactions arising from the porphyrin-fullerene end-on orientation appear to be favorable for achieving a larger $V_{\text{OC}}$ than the co-facial CT. In layers containing both the orientations between nearest neighbor porphyrin and fullerene molecules, the achievable CT energy may exhibit a wide range of 0.6 – 0.75 eV. The exciton binding energy for the lowest CT state is lowered by approximately 0.6 eV in going from a co-facial geometry to an end-on orientation for both $C_{60}/\text{TPP}$ and $C_{60}/\text{ZnTPP}$, which mainly accounts for the large change in CT excitation energy. Additionally, the change in relative donor-acceptor geometrical orientation has a larger impact on the CT energy than changes in the relative donor-acceptor distance. Changing the donor component of the porphyrin-fullerene dyad to include a transition metal in going from base-TPP to ZnTPP had a negligible effect on the CT energetics.
A fundamental requirement for donor-acceptor frontier orbital energy level offsets to achieve efficient charge photogeneration in organic photovoltaic systems is a relative energy ordering which creates a downhill energetic driving force conducive to the transferring of an electron from the donor molecule to the acceptor moiety. In particular, the charge-transfer state must be the lowest energy excited state in the system. Since finding the ideal donor-acceptor HOMO/LUMO level offset is not straightforward, it is of great importance to optimize the energy level positions of the donor and acceptor to allow efficient charge separation without losing the photo-generated voltage. An attractive quality in employing pi-conjugated macrocycles as chromophores in organic photovoltaic devices is the flexible incorporation of electron-rich and electron-deficient functional units along the conjugated periphery, where a variation of their strength allows for a systematic tuning of the molecular frontier orbital energy levels. The HOMO/LUMO level offset can be tailored by lowering the LUMO and/or raising the HOMO energy level of the molecule to obtain a minimum offset required to dissociate the Coulombically bound exciton at the donor-acceptor interface. This approach was applied in the sulfonation of the zinc-phthalocyanine (ZnPc) molecule at the ortho- and meta- positions of the macrocycle periphery with the objective of tuning the solubility and photocurrent properties of ZnPc/C\textsubscript{60}-based donor-acceptor organic solar cells, where altering the number of sulfonate substituent groups led to varying contributions to the device photocurrent.

Similar to the device performance obtained for the CuPc-S4/C\textsubscript{60} donor-acceptor pairs, the zinc analogue of the water-soluble sulfonated Pc donor component in the ZnPc-S4/C\textsubscript{60} system yielded a negligible contribution to the device photocurrent\textsuperscript{16,140} Decreasing the number of sulfonate substituent groups for ZnPc resulted in an increasing contribution to the photocurrent, accompanied by a noticeable reduction in the open circuit voltage.\textsuperscript{140} The lack of photocurrent exhibited by the device composed of ZnPc-S4/C\textsubscript{60} donor-acceptor pairs was attributed to a reduced free energy at the ZnPc-S4-C\textsubscript{60} interface, where the difference in donor and acceptor LUMO levels does not exceed the attractive Coulombic force of the photogenerated exciton necessary for charge separation at the interface. In turn, a comparison between the degree of sulfonation and the measured device $V_{OC}$ did not result in the
expected pattern of values. If the device $V_{OC}$ is taken to be proportional to the difference in energy between the HOMO level of the donor and the LUMO level of the acceptor, the device exhibiting the lowest $V_{OC}$ among the set of ZnPc sulfonated systems should be the disubstituted ZnPc-S2 system. Experimental measurements show that the $V_{OC}$ is largest for ZnPc-S4 and lowest for ZnPc-S3 with ZnPc-S2 having an intermediate value. Differences in morphology account for the irregular pattern of $V_{OC}$ values, where a marked difference in morphology between the ZnPc-S4 film and the di- and tri-sulfonated ZnPc films is revealed by atomic force microscopy. Therefore, several loss processes related to smaller exciton diffusion lengths for the ZnPc-S2 and ZnPc-S3 systems may lead to the lower device Voc observed for ZnPc-S2/C$_{60}$ and ZnPc-S3/C$_{60}$.

In order to gain insight into the charge transfer processes for the ZnPcS/C$_{60}$ donor-acceptor pairs, we have performed ground-state and excited-state calculations on four different water-soluble sulfonated zinc-phthalocyanine (ZnPcS) donor molecules coupled to C$_{60}$ (figure 13). The four ZnPcS donor
molecules (denoted as ZnPcS2A, ZnPcS2, ZnPcS3, and ZnPcS4) are shown in figure 14. From ground-state calculations of the ZnPcS donor and the C60 fullerene acceptor in isolation and in complex, we can estimate the effect on the HOMO/LUMO energy level ordering of donor and acceptor component in forming a bound complex. In varying substituent groups on the donor molecules with the aim of

![Figure 14. Four different water-soluble sulfonated (zinc)phthalocyanine molecules. The di-sulfonated moieties are denoted as S2 and S2A. The tri- and tetra- sulfonated compounds are labeled S3 and S4, respectively. Mixed ortho- and meta- substitution positions are shown for S4.](image)

shifting the frontier orbital energy level ordering and the CT excitation energies, the substituent type and position (ortho-, meta-) are important considerations. For instance, spectroscopic measurements indicate that electronegative substituent groups such as sulfonates shift the visible-spectrum Q-band absorption peaks (HOMO-to-LUMO and HOMO-to-LUMO+1 transitions) of ZnPc donor macrocycles.

In addition, the different substituent positions shift the Q-band of the ZnPc macrocycle by varying degree. Therefore, varying the number of sulfonate substituents and substituent position in the ZnPc molecule will influence the frontier orbitals of the donor and the CT excitation energy of the donor-acceptor complex. In the present study, we have calculated several low-lying charge transfer
excited-state energies for non-covalently bound ZnPcS/C$_{60}$ dyads in two different donor sulfonate substitution settings: (1) all sulfonate substituents at a meta-position and (2) sulfonate substituents at mixed meta- and ortho-positions.

Several experimental and computational studies have addressed important concepts and developments in a current major area of investigation in organic photovoltaics that deals with understanding the physicochemical processes at the donor-acceptor interface. A complete description of the charge dissociation process in donor-acceptor based organic solar cells requires an understanding of the behavior and characteristics of various electronic processes and energy levels with respect to changes in donor-acceptor distance and relative orientation, electronic coupling, strength of the non-covalent interaction, and polarization effects arising from the donor-acceptor interface. In regard to the relative geometrical orientation between donor and acceptor component, two different orientations (shown in figure 15 as co-facial and end-on) for the dyad system were studied for the ZnPcS2A/C$_{60}$ donor-acceptor system. Since several donor-acceptor relative orientations may co-exist at a given planar- and bulk-heterojunction interface, studying both the co-facial and end-on configuration for the ZnPcSA/C$_{60}$ dyad gives insight into the effect of geometrical orientation on the CT excitation energy. In going from the co-facial orientation to the end-on orientation, dispersion effects resulting from pi-pi stacking between the phthalocyanine macrocycle and the curved C$_{60}$ surface and other polarization effects will decrease. This change in polarization will influence the frontier orbital energy levels for each of the four donor-acceptor pairs. The difference in CT excitation energies between co-facial and end-on orientations will reflect the change in strength of the polarization effects and provide a reasonable estimate for the range in charge transfer excitation energies arising from several different co-existing relative dyad orientations at a donor-acceptor interface. In addition to varying donor-acceptor orientations present at the heterojunction interface, the intermolecular donor-acceptor distance will have a significant impact on the charge transfer energetics. Therefore, we have calculated the CT excitation energy as a function of donor-acceptor intermolecular distance spanning a range of 2.5 Å (figure 16). The intermolecular distance ($R_{\text{co-facial}}$ and $R_{\text{end-on}}$) CT calculations were performed for both the end-on and co-facial orientations of the ZnPcS2A/C$_{60}$ donor-acceptor pair. These calculations will provide a
reasonable estimate of the range in CT excitation energies arising from the various donor-acceptor distances and orientations that will likely be present at the heterojunction interface of ZnPcS2A/C\textsubscript{60}-based organic solar cells.

Figure 15. The left panel displays the co-facial orientation for the ZnPcS2A/C\textsubscript{60} dyad. The right panel shows the end-on orientation for the ZnPcS2A/C\textsubscript{60} dyad.

We also performed time-dependent Density Functional Theory (TDDFT) excited state calculations on each of the four different sulfonated zinc-phthalocyanine donor molecules in the various substituent patterns described above (figure 14). A strong absorption band (Q-band) resolved in a large number of phthalocyanine systems lies in the visible region at wavelengths between 650 nm to 670 nm, where symmetry plays an important role in determining the shape of the absorption peak for phthalocyanine-based macrocycles. Additionally, the substituent group type and the particular substituent ring positions influence the Q-band absorption energies. For instance, electron-withdrawing groups, such as sulfonyl and carboxyl groups, shift the Q-band to the red region of the visible spectrum. Group functionalization at the ortho- positions of the Pc macrocycle has a larger impact on the absorption spectra in comparison to similar meta- substituted complexes. The combination of ortho- and meta- substitution groups on the Pc macrocycle produces the largest Q-band shifts in the absorption spectra. Our results show that the di-sulfonated zinc-Pc molecules exhibit the largest red-shift relative to the non-substituted zinc-Pc molecule. We examine the effect of strict ortho- and meta- substitution and mixed ortho-/meta- substitution on the Q-band absorption (corresponding to HOMO-to-LUMO and HOMO-to-LUMO+1 transitions) of the sulfonated-ZnPc macrocycle chromophores.
Figure 16. The left and right panels display the intermolecular distance scans ($R_{co-facial}$ and $R_{end-on}$) used in evaluating charge-transfer energies as a function of particle-hole distance.

6.1 **Computational Method**

The calculations reported here were carried out using Density Functional Theory (DFT) as implemented in the NRLMOL (Naval Research Laboratory Molecular Orbital Library) suite of codes. We employed the Perdew, Burke, and Ernzerhof (PBE) exchange-correlation energy functional within the generalized gradient approximation for all calculations reported here. 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. 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 of the exponents are given in Table I. This basis set resulted in a total of ~4420 basis functions for the ZnPcS/C$_{60}$ dyads studied here. All ground-state and excited-state calculations were performed using spin-polarized wavefunctions. The P-$\Delta$SCF excited state DFT method has been implemented in the NRLMOL code and used here to determine the energies of the charge transfer excited state transitions. To obtain the excitation energy, an electron from an occupied state is placed in an unoccupied orbital and the self-consistent problem is solved using the perturbative $\Delta$SCF method. The energy of the triplet state is obtained if the two unpaired electrons in the particle-hole state are of the same spin. However, if two unpaired electrons in the particle-hole state 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 may be calculated using the Ziegler-Rauk post-SCF spin-purification correction by subtracting the triplet energy from two times the energy...
of the mixed state. The P-ΔSCF method provides accurate estimates of the experimentally obtained charge transfer excited state energies for a set of 12 supramolecular Tetracyanoethylene (TCNE)-hydrocarbon dyads. Previously calculated CT excitation energies for porphyrin-C\textsubscript{60} co-facial dyads are in excellent agreement with the range of experimental values reported in the literature for similar porphyrin-fullerene systems. The method has also been applied to the study of charge transfer energetics in relation to varying geometrical orientation of the tetraphenyl-porphyrin/C\textsubscript{60} (TPP/C\textsubscript{60}) and (zinc)tetraphenyl-porphyrin/C\textsubscript{60} (ZnTPP/C\textsubscript{60}) supramolecular dyads. The excitation energy and oscillator strength calculations were carried out using time-dependent density functional response theory as implemented in the Gaussian09 program. The TDDFT calculations, carried out at the PBEPBE/6-311+G(d,p) optimized structures, were done using the same basis set as those used in the ground-state DFT calculations for the four ZnPcS donor molecules shown in figure 14. A previous TDDFT study on zinc-phthalocyanine showed that increasing the basis set size by adding diffuse functions and using larger triple-zeta basis sets had a small effect on the calculated excitation energies and oscillator strengths.

TABLE VIII. 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.

<table>
<thead>
<tr>
<th>Atom</th>
<th>s-type</th>
<th>p-type</th>
<th>d-type</th>
<th>Primitives</th>
<th>Exponent Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>12</td>
<td>2.22 x 10\textsuperscript{4} – 0.077</td>
</tr>
<tr>
<td>H</td>
<td>4</td>
<td>3</td>
<td>1</td>
<td>6</td>
<td>7.78 x 10 – 0.075</td>
</tr>
<tr>
<td>N</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>13</td>
<td>5.18 x 10\textsuperscript{4} – 0.25</td>
</tr>
<tr>
<td>O</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>13</td>
<td>6.12 x 10\textsuperscript{4} – 0.10</td>
</tr>
<tr>
<td>S</td>
<td>6</td>
<td>5</td>
<td>3</td>
<td>17</td>
<td>6.72 x 10\textsuperscript{5} – 0.07</td>
</tr>
<tr>
<td>Zn</td>
<td>7</td>
<td>5</td>
<td>4</td>
<td>20</td>
<td>5.0 x 10\textsuperscript{6} – 0.055</td>
</tr>
</tbody>
</table>

6.2 RESULTS AND DISCUSSION

TDDFT Calculations

An important characteristic of phthalocyanine macrocycles is its metallation capacity that spans ample chemical space from main group metals to transition metals and lanthanides to actinides. A range in the Q-band peak between 620 nm and 720 nm is observed for metallated Pc molecules with varying
metal size, coordination, and oxidation state. Phthalocyanine molecules containing closed-shell metal atoms, such as zinc(II), show a maximum absorption peak near 670 nm. On the other hand, open-shell metal ions may interact strongly with the phthalocyanine ring and result in blue-shifted Q-bands with absorption maxima at around 630 nm to 650 nm. Metallated phthalocyanines adopt a higher symmetry than the corresponding free base phthalocyanine system with the incorporation of a metal ion inside the central cavity. This leads to a single peak Q-band in the visible range. The spectra of the corresponding free-base Pc molecules of lower symmetry yields a split Q-band. Also, substituent groups that preserve an overall symmetric metallated-phthalocyanine macrocycle exhibit only one absorption peak for the corresponding Q-band, whereas non-symmetric substitution breaks the molecular symmetry and gives rise to a split Q-band.

The spectral assignments of ZnPc (Q, B, N, L, and M bands) were first reported by Edward et al. based on broad gas-phase high-temperature spectra. Previous studies of the broad-range absorption spectrum for ZnPc using the time-dependent extension of DFT (TDDFT) gave results in excellent agreement with various experimental spectra. Since the zinc-phthalocyanine (ZnPc) macrocycle structure can be derived from the zinc-porphyrin (ZnP) molecular structure through combined tetraaza substitutions and tetrabenzo annulations, a particular TDDFT study of the combined effects of tetraaza and tetrabenzo groups on the structure and spectrum of ZnP showed a significant difference. Mainly, the near degeneracy of the HOMO and HOMO-1 orbitals of ZnP, which provides the basis for Gouterman’s four-orbital model description of the frontier orbital transitions, breaks down for the ZnPc macrocycle. In zinc-phthalocyanine (ZnPc), the near degeneracy of the \(a_{2u}\) orbitals with other occupied orbitals gives rise to a complex structure in the higher energy regions of the spectra. Consequently, the orbitals lying lower in energy than the HOMO level are found to be well (2.57 eV) separated from the HOMO, where the HOMO and lower occupied orbitals of ZnPc all have a significant pi contribution from the benzo rings. For orbitals that are known to give rise to specific well-characterized transitions such as the Q-band absorption peak(s), the energy shifts are useful in interpreting the variation in excitation energies and intensity produced by different substituents.
Our TDDFT calculation at the PBEPBE/6-311+G(d,p) level of theory for zinc-phthalocyanine gave a Q-band absorption peak value of 1.88 eV in excellent agreement with the experimentally determined value of 1.89 eV (gas-phase spectrum). This level of theory was used to calculate the near Q-band absorption spectrum of all sulfonated-phthalocyanine donor molecules shown in figure 14. The TDDFT calculations show that the absorption peak for one of the two disulfonated zinc-phthalocyanine molecule conformers (ZnPcS2 shown in the left-side of figure 17) yields a split Q-band of 0.12 eV with respect to the non-sulfonated zinc-phthalocyanine molecule. Interestingly, the HOMO-to-LUMO transition (661 nm) is red-shifted with respect to the calculated single-peak value of ZnPc (639 nm), whereas the HOMO-to-LUMO+1 transition (621 nm) exhibits a blue-shift. In contrast, the other disulfonated isomer (ZnPcS2A shown in the right-side of figure 17) displays a negligible change in absorption shape and magnitude in comparison to the single-peaked Q-band absorption of the ZnPc macrocycle. Table I shows the calculated Q-band absorption values for each of the four sulfonated donor molecules (ZnPcS2A, ZnPcS2, ZnPcS3, and ZnPcS4) and the non-sulfonated ZnPc molecule. For the tetra-sulfonated donor molecule (ZnPcS4), a molecule which contains sulfonate substituents at the
meta- and ortho- positions, the Q-band exhibits a split similar to the ZnPcS2 donor molecule but smaller in magnitude. The tri-sulfonated system (ZnPcS3) shows a small (~0.03 eV) red-shift for both the absorption transition peaks originating from the HOMO orbital.

Table IX. Transitions calculated by the TDDFT method at the PBEPBE/6-311+G(d,p) level of theory.

<table>
<thead>
<tr>
<th>Q-Band Absorption (nm)</th>
<th>ZnPc Base</th>
<th>ZnPcS2A</th>
<th>ZnPcS2</th>
<th>ZnPcS3</th>
<th>ZnPcS4</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO → LUMO (mixed)</td>
<td>639.67</td>
<td>642.47</td>
<td>661.42</td>
<td>657.26</td>
<td>643.75</td>
</tr>
<tr>
<td>HOMO → LUMO+1 (mixed)</td>
<td>638.63</td>
<td>637.60</td>
<td>621.43</td>
<td>646.46</td>
<td>633.18</td>
</tr>
</tbody>
</table>

Ground State Calculations

For the four distinct sulfonated ZnPc molecules, upon forming a complex with the C$_{60}$ fullerene, the HOMO orbital becomes the HOMO orbital of the phthalocyanine-fullerene complex. However, increasing the degree of sulfonation in the Zn-phthalocyanine macrocycle reduces the mismatch in energy between the HOMO level of the isolated ZnPcS-donor and the HOMO levels of the isolated C$_{60}$-acceptor, where the energy difference between the tetra-sulfonated ZnPc HOMO level and the C$_{60}$ 5-fold degenerate HOMOs in the complex is less than 0.1 eV. The five-fold degenerate HOMO orbitals for the isolated C$_{60}$ fullerene form the HOMO-1 to HOMO-5 orbitals in the complexes with each of the ZnPcS donor molecules. From the DFT ground-state calculations for each of the four co-facial ZnPcS/C$_{60}$ non-covalently bound dyads, figures 18 and 19 show the corresponding orbital energy diagrams with the orbital range spanning from HOMO-5 to LUMO+5 for both donor and acceptor molecule in isolation and in complex. Figure 18 displays a side-by-side comparison of the energy level ordering between a di-sulfonated ZnPc donor molecule (ZnPcS2) and the tri-sulfonated ZnPc (ZnPcS3) molecule and figure 19 compares the isomeric di-sulfonated ZnPc (ZnPcS2A) moiety with the tetra-sulfonated ZnPc (ZnPcS4) donor molecule. Since the energy ordering is similar for both di-sulfonated ZnPc systems, the comparisons emphasize the shift in the frontier orbital energy levels of the sulfonated
ZnPc molecules in increasing the number of sulfonate substituent groups from two (ZnPcS2A and ZnPcS2) to three (ZnPcS3) and four (ZnPcS4) groups.

![Diagram of orbital energy levels](image)

Figure 18. The left panel displays the orbital energy level ordering for the donor (left) and acceptor (right) molecule in isolation and in complex (middle) for the ZnPcS2A/C₆₀ system. Likewise, the right panel shows the energy ordering for the ZnPcS3/C₆₀ system.

The most important feature in the comparison of the energy level diagrams in regard to the frontier orbital energies known to impact the photovoltaic properties of a D/A-based organic solar cell is that both the HOMO and LUMO/LUMO+1 energy levels of the donor molecule in isolation incur a substantial lowering in energy in going from the di-sulfonated ZnPc system to the tri- and tetra-sulfonated ZnPc molecules. In both the isolated ZnPcS3 and ZnPcS4 ground-state systems, the LUMO
and LUMO+1 orbitals are lower in energy than the 3-fold degenerate isolated-C$_{60}$ fullerene LUMO level. Moreover, the energy of the HOMO orbital for both the ZnPcS3 and ZnPcS4 molecules is very close to the energy of the 5-fold degenerate C$_{60}$ HOMO level. Despite a seemingly unfavorable donor/acceptor HOMO/LUMO energy level offset between the ZnPcS3/ZnPcS4 and C$_{60}$ molecular systems, in forming a bound phthalocyanine-fullerene complex the triply degenerate LUMO levels of the isolated C$_{60}$ molecule become the lowest lying LUMO orbitals of the complex in the ground state (as indicated by red arrows in figures 18 and 19). The LUMO/LUMO+1 orbitals of the sulfonated
(zinc)phthalocyanine donor molecules become the higher-lying LUMO+3/LUMO+4 orbitals in the donor/acceptor complex.

In Table II we show the DFT calculated ionization potential of the donor and electron affinity of the acceptor in isolation and in complexes. For a neutral molecule with N electrons, the ionization potential (IP) can be calculated from the following expression:

$$\text{IP} = E(N-1) - E(N)$$

where $E(N)$ is the self-consistent total energy of the molecule in the ground state and $E(N-1)$ is the total energy of the cation. If the ionization process is rapid with respect to structural relaxation, then the energy of the cation $E(N-1)$ may be calculated using the geometry of the neutral system and the resultant ionization energy is called the vertical IP. Similarly, the electron affinity (EA) can be calculated using the following definition:

$$\text{EA} = E(N) - E(N+1)$$

where $E(N+1)$ is the self-consistent total energy of the anion calculated using the geometry of the neutral system. The IP and EA values reported in Table II were calculated within this ∆SCF scheme.

<table>
<thead>
<tr>
<th></th>
<th>S2</th>
<th>S2A</th>
<th>S3</th>
<th>S4</th>
<th>C60</th>
<th>S2/C60</th>
<th>S2A/C60</th>
<th>S3/C60</th>
<th>S4/C60</th>
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<tr>
<td>IP</td>
<td>6.79</td>
<td>6.82</td>
<td>7.00</td>
<td>7.14</td>
<td>6.59</td>
<td>6.64</td>
<td>6.77</td>
<td>6.90</td>
<td></td>
</tr>
<tr>
<td>EA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.67</td>
<td>3.13</td>
<td>3.13</td>
<td>3.28</td>
<td>3.37</td>
</tr>
<tr>
<td>IP-EA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.46</td>
<td>3.51</td>
<td>3.49</td>
<td>3.52</td>
<td></td>
</tr>
<tr>
<td>EBE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.05</td>
<td>2.00</td>
<td>2.04</td>
<td>1.95</td>
<td></td>
</tr>
</tbody>
</table>

Table X. The ionization potential (IP) for each of the four donor molecules and the electron affinity (EA) of the C60 acceptor molecule in isolation and in complex. The IP-EA value gives the quasi-particle gap. The exciton binding energy (EBE) is given.

The table shows that the IP value increases with the number of added sulfonate substituent groups to the zinc-phthalocyanine macrocycle. This is reflected in the energy level diagrams given in figures 18 and 19, where the HOMO level of the donor component is lower in energy for the tri- and tetra-sulfonated ZnPc molecules (ZnPcS3 and ZnPcS4; right-panel of figures 18 and 19) in comparison.
to the di-sulfonated systems (ZnPcS2 and ZnPcS2A; left panel of figures 18 and 19). In forming a complex with the C\textsubscript{60} fullerene, the four sulfonated-ZnPc systems (ZnPcS2, ZnPcS2A, ZnPcS3, and ZnPcS4) exhibit a lowering in energy of the IP level by approximately 0.2 eV. The EA level of the acceptor component is shifted upward in energy in forming a complex with the ZnPcS donor molecules, where a larger shift takes place for the ZnPcS3/C\textsubscript{60} and ZnPcS4/C\textsubscript{60} dyads with a significant change of \~0.7 eV. In figure 20 we show an isosurface of the difference between the ground state electron density of the dyad at equilibrium separation and the densities of the isolated components. The blue (grey) surface shows the region where the density difference is negative (positive). From the figure it is seen that substantial charge redistribution takes place on the curved fullerene surface near the interface with the semi-planar phthalocyanine macrocycle plane. The polarization of the fullerene thus contributes to the formation of the interfacial dipole. Overall, the quasi-particle gap, calculated as the IP\textsubscript{dyad}-EA\textsubscript{dyad}, and the exciton binding energy (EBE) are similar in value for the group of four ZnPcS/C\textsubscript{60} dyads (Table II). The exciton binding energy (EBE) was calculated using the quasi-particle gap and the lowest charge transfer excitation energy (CT\textsubscript{lowest}) according to the following equation:

$$\text{EBE} = (\text{quasi-particle gap}) - \text{CT}\textsubscript{lowest} = (\text{IP-EA})\textsubscript{dyad} - \text{CT}\textsubscript{lowest}$$

Figure 20. The difference in ground state density of the ZnPcS2/C\textsubscript{60} dyad and its isolated components.
Charge Transfer Excited State Calculations

By calculating several low-lying charge transfer excited-state energies for the four different non-covalently bound dyads, we examine the relationship between the degree of sulfonation for the donor component of the charge transfer complex and the donor-acceptor charge transfer excitation energy. This understanding is important from the perspective of device performance efficiency, where the device $V_{OC}$ is largely determined by the CT excitation energy. The power conversion efficiency of a donor-acceptor based organic solar cell is directly proportional to the $V_{OC}$ as shown in equation 1:

$$\text{Power Conversion Efficiency: } \eta = V_{OC}J_{SC}FF/P_{in} \quad (1)$$

Equation (1) shows three widely used parameters in the characterization of a solar cell: the short-circuit current density ($J_{SC}$), the open-circuit voltage ($V_{OC}$), and the fill factor (FF). $J_{SC}$ is a measure of the effectiveness of the organic semiconductor in converting absorbed photons into charge carriers and the FF term describes the quality of the solar cell in terms of photogenerated charge carriers reaching the electrodes. In regard to the $V_{OC}$, a dependence on the energy ordering of the donor-acceptor frontier orbitals allows for the tuning of $V_{OC}$ by combining various donor and acceptor molecules with HOMO-LUMO energy differences within a targeted range. Another way of tuning the energy levels of the frontier orbitals is by controlling the relative orientation between the donor and acceptor molecule. In using group functionalization of organic molecules to create increasingly favorable donor-acceptor energy band offsets, accurate CT excited state calculations complement the experimental molecular tuning of important photovoltaic properties by giving insight into the effect of varying donor substituent groups and varying donor-acceptor distance/orientation on the CT energetics of donor-acceptor complexes.

Figure 21 depicts the lowest few CT excited state transitions for the di-sulfonated phthalocyanine (ZnPcS2A) HOMO orbital to the C$_{60}$ LUMOs for the co-facial ZnPcS2A/C$_{60}$ complex by arrows originating from the donor states shown on the left side to the corresponding C$_{60}$ acceptor states displayed on the right side of the figure. The calculated singlet/triplet excitation energies for the CT excited state transitions between the ZnPcS-localized donor states and the C$_{60}$-localized acceptor states and the donor/acceptor local excitations are displayed in figure 22. The singlet excitation energies are calculated following the prescription given by Ziegler et al., that is, by subtracting the triplet energy
from twice the energy of the mixed state. A comparison between the singlet and triplet excitation energies is made side by side in figure 22 for each of the four different co-facial ZnPcS/C\textsubscript{60} dyads (ZnPcS2/C\textsubscript{60}, ZnPcS2A/C\textsubscript{60}, ZnPcS3/C\textsubscript{60}, and ZnPcS4/C\textsubscript{60}). The labeled Charge Transfer (CT) and Local Excitation (PE and FE) transitions are assignments to the di-sulfonated ZnPcS2A/C\textsubscript{60} and ZnPcS2/C\textsubscript{60} dyad systems, where the HOMO→LUMO, HOMO→LUMO+1, and HOMO→LUMO+2 excited state transitions correspond to donor-acceptor charge-transfer states. In turn, the HOMO→LUMO+3 and HOMO→LUMO+4 transitions correspond to local sulfonated-(zinc)phthalocyanine donor excitations for the ZnPcS2A/C\textsubscript{60} and ZnPcS2A/C\textsubscript{60} complexes.

Our calculations give a lowest CT excited state lower in energy than the lowest-lying local donor excitations for the di-sulfonated systems, which may serve as an energy-level setting conducive to CT excited state transitions. In contrast, an energy level re-ordering (reversal) takes place among the

Figure 21. CT excited state transitions (in eV) for co-facial ZnPcS2A/C\textsubscript{60}. Transitions are depicted by arrows originating from the ZnPcS2A donor state shown on the left (blue) to the corresponding C\textsubscript{60} acceptor states (red) displayed on the right.
Figure 22. Calculated energies (in eV) for the charge transfer excited state transitions between the ZnPcS-localized donor states and the C$_{60}$-localized acceptor states and calculated energies for local donor/acceptor excitations.

frontier orbitals of the tetra-sulfonated dyad system (ZnPcS$_4$/C$_{60}$), leading to the local donor excitation (1.53 eV) lying lower in energy than the ZnPcS$_4$/C$_{60}$ CT band (1.57 eV). Thus, the CT excited state is not energetically favored in comparison to competing local donor excitation transition pathways for the ZnPcS$_4$/C$_{60}$ donor-acceptor pair. Our excited state calculation results are in line with previous experimental studies on sulfonated (zinc)-phthalocyanine-C$_{60}$ molecular dyads employed in solar cells, and the related sulfonated (copper)-phthalocyanine-C$_{60}$ dyads, which show a negligible contribution to device photocurrent from the tetra-sulfonated systems and a corresponding improvement in device performance for di- and tri-sulfonated systems. Thus, the molecular tuning of CT states to obtain increasingly favorable frontier orbital energy offsets in donor/acceptor systems can be achieved through
a systematic and judicious use of group functionalization of well-established pi-conjugated organic chromophore molecules such as porphyrin- and phthalocyanine-based macrocycles.

Figure 23. CT excited state transitions (in eV) for end-on ZnPcS2A/C\textsubscript{60}. Transitions are depicted by arrows originating from the ZnPcS2A donor state shown on the left (blue) to the corresponding C\textsubscript{60} acceptor states (red) displayed on the right.

The relative donor-acceptor orientation plays an important role in determining photophysical properties of charge transfer complexes. Several experimental and theoretical studies have shown that the relative position of the donor and acceptor components significantly impacts the interfacial electronic processes in organic solar cells. The different possible orientations at a heterojunction interface of phthalocyanine-fullerene supramolecular dyads will generate varied associated local electric fields which influence the charge transfer energetics. Additionally, the strength of the stabilizing non-covalent pi-pi interaction between a (zinc)phthalocyanine-C\textsubscript{60} dyad is expected to be maximal for the cofacial orientation, where the donor-acceptor surface-to-surface interaction is largest, and minimal for the
end-on configuration. Dispersive-related polarization effects originating from the interaction between the sulfonated (zinc)phthalocyanine and fullerene charge distributions will also decrease in going from the co-facial orientation to the end-on configuration. Thus, calculating the charge transfer excitation energies for both the co-facial and end-on ZnPcS2A/C₆₀ supramolecular dyad may provide a reliable estimate for a range of achievable open-circuit voltage in a donor-acceptor based photovoltaic cell. In figure 23, we show the calculated excitation energy for the three lowest-lying CT states of the ZnPcS2A/C₆₀ molecular dyad in an end-on orientation. The calculated lowest-lying CT excitation energies are larger for the end-on orientation in comparison to the co-facial structure by ~1.5 eV, which primarily occurs due to a decrease in exciton binding energy in going from the co-facial to the end-on orientation, where the calculated exciton binding energy (EBE) for the ZnPcS2A/C₆₀ end-on orientation (0.46 eV) is much smaller than the EBE of its counterpart co-facial ZnPcS2A/C₆₀ orientation (2.00 eV).

A comparison between the CT energetics of the di-sulfonated (zinc)phthalocyanine/C₆₀ (ZnPcS2A/C₆₀) dyad and the (zinc)tetraphenyl-porphyrin/C₆₀ (ZnTPP/C₆₀) dyad shows that the exciton binding energy difference in going from a co-facial orientation to an end-on orientation is two times larger for the ZnPcS2A/C₆₀ complex (1.54 eV) than the ZnTPP/C₆₀ system (0.70 eV).

We further studied the effect on the CT excitation energy of varying the phthalocyanine-fullerene intermolecular distance for both the co-facial and end-on orientation of ZnPcS2A/C₆₀. In order to examine the behavior of the CT excitation energy as a function of particle-hole distance, we have calculated the lowest HOMO to LUMO CT energies of the ZnPcS2A/C₆₀ dyad for both co-facial and end-on orientations as a function of increasing ZnPcS2A-fullerene intermolecular distance spanning a range of 2.5 Å in five increments of 0.5 Å (figure 24). The co-facial intermolecular scan consisted of a C₆₀ (6:6)-bond to Pc-center distance of 2.0 Å to 4.5 Å and the end-on scan spanned an edge-to-edge distance of 7.0 Å to 9.5 Å. In figure 24, the end-on distance scan was shifted to match the co-facial scan in x-axis values in order to draw a comparison between both orientations. The steepness of the co-facial curve in comparison to the end-on curve is indicative of a stronger particle-hole polarization interaction for the co-facial orientation. The calculated range in CT energy for the end-on intermolecular distance scan of the ZnPcS2A/C₆₀ dyad is 0.27 eV, whereas the range in CT energy for the co-facial
intermolecular distance scan is 1.16 eV. A comparison between the CT energy distance-scan of the di-sulfonated (zinc)phthalocyanine/C₆₀ (ZnPcS₂A/C₆₀) dyad and the (zinc)tetraphenyl-porphyrin/C₆₀ (ZnTPP/C₆₀) dyad shows that the range of CT excitation energies is two times larger for the ZnPcS₂A/C₆₀ complex (1.16 eV) than the ZnTPP/C₆₀ system (0.60 eV).

Figure 24. The HOMO-to-LUMO CT excited state energy (in eV) as a function of intermolecular separation for the co-facial and end-on orientation of ZnPcS₂A/C₆₀.

6.3 CONCLUSIONS

One approach to tuning the frontier orbital energy level ordering is through the use of group functionalization in organic molecules. This approach was utilized in the synthesis of water-soluble sulfonated zinc-phthalocyanine (ZnPc) molecules for use in organic solar cells, where the addition of sulfonate groups increased the solubility of the zinc-phthalocyanine macrocycle in aqueous solution. In turn, increasing the number of sulfonate groups alters the frontier orbital energy levels by lowering the HOMO and LUMO/LUMO+1 levels of the ZnPc donor molecule. In order to examine the effect of increasing the number of ZnPc sulfonate substituents on the photophysical properties relevant to
phthalocyanine/C$_{60}$-based organic solar cells, we studied the excited states of four distinct sulfonated-ZnPc donor molecules (di-, tri-, and tetra-sulfonated ZnPc) in isolation and coupled to C$_{60}$ as a donor-acceptor pair. Our TDDFT calculations of the isolated sulfonated ZnPc donor molecules exhibit a significant shift in the Q-band levels (HOMO and LUMO/LUMO+1) for only one of the systems, namely the di-sulfonated ZnPcS$_2$A molecule. In contrast, the CT excitation energies exhibited a significant change in ordering for the tetra-sulfonated system (ZnPcS$_4$/C$_{60}$), where the lowest CT state lies higher in energy than the lowest local sulfonated zinc-phthalocyanine excited state. For the di- and tri-sulfonated dyad systems, the CT state is the lowest excited state in the system. Although the tetra-sulfonated phthalocyanine-C$_{60}$ may achieve the largest solubility in water, its corresponding frontier orbital energy level ordering is not favorable for charge separation. Since several different donor-acceptor distances and orientations are present at an organic heterojunction interface, we obtained an estimate for the range in CT energies resulting from the various orientations by calculating several low-lying CT excitation energies for both the co-facial and end-on orientation of the ZnPcS$_2$A/C$_{60}$ complex. Our calculations show a substantial increase in CT energies of ~1.5 eV in going from the co-facial orientation to the end-on orientation, which is attributed to a lower exciton binding energy for the end-on orientation. In calculating the CT energy as a function of particle-hole distance for both the co-facial and end-on orientation, we find a variation of ~1.16 eV in CT energy for a co-facial intermolecular distance range of 2.5 Å and a variation of 0.27 eV for the end-on orientation distance scan (2.5 Å).
Chapter 7: The Effect of Structural Conformational Changes on Charge Transfer States in a Light-Harvesting Carotenoid-diaryl-Porphyrin-C$_{60}$ Molecular Triad

In natural photosynthetic systems, a high quantum yield of the final charge separated state is achieved through a series of short-range, fast, and efficient electron transfer transitions.\(^{141}\) This strategy was exploited in the design of the CPC$_{60}$ molecular photovoltaic triad by employing two electron donors and one acceptor, in which two sequential electron transfers lead to a long-lived charge separated state.\(^{142}\) 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.\(^{142, 143}\) The large distance between the donor and acceptor components in the CPC$_{60}$ triad leads to weak electronic coupling and slows the charge recombination process.\(^{143}\)

The synthesis and photochemistry of the CPC$_{60}$ molecular triad established that fullerenes can act as effective primary electron acceptors in multi-component systems larger than porphyrin-fullerene dyads.\(^{142}\) The molecular triad generated long-lived charge-separated states with high quantum yields even at low temperature. A salient photochemical feature observed in the CPC$_{60}$ triad is that the $C^\bullet-P-C_60^\bullet\text{-}\text{charge-separated state}$ recombines to yield a carotenoid triplet state rather than the molecular ground state, similar to photosynthetic reaction centers.\(^{143}\) For the CPC$_{60}$ triad, the charge transfer $C^\bullet-P-C_60^\bullet\text{-}\text{transition}$ yields a singlet radical pair state which evolves into a CT triplet radical pair. The excited state triplet radical pair recombines to yield a $3\text{C-P-C}_60$ triplet carotenoid state.\(^{143}\)

The main charge-transfer transition pathway between the ground-state and the final $CPC_{60}^\bullet\text{-}\text{charge-separated state}$ involves a local excitation on the porphyrin moiety, followed by electron transfer to the adjacent C$_{60}$ component. Next, the carotenoid transfers an electron to the positively charged porphyrin to yield the final charge-separated state. A recent study suggests that the photoinduced charge separation process of the triad is driven by correlated motion of electrons and nuclei.\(^{144}\) The experimentally determined lifetime for the $CPC_{60}^\bullet\text{-}\text{charge separated state}$ is $\sim$170 nanoseconds in a 2-methyltetrahydrofuran solution.\(^{142}\) In 2003, Smirnov and co-workers employed a transient dc photocurrent technique to study transient dipoles formed upon excitation of the porphyrin chromophore in the CPC$_{60}$ triad.\(^{145}\) 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 C\textsubscript{60} fullerene at a large particle-hole separation (>30 Å).

A previous 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\textsuperscript{146}. It was determined that the linear triad is energetically more stable than its elbow-shaped conformer counterpart\textsuperscript{146}. The ground-state CPC\textsubscript{60} structure consists of a pyrole-C\textsubscript{60} 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 (pyrole-C\textsubscript{60}, 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\textsuperscript{146}. 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 (TD-DFT) formalism\textsuperscript{54}. 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\textsuperscript{54}.

In another study, the P-\(\Delta\)SCF excited state method was applied to the study of charge transfer excitations in the CPC\textsubscript{60} molecular triad\textsuperscript{96}. The large particle-hole distance in the final \(\text{+CPC}_{60}\) 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-\(\Delta\)SCF excited state method gives an excitation energy of 2.46 eV for the \(\text{+CPC}_{60}\) charge separated state in gas-phase, which is in good agreement with the point-
charge estimate (IP-EA-1/R) of 2.5 eV.\textsuperscript{96} The P-\textDelta SCF study of CPC\textsubscript{60} 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.\textsuperscript{96} The importance of solvent polarization is also brought out by the experimental study of Gust et al.\textsuperscript{142} in which charge separation was observed in benzonitrile and (2-methyl)-tetrahydrofuran but not observed in toluene. The effect of the solvent is significant as the experimental CT energy of the \(^{+}\text{CPC}_{60}^{-}\) state is significantly smaller than the gas-phase calculated value.\textsuperscript{96, 147}

The magnitude of the excited state dipole moment for the triad is 153 D, where experimental estimates were made in deriving the dipole value.\textsuperscript{145} The approximations 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. In regard to molecular shape, an alternative evaluation consisting of a decomposition of the total dipole moment into solute and solvent polarization contributions gave an experimental estimate of 163 D, which corresponds to a particle separation of \(\sim 34\) Å.\textsuperscript{145} 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 \(\text{C}_{60}\) 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 \(\sim 110\) D.\textsuperscript{148} The conformational changes of the triad in water were studied by Cheung et al.\textsuperscript{149} 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 conformational changes in solution.
In the present investigation, we extend our two previous DFT studies of the CPC\textsubscript{60} triad with a combined ground- and excited-state electronic structure study of various conformational configurations of the linear-shaped triad. Since entropy changes in the triad/solvent system control the excited state charge transfer process, it becomes important to study the excited state properties of several different triad conformations. Since our calculations are on the gas-phase triad, this study brings out the changes in the CT energy due to the conformational changes only, separate from the electronic polarization effects due to the polar solvents. In order to gain insight into the large differences in structural conformation (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 19 distinct triad conformations. For each conformer, the calculated lowest excited state transition corresponds to the lowest CT state. In order to study changes in the CT energy due strictly to conformational variations, single-point calculations were performed for the structures reported in the present study. To the best of our knowledge, rigorous all-electron calculations have not been carried out for a series of triad conformers, mainly due to the large computational expense involved in the ground- and excited-state calculations of systems as large as the CPC\textsubscript{60} triad (207 atoms).

7.1 Computational Method

The calculations reported here were carried out using Density Functional Theory (DFT) as implemented in the NRLMOL (Naval Research Laboratory Molecular Orbital Library) suite of codes.\textsuperscript{83, 87, 98} We employed the Perdew, Burke, and Ernzerhof (PBE) exchange-correlation energy functional within the generalized gradient approximation for all calculations reported here.\textsuperscript{86, 137} 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.\textsuperscript{87} 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 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-\DeltaSCF excited state DFT
method\textsuperscript{134, 135} has been implemented in the NRLMOL code and used here to determine the energies of the charge transfer excited state transitions. To obtain the excitation energy, an electron from the HOMO is placed in the LUMO and the self-consistent problem is solved using the perturbative $\Delta$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.\textsuperscript{150} The energy of the singlet state may calculated using the Ziegler-Rauk method by subtracting the triplet energy from two times the energy of the mixed state.\textsuperscript{110} For the linear-shaped molecular triad, we found that the Ziegler-Rauk post-SCF spin-purification correction was small due to the triplet and mixed excited states lying close in energy. Therefore, due to the large computational expense for the triad, we have calculated only the mixed excitation energies for all of the triad conformers reported in the present study. The P-$\Delta$SCF method provides accurate estimates of the experimentally obtained charge transfer excited state energies for a set of 12 supramolecular Tetracyanoethylene (TCNE)-hydrocarbon dyads.\textsuperscript{134} Previously calculated CT excitation energies for porphyrin-C\textsubscript{60} co-facial dyads are in excellent agreement with the range of experimental values reported in the literature for similar porphyrin-fullerene systems.\textsuperscript{136} The method has also been applied to the study of charge transfer energetics in relation to varying geometrical orientation of the tetraphenyl-porphyrin/C\textsubscript{60} (TPP/C\textsubscript{60}) and (zinc)tetraphenyl-porphyrin/C\textsubscript{60} (ZnTPP/C\textsubscript{60}) supramolecular dyads.\textsuperscript{151}

### TABLE XI

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.

<table>
<thead>
<tr>
<th>Atom</th>
<th>s-type</th>
<th>p-type</th>
<th>d-type</th>
<th>Primitives</th>
<th>Exponent Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>12</td>
<td>$2.22 \times 10^3 - 0.077$</td>
</tr>
<tr>
<td>H</td>
<td>4</td>
<td>3</td>
<td>1</td>
<td>6</td>
<td>$7.78 \times 10 - 0.075$</td>
</tr>
<tr>
<td>N</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>13</td>
<td>$5.18 \times 10^4 - 0.25$</td>
</tr>
<tr>
<td>O</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>13</td>
<td>$6.12 \times 10^{4.10}$</td>
</tr>
</tbody>
</table>
7.2 RESULTS AND DISCUSSION

The importance of studying various structural conformations of the CPC$_{60}$ 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.$^6,^{152}$ 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.$^{153,154}$ 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.$^{153,154}$

In the present study, we undertook a systematic structural search for conformers resulting from torsions using the DFT method. Two different dihedral segments from the CPC$_{60}$ molecular structure were selected, denoted as PF and CP, through which various conformer structures were generated by dihedral-angle rotations about each of the chosen 4-atom dihedral segments (shown in figures 25 and 27). The PF (porphyrin/fullerene) designation corresponds to triad configuration variations where the structural modifications originate from torsions about the '(C$_{60}$-pyrrole)-porphyrin' linkage. Similarly, the CP (carotenoid/porphyrin) designation describes structural changes effectuated through torsions about the 'porphyrin-carotene' amide linkage. For each dihedral segment, 7 distinct triad conformations were generated by successively incrementing the corresponding dihedral angle of the linear triad by 45 degrees for a full 360 degree torsion scan.

In figure 25 we show a dihedral segment of the CPC$_{60}$ triad at the linkage between the carotenoid and porphyrin subunits. The dihedral segment was scanned for full 360 degree torsion in increments of 45 degrees. 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 26). 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 report the calculated ground- and excited-state dipole moment magnitudes. The calculated CT energies lie within
Figure 25. The 4-atom dihedral segment (colored 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.

Figure 26. The angle (θ), charge transfer energy (CTE), and dipole magnitude values are shown for each of the 7 distinct CP conformers.
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.

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

<table>
<thead>
<tr>
<th>Triad Conformer</th>
<th>CT Excitation Energy</th>
<th>Ground State Dipole</th>
<th>Excited State Dipole</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP 45°</td>
<td>2.46</td>
<td>7.9</td>
<td>165.6</td>
</tr>
<tr>
<td>CP 90°</td>
<td>2.50</td>
<td>9.2</td>
<td>168.0</td>
</tr>
<tr>
<td>CP 135°</td>
<td>2.49</td>
<td>9.0</td>
<td>169.4</td>
</tr>
<tr>
<td>CP 180°</td>
<td>2.47</td>
<td>8.0</td>
<td>171.1</td>
</tr>
<tr>
<td>CP 225°</td>
<td>2.48</td>
<td>8.4</td>
<td>173.7</td>
</tr>
<tr>
<td>CP 270°</td>
<td>2.50</td>
<td>9.3</td>
<td>174.6</td>
</tr>
<tr>
<td>CP 315°</td>
<td>2.48</td>
<td>8.6</td>
<td>171.7</td>
</tr>
</tbody>
</table>

Figure 27. The 4-atom dihedral segment (colored 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.
For the torsion displayed in figure 27 we have evaluated the CT energy at 7 dihedral steps in increments of 45 degrees 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 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 28 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.

![PF Conformers](image)

Figure 28. The angle (θ), charge transfer energy (CTE), and dipole magnitude values are shown for each of the 7 distinct PF conformers.
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\textsuperscript{155, 156} quantum chemistry software package where a similar energy ordering was obtained across the different semi-empirical methods. From the semi-empirical calculations of the 14 conformers and the linear triad, a set of 5 conformer structures with energies within a ~0.5 eV 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 C\textsubscript{60} 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.

Table XIII. 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.

<table>
<thead>
<tr>
<th>Triad Conformer</th>
<th>CT Excitation Energy</th>
<th>Ground State Dipole</th>
<th>Excited State Dipole</th>
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<tbody>
<tr>
<td>PF 45°</td>
<td>2.55</td>
<td>8.8</td>
<td>174.9</td>
</tr>
<tr>
<td>PF 90°</td>
<td>2.58</td>
<td>10.6</td>
<td>185.4</td>
</tr>
<tr>
<td>PF 135°</td>
<td>2.57</td>
<td>10.5</td>
<td>188.7</td>
</tr>
<tr>
<td>PF 180°</td>
<td>2.57</td>
<td>9.7</td>
<td>187.2</td>
</tr>
<tr>
<td>PF 225°</td>
<td>2.56</td>
<td>9.4</td>
<td>181.8</td>
</tr>
<tr>
<td>PF 270°</td>
<td>2.58</td>
<td>10.6</td>
<td>182.1</td>
</tr>
<tr>
<td>PF 315°</td>
<td>2.51</td>
<td>9.5</td>
<td>176.5</td>
</tr>
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In the CPC\textsubscript{60} 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°<O<90° 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 29). 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. Studies have addressed this issue by attempting to disrupt extended conjugative interactions by placing alkyl substituents at beta-pyrrolic positions. 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. 

Figure 29. Simple Hückel type representations of the cyclic pi-conjugation exhibited by porphyrin and aryl systems.

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 30. The dihedral parameter is evaluated, with respect to the ground-state dihedral, in 4 increments of 45 degrees for a total torsional scan of 180 degrees. 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 several low-lying 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.

![Figure 30. 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.](image)

<table>
<thead>
<tr>
<th>Triad Conformer</th>
<th>CT Excitation Energy</th>
<th>Ground State Dipole</th>
<th>Excited State Dipole</th>
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<tr>
<td>Dihedral 45°</td>
<td>2.48</td>
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<td>Dihedral 90°</td>
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<td>Dihedral 135°</td>
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<td>9.4</td>
<td>166.6</td>
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<tr>
<td>Dihedral 180°</td>
<td>2.50</td>
<td>9.2</td>
<td>176.0</td>
</tr>
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</table>
Since the excited state dipole moments of all the conformers show large dipole moments, we constructed a folded geometry which is likely to possess a significantly lower excited state dipole moment as shown by experiment (~110 D).\textsuperscript{148} In the folded configuration, the porphyrin-carotene extension wraps closely around the fullerene component where the C\textsubscript{60}-carotene particle-hole distance is ~19 Å (shown in figure 31). The magnitude of the dipole moment for the +CPC\textsubscript{60} - charge-separated state of such a folded conformer would be smaller, which may reduce the photovoltaic efficiency in comparison to its larger dipole moment conformational counterparts. Also, the solvent stabilization of the charge transfer state would be less in comparison to the stabilization resulting from a larger molecular dipole such as in the linear triad conformation. Our calculated value for the CT excitation energy of the folded conformation yields a value of 2.16 eV, which is ~0.4 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 Debye) in comparison to the average dipole value for the CP and PF

Figure 31. Folded triad conformation exhibiting a close interaction between the particle and hole states in the excited state (~19 Å). The Charge Transfer Energy (CTE) of 2.16 eV and the dipole moment value of 88 Debye are shown.
conformers. The energy of the C\(^+\)PC\(_{60}\)\(^-\) charge transfer excited state is reported to be 1.20 eV by Gust and co-workers\(^{147}\), 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 conformational changes can reduce the energy of the CT state in the gas-phase by a few tenths of an electron-volt even for conformers where the excited state dipole is significantly smaller. The remaining difference is likely to be due to the electronic polarization effects due to the polar solvent molecules.

7.3 CONCLUSIONS

We have examined the effect of structural conformational changes on the CT excited states of the CPC\(_{60}\) molecular triad. 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 conformers through torsional scans about the carotene/porphyrin (CP) linkage and the porphyrin/fullerene (PF) linkage. In addition, we studied a folded conformation 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 CPC\(_{60}\) 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 conformation varies by ~0.4 eV with a value of 2.16 eV and the excited state dipole magnitude is reduced by half. Such a folded conformation will have strong implications on the CT excited state dynamics of the triad in solution since the reduced dipole magnitude will decrease the solvent-polarization induced stabilization of the CT state. Due to the structural flexibility of the CPC\(_{60}\) triad, we also examined a conformational 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. By studying the CT excited states of several triad conformations in the gas phase, we have decoupled the effect of structural changes on the CT excitation energy from solvent effects on the CT energy. Since the calculated gas phase values for the CT energy differ from the reported experimental value, the solvent induced stabilization of the CT state becomes important.
Chapter 8: A Combined Quantum Mechanical and Molecular Mechanical (QM/MM) Study of Solvent Effects on the Charge Transfer Excited States of a Carotene-Porphyrin-C_{60} Molecular Triad

Employing functionalized fullerenes as electron donors in bulk heterojunctons (BHJ) may serve as a promising avenue in the development of efficient energy conversion systems in organic solar cells. By functionalizing the fullerene with an appropriate electron-donating ligand(s) to induce an intramolecular charge separated state, it may be possible to fabricate an active layer consisting of a single molecular component, where the photocurrent generation may be maximized through the selection of a suitable solvent. The careful selection of a fullerene derivative and its coupling to a solvent environment can be used strategically to obtain a state similar to a pre-dissociation of an exciton through efficient, long-range intramolecular charge transfer. As an example, the calculated exciton binding energy ([IP-EA\_D/A-CT\_lowest]) for the carotene-C_{60} CT excited state at a large particle-hole distance of ~34 Å in the carotene-porphyrin-C_{60} (CPC_{60}) molecular triad is near zero. In most implementations of fullerene-based BHJ solar cells to date, the active layer consists of fullerene/polymer blends and supramolecular fullerene/macrocycle blends. In an organic photovoltaic device composed of a single molecular component, the donor and acceptor phase may self-segregate into amorphous regions without intrinsic ordering, which is characteristic of BHJ type solar cells. The selective photoexcitation of an exciton in the donor phase can lead to a long-range charge separated state capable of being converted into electrical current given the following conditions: (1) the exciton is sufficiently long-lived, (2) the diffusive path of the exciton intersects a donor/acceptor phase interface, and (3) the energy level distributions of the donor and acceptor support efficient charge transfer. The CPC_{60} molecular photovoltaic introduced and studied in the previous chapter satisfies the first and third aforementioned criterion, where experimental studies have measured a long-lived, solvent-stabilized charge separated state of 170 ns in a 2-methyltetrahydrofuran solution. The second criterion, the donor-acceptor interface, is challenging to determine in BHJ devices. The solvent environment is a readily tunable degree of freedom that has a large impact on the stabilization of molecular electronic structures and dynamics, particularly states exhibiting a large dipole moment as is characteristic of CT excited states. In the context of designing efficient BHJ solar cells, we propose that the solvent can facilitate the pre-
dissociation of an exciton through efficient intramolecular CT, which can then be used to mitigate voltage drops that arise from a mismatch in the intermolecular frontier orbital energy offset at organic heterojunctions. As an application of this concept, we undertake a combined quantum mechanical (QM) and molecular mechanical (MM) study of the solvent induced stabilization of the CT excited state in the CPC$_{60}$ molecular triad, where polar solvents lower the energy of the CT state relative to the gas-phase energy level ordering.

8.1 BACKGROUND

The underlying motive in the development of hybrid quantum mechanical (QM) and molecular mechanical (MM) approaches is the general formulation of a large chemical ensemble, such as a solute-solvent system, partitioned into an electronically important region requiring a quantum mechanical treatment and the remaining system which acts in a perturbative fashion and thus admits a classical description. The perturbation may be considered mechanical if the effect of the classical region consists mainly of forcing the quantum region into a particular geometry. A different perturbation type comprises electronic effects such as electrostatics and polarization. According to this formulation, a solute-solvent conformational analysis may be treated as a structural transformation involving the QM-region reactive center influenced by its environment (solvent MM region). This concept is closely related to the physicochemical argumentation for the stabilization of molecular CT states in polar media, where the CT excited state induces a reaction field on the surrounding polar solvent molecules which, in turn, stabilize the solute molecular dipole associated to a particular CT state.

The explicit description of the solvent leads to very large systems, and the use of quantum mechanical potentials in MD simulations for such systems become computationally prohibitive. Empirical force fields have been employed successfully in many types of MD simulations, with the only main deficiency stemming from its lack of capturing chemical reactivity. The accuracy of a classical force field strongly depends on the careful calibration of a large number of parameters against experimental reference data or high-level quantum mechanical calculations. This ensures the reliability and accuracy of a given MM approach, but restricts its application to classes of molecules employed in
the training set. Therefore, many force fields match or outperform simple QM models in accuracy because tailored potential functions and flexible parameterizations allow for good quantitative reproduction of experimental data. A further advantage of MM force fields is the computational efficiency afforded by solving analytical expressions for the equations of motion, which makes them particularly attractive for MD simulations. Classical MD simulations are faster than QM approaches and show a modest scaling of the cpu requirements with increasing system size. On the other hand, QM models are more generally applicable and allow for an accurate description of ground- and excited-state electronic properties such as the ionization potential, the electron affinity, and CT excitation energies. This motivates the use of hybrid quantum mechanical (QM) and molecular mechanical (MM) models which combine the merits of both the quantum and the classical approach for the study of large systems such as solute-solvent interactions.

8.2 Methodology

The parameters for the structural Hamiltonian were generated by the ForceField Toolkit (one of the plugins in the Visual Molecular Dynamics (VMD) software) using the CHARMM General Force Field (CGenFF), and the initial charges were taken from a DFT calculation based on a single extended conformation (6157 basis functions). Since the current version of the CGenFF has parameters available for carotene and the C60 fullerene was kept fixed throughout the simulation, the bonded potential energy parameters missing to fully describe the triad stemmed from the diarylporphyrin component and the five-membered ring connecting the porphyrin to the fullerene. The missing bonded potential energy terms for the triad were parameterized according to the CHARMM parameterization protocol, where the bond and angle terms are fitted to the Hessian and the dihedral terms are obtained via a fitting to dihedral scans in a simulated annealing simulation. The newly obtained parameters for the triad employed in the current study are listed below. In addition, the Grifalco non-bonded carbon atomic term was used for the aromatic carbons comprising the C60 fullerene component. Rigid water was applied using the SHAKE algorithm in accordance to the TIP3P parameterization. Also, bonds between hydrogen atoms and heavy atoms were constrained to their nominal length during integration using
SHAKE. The integration time step was 1 fs and the damping coefficient for the Langevin dynamics was set to 1 ps\(^{-1}\). For the bulk system, the switching distance for van der Waals forces was set to 12 Å, and the cutoff was set to 24 Å. The electrostatic interactions were calculated using the particle mesh Ewald (PME) method. The triad was solvated with TIP3P water in a rectangular periodic boundary box (10 nm \(\times 10\) nm \(\times 7\) nm). The energy of this bulk solute-solvent system was first minimized using a conjugate gradient method and then equilibrated in three steps by using NAMD as follows: (1) gradually heat up water molecules to 300 K while keeping the triad fixed in space; (2) gradually heat up the system to 300 K with a temperature step of 1 K and run a 3-ps simulation per temperature step under constant NVT conditions using Langevin dynamics; (3) equilibrate and execute production level run of the solute-solvent system at 300 K under constant NVT conditions using Langevin dynamics for 10 ns.

**BONDS**

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**ANGLES**

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CG2DC1 CG2R52 NG2R50 CG251O 1.4370 2 180.00
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8.3 RESULTS AND DISCUSSION

Solvent effects play an important role in the charge transfer processes of the CPC$_{60}$ triad in solution by stabilizing the excited state dipole moment of the CT excited state. This results in a shift in the CT energy with respect to the CT energy calculated for the gas phase structure. To account for electrostatic effects of polar solvents on the CT energetics, we adopt a simulation scheme belonging to the widely used class of QM/MM hybrid methodology, where the solvent molecules are treated with molecular mechanics and the donor-acceptor solute will be treated quantum mechanically. The MM component will consist of NAMD (Not Another Molecular Dynamics code) simulations employing the CHARMM General Force Field (CGenFF) for the molecular triad and the TIP3P model for water. The QM region will be described by the Kohn-Sham density functional approximation scheme as implemented in the NRLMOL code.

Three different types of calculations were undertaken in the following study of solvation: (1) Full-step NAMD production simulations (Minimization, Gradual Heating, System Equilibration, and Production Run) of the donor-acceptor system as the solute centered in a box of solvent; (2) Spin-polarized ground state calculations for a donor-acceptor system containing 207 atoms at the all-electron level using a large basis set more than twice the size of the commonly used 6-31+G(d,p) basis; and (3) Charge transfer excited state calculations of large donor-acceptor complexes using the spin-polarized ground-state wavefunction as a starting point for generating an excited state wavefunction.

The following details our solvation strategy:

**Step 1:** Run multi-step Molecular Dynamics production simulations using the NAMD software for solute-solvent configurations consisting of the CPC$_{60}$ donor-acceptor system in explicit solvent using Periodic Boundary Conditions with a box size of 100 Å x 100 Å x 70 Å (figure 32). The total number of atoms in a simulation will vary between 50,000 and 100,000 atoms depending on the solvent density. Moreover, four different solvents (water, chloroform, toluene, and benzonitrile) will be studied in order to gain insight into the effect of solvent polarity strength on the CT energetics. The final production run will consist of a 10-nanosecond NVT-ensemble simulation.
Step 2: At this point, structural solute-solvent configurations will be selected at evenly spaced intervals along the 10-ns production run trajectory, yielding a total of 100 different structural configurations. Next, a solvation sphere surrounding the solute will be cut-out from each of the selected trajectory snapshots in order to reduce the total number of atoms for a subsequent partial charge calculation.
partial charges of the new solute-solvent cut-out will be derived from either single-point semi-empirical calculations or the Charge Equilibration method.

**Step 3:** QM/MM calculations will be performed to relax the donor-acceptor geometry in the presence of solvent molecules. The solute is optimized at the DFT level and the surrounding solvent shell obtained from the MD simulation is accounted for by including the solvent interaction energies as point charges in the Hamiltonian in a self-consistent iterative minimization. The relaxation of the density matrix due to the solvent external perturbation may be identified as the polarization of the QM region.

**Step 4:** This final step is the most computationally demanding. The 100 optimized donor-acceptor geometries given by the previous QM/MM calculations will be submitted for excited state calculations using the Perturbative $\Delta$SCF method. Usually, several localized states on both donor and acceptor components participate in CT transitions. Therefore, a set of 6 separate excited state calculations will be run for each of the 100 QM/MM-optimized solute geometries for both singlet and triplet excited state electronic configurations. This step totals 1,200 different excited state calculations.

In figure 33, a comparison of various calculated excited state levels for the triad in vacuum is made to experimentally determined excitations of the triad in a polar solvent. The figure highlights a significant difference in excited state energy level ordering between the triad in the gas-phase and in solution by lines stretching from the left-side diagram (vacuum) to the right-side diagram (solution). Two main factors may account for the discrepancy of ~1.0 eV between our calculated gas-phase CT energy and the experimental value: (1) the triad undergoes various structural changes in solution which alter the frontier orbital energies and (2) the solvent stabilization has a large impact on the CT energies. Our extensive conformational study in the previous chapter of the triad in gas-phase resulted in a maximum variation of 0.4 eV in CT energies. In our solute-solvent QM/MM calculations, we obtain a lowering of the CT excited state energy for one of the snapshots by 0.4 eV.
Figure 33. A comparison of various calculated excited state levels for the triad in vacuum (left diagram) with experimentally determined excitations of the triad in a polar solvent (right diagram).
References

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Vita

Marco Augusto Olguin, born on July 20, 1982 in El Paso, Texas, USA, is the child of Sara Esther Fortuño Villaseñor. He obtained his Bachelor of Science degree in Chemistry on May 2007 from the University of Texas at El Paso (UTEP). In the summer of 2007, he entered the graduate program of UTEP as a Chemistry major with a Teaching Assistantship. During the course of five consecutive semesters as a Teaching Assistant, he implemented and taught an undergraduate computational chemistry class in the Chemistry Department using various quantum chemistry software packages. During his graduate studies in Chemistry, his research focus was on aromaticity using quantum chemical methods. He decided to pursue a Ph.D. degree in Computational Science at UTEP. The doctoral level research was focused on the study of charge transfer energetics in organic photovoltaic systems.

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