Electronic structure and charge transfer excited states of a multichromophoric antenna

Luis Basurto\textsuperscript{1}, Rajendra R. Zope\textsuperscript{2}, and Tunna Baruah\textsuperscript{1,2}\textsuperscript{*}

\textsuperscript{1}Computational Science Program, The University of Texas at El Paso, El Paso, TX 79958, USA and
\textsuperscript{2}Department of Physics, The University of Texas at El Paso, El Paso, TX 79958, USA

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Abstract

The electronic structure of a multichromophoric molecular complex containing two of each borondipyrromethane dye, Zn-tetraphenyl-porphyrin, bisphenyl anthracene and a fullerene are studied using density functional theory. The snowflake shaped molecule behaves like an antenna capturing photon at different frequencies and transferring the photon energy to the porphyrin where electron transfer occurs from the porphyrin to the fullerene. Molecular structure of this large complex is first optimized using plane wave projector augmented wave methodology. Subsequent electronic structure calculations are performed using the real space methodology using an all electron pseudopotential basis set containing total of 12478 basis functions. The results show that the HOMO and a state below the HOMO are primarily localized on one of the porphyrins while the LUMO resides mainly on the fullerene component of the complex. The energies of the HOMO and LUMO states in the complex, as adjudged by the ionization potential and the electron affinity values, show significant differences with respect to their values in participating subunits in isolation. We have systematically examined the effect of structural strain and the presence of ligands on the ionization energy and the electron affinity. Finally, we have calculated a few lowest charge transfer energies involving electronic transitions from a the porphyrin component to the fullerene subunit of the complex using the perturbative delta-SCF method. Our predicted value of the lowest charge transfer excited state (1.67 eV) is comparable to the experimental estimate of the charge transfer energy of a similar complex.

\textsuperscript{*} Corresponding author: tbaruah@utep.edu
I. INTRODUCTION

The organic heterojunction photovoltaics are often designed as a donor-acceptor complex that consists of a p-type and an n-type semiconductor. These materials can be in molecular or polymeric form [1–6]. However, often the absorption band is limited to that of the donor material. One way to overcome this limitation is to modify the electronic structure of the chromophore through chemical groups to broaden the absorption spectrum. Another way that has been pursued by a few groups is to use an antenna-like construct [7–13]. Such molecular antennas are made to mimic the action of biological antennas seen in plants. The function of biological antenna is to capture solar energy at different wavelengths and funnel the energy to the reaction center. One such interesting artificial molecular antenna was synthesized recently by Gust and co-workers [13]. This molecular antenna contains a wheel shaped hexaphenylbenzene core where each of the phenyl rings is connected to a chromophore forming a hexad. The supramolecule contains two of each of the chromophores: porphyrin (either H2 or Zn), bis(phenylethynyl)anthracene (BPEA), and borondipyrromethane (BODIPY). Both the BPEA and BODIPY units function by absorbing photons at different wavelengths and subsequently funneling the absorbed photon energy to one of the porphyrins. One advantage of such a construct is that together the BPEA and BODIPY widen the absorption band to the region where porphyrin absorption is weak. The BPEA moieties absorb in 430-475 nm region which is between the porphyrin Soret and Q-bands. On the other hand BODIPY absorb in the 475-530 nm and 330-430nm region. Thus the absorption range is quite extended for this complex. Another advantage is that singlet-singlet energy transfer takes place from both the BPEA and BODIPY to the porphyrin. Similar to the reaction center in natural light-harvesting systems, an electron transfer takes place from the porphyrin to the fullerene. The dynamics in the base porphyrin hexad without the fullerene moieties is slightly different from that of the Zn-porphyrin hexad. In the absence of an acceptor moieties, an electron transfer takes place from the Zn-porphyrin to BODIPY. However, in the presence of a C60 molecule, rapid electron transfer takes place from the porphyrin to the C60. The experiments were performed in 1,2 difluorobenzene and 2-methyltetrahydrofuran both of which are polar solvents with 1,2 difluorobenzene ($\epsilon = 13.8$) being more polar than 2-methyltetrahydrofuran ($\epsilon = 7.36$).

The dynamics of the electron and energy transfer in this system makes it very interesting. The present article reports a density functional theory [14, 15] (DFT) based electronic structure study of the hexad in its ground state and the lowest charge transfer state. We have recently developed a perturbative $\Delta$-SCF methodology to describe the charge transfer states of donor-acceptor systems. The initial applications on smaller systems showed excellent agreement with experiment [16]. In this article, we present a study of the lowest charge transfer state in the complex using the perturbative delta-SCF method. In the next section we describe the computational methods followed by results and discussions of our study.
II. COMPUTATIONAL METHOD

All the calculations reported here are done using the density functional theory using the PBE exchange-correlation functional within the generalized gradient approximation (GGA) \[17\]. The large size of the complex presents challenges for quantum mechanical calculations. To reduce the computational costs, the methyl groups are replaced by hydrogens resulting in a complex with 421 atoms. The structure optimization of the heptad was carried out using PAW pseudopotentials as implemented in the VASP code \[18\] \[23\]. The VASP optimized structure is then used to derive all the results reported here using the NRLMOL code \[24\] \[27\]. The NRLMOL code has previously been used to study large light-harvesting systems \[28\] \[30\]. In this work, we have used both the all-electron formalism and pseudopotential formalism wherever all-electron approach was difficult to apply due to the large size of the molecule. We used a mixed all-electron and pseudopotential approach for the ground state calculations. In the ground state calculation, all-electron basis is used for the hydrogens and the zinc atoms whereas for all the other types of atoms pseudopotential given by Bachelet, Hammam and Schluter is used \[31\].

The numbers of the primitive Gaussians, s-type, p-type and d-type functions along with the range of the exponents for each type of atoms are given in table I. All the contracted basis functions for a given atom are derived from the same set of primitive Gaussians. The mixed basis set contained 12478 basis functions in total. The all-electron basis set used in this work were optimized for PBE-GGA functional \[32\]. In a similar way, the pseudopotential basis is also optimized for the BHS pseudopotential. The basis set used here is larger than the typical 6-311G basis set used for moderate size molecules. Our efforts to perform calculations at the all-electron level with the 6-311G basis showed numerical instability forcing the convergence criteria to be reduced. Because of the numerical errors, we performed the ground state calculations with the mixed pseudopotential and all-electron approach using the NRLMOL basis functions only. To reduce the computational cost, only spin-restricted calculations are done. The intramolecular excitation energies for the electronic transitions occurring on the same part of the molecule are studied using the time dependent theory as implemented in Gaussian09 \[33\]. The charge transfer excitations are not well described by the TDDFT unless specially optimized range corrected functionals are used. However, perturbative delta SCF method as illustrated in our recent article \[16\] \[34\] provides satisfactory description of charge transfer excitations. The method reproduces experimental values of charge transfer excitation energies for a database of tetracyanoethylene-hydrocarbon complexes and other model organic photovoltaic complexes within 0.3 eV or less. This set also includes a porphyrin fullerene complex which are the units involving charge transfer in the present study. 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. The method has been previously
used to study the charge transfer excitations in a few fullerene porphyrin dyads[35, 36] and carotene-porphyrin-fullerene triad[34]. Its predictions on C70 porphyrin[36] are consistent with recent many-body Green’s function GW study[37]. For the details of the method and its performance we refer reader to our recent articles Ref. 16, 34. Since the excited state calculations require larger memory, we have used a triad cutout of the heptad for the excited state calculations. The calculations on both the ground and excited states of the triad cutout was carried out at the all electron level. We have further verified that the charge transfer excited state energy using the pseudopotential differs from the all-electron approach by only 0.04 eV.

III. RESULTS AND DISCUSSION

The heptad molecule contains a hexaphenylbenzene core where the phenyl rings lie at nearly 90° angle to the central benzene ring. The planes of the anthracenes are at ~ 90° angle to the phenyl ring of the core whereas those of the BODIPY are in plane with their corresponding phenyl rings. On the other hand the porphyrins are strained such that the rings connected to the porphyrins are distorted from 90° angle. The DFT optimized structure of the heptad molecule is shown in Fig. 1. The electron donor (zinc-tetraphenyl porphyrins) and acceptor(fullerene) moieties are connected through a pyridine with a separation of roughly 6.8 Å between the Zn ion at the porphyrin center and the nearest fullerene surface. The two pyridines are connected through a single carbon on top of a 6:6 bond of the fullerene. The fullerene molecule is rigidly wedged between the two porphyrins such that torsions of the fullerene-porphyrin linker is unlikely to occur. Since the structure of the electron donor-acceptor part of the complex is rigid, the possibility of isomerization in the presence of a solvent is much lower [13].

The calculated density of states of the gas-phase heptad is shown in Fig. 2. The fermi
FIG. 1: (Color online) The structure of the heptad complex.

energy is marked as a straight line in the plots. The site-decomposed DOS is also presented for the various distinct units of the supramolecule - the hexaphenyl benzene core, Zn-porphyrin, BODIPY, BPEA and the fullerene. Since the DOS belonging to the two components of Zn-porphyrin, BODIPY, and BPEA are identical, only one set of DOS for each of these units are shown. The pyridine units are considered as part of the porphyrin moieties for plotting the DOS. Since the molecule has two symmetrically placed porphyrins, the highest two occupied molecular orbitals, HOMO and HOMO-1 of the heptad, are localized on the porphyrins are nearly degenerate. They are predominantly located on one of the porphyrins with some orbital density also on the other counterpart. The fullerene LUMOs form the lowest three LUMO of the heptad which split into a doublet and a singlet with an energy spacing of 0.24 eV between them at DFT GGA level. Thus the lowest charge transfer occurs from one of the porphyrins to the fullerene. The HOMO of BPEA lies in between the two occupied Gouterman orbitals of the porphyrins whereas the HOMO of the BODIPY is lies deeper than the porphyrin Gouterman orbitals. The HOMO of the BODIPY is about 0.3 eV lower than the HOMO-2 of the Zn-porphyrin. However, the LUMO of the BODIPY is only slightly higher than fullerene LUMOs as seen from the Fig. 2. The HOMO-LUMO separation for these different units of the heptad as given by the KS-DFT ground state calculation are about 1.5 eV for Zn-porphyrin, 1.5 eV for fullerene, 2.0 eV for BODIPY and 1.3 eV for BPEA. These gaps are underestimated in the KS-DFT calculations due to the self-interaction errors and missing derivative discontinuities in DFT functionals but it qualitatively shows the relative ordering of the orbitals belonging to different units.
FIG. 2: (Color online) The density of states of the heptad molecule. The site projected density of states on the various components are shown.

The ordering seen in the orbitals localized on different units supports the fact in the absence of the fullerene moieties, charge transfer occurs from the porphyrin to the BODIPY which was noted by Gust et al. [13].

The dipole moment of the heptad in its ground state is small due to its symmetrical structure. Our calculated value for the dipole is 3.98 Debye which points from the fullerene to the hexaphenyl-benzene core.

In the heptad molecule the pyridine ligands attached to the fullerene binds to the zinc ions in the ZnTPPs. Thus the Zn ions are in five-fold coordination in this compound. The porphyrins in the heptad molecule are strained. We have relaxed the structure of a free ZnTPP molecule with an axial pyridine ligand. The ligand changes the structure such that the phenyl rings are twisted (Cf. Fig. [3]). The porphyrin plane itself also puckers out. Such puckering of the porphyrin plane was reported earlier in a number of studies [39][41].

Relaxation of the free porphyrin structure as present in the heptad reduces the energy of the pyridine ligated Zn tetrapenylporphyrin by 0.51 eV. These results not only bring out the impact of the pyridine ring on the electronic structure of the porphyrin but are also indicative of the strain on the pyridine-porphyrin units in the heptad molecule. One of the effects of the structural distortion is to reduce the HOMO-LUMO gap. We have employed both the TDDFT method and also a perturbative delta-self-consistent field method at the all-electron spin-polarized formalism to calculate the excitation energies of the pyridine-ligated ZnTPP and free ZnTPP without the axial ligand. The first singlet excitation of a free ZnTPP with no axial ligand is calculated to be at 2.03 eV using the perturbative delta-SCF. This energy is close to the value of 2.01 eV for the lowest singlet excited state obtained from TDDFT. For an isolated relaxed ZnTPP with the axial pyridine, the calculated energy of the lowest
singlet excited state using the perurbative delta-SCF method is 1.84 eV. The other singlet excitations in free pyridine-ligated-porphyrin are 1.90 eV (H→L+1), 2.17 (H-1→L), 2.21 eV (H-1→L+1), and 2.99 eV (H→L+2). Since mixed characters of excited states are not well reproduced by this method, we have also calculated these excited state energies using TDDFT method. The TDDFT calculation was carried out using the Gaussian09 code[33]. The TDDFT calculation shows that the lowest singlet is a mixing of H→L, H→L+2, H-1→L+1 excitations with an excitation energy of 1.99 eV. The next singlet is at 2.01 eV. The mixing of the states in the pyridine-porphyrin is different from the free ZnTPP. In free ZnTPP the lowest singlet is comprised of H→L, H→L+1, H-1→L, and H-1→L+1 excitations. The lowest singlet excited state of pyridine-ligated-Zn-porphyrin in the heptad molecule was estimated at 2.03 eV by Gust et al. [13]. The ZnTPP Q band is reported to show a red-shift of ∼ 15 nm due to the appended pyridine coordinated to the metal atom [42, 44].

Our calculated value for the porphyrin local excitation in the (ZnTPP)₂-C₆₀ is 1.75 eV and the excitation from the porphyrin HOMO-1 to porphyrin LUMO occurs at 2.13 eV. These energies are slightly lower than those for the free pyridined-porphyrin mostly due to strain. This was confirmed by calculating the lowest excitation in the strained pyridine ligated porphyrin. Mixing of the states similar to that predicted by TDDFT method for
free pyridined-porphyrin is likely increase the energy of the lowest singlet excited state. The TDDFT calculations on triad could not be carried out due to its large size.

The calculated ionization potential (IP) of the triad cutout is also much smaller compared to the free ZnTPP. This happens possibly due to the fact that the HOMO is delocalized with substantial density on the second porphyrin and also due to the presence of the axial ligation to the pyridine connecting the porphyrin to the C$_{60}$. The HOMOs of the two porphyrins are degenerate. Our calculated ionization potential of a single porphyrin with an axial pyridine on top shows that the IP changes from 6.34 eV for a free ZnTPP to 6.00 eV for the pyridine-ligated-porphyrin. Lack of experimental data on ultraviolet photoelectron spectra of pyridine-ligated porphyrin hinders a direct comparison. The electrochemical measurements are done in solution in which the choice of the solvent is important. Experimentally, a change of $\sim 0.11$ eV was reported in the oxidation potential of Zn-tetraphenyl porphyrin in pyridine in electrochemical measurements in solution [45, 46]. Strain on the porphyrin plane, similar to that present in the heptad, further reduces it to 5.86 eV. The calculated value of the IP of the (ZnTPP)$_2$-C$_{60}$ at all-electron level is 5.54 eV. The IP of the full heptad molecule using mixed pseudopotential and all-electron approach differs only slightly at 5.49 eV. The HOMO level is spread over both the porphyrins although it is mostly localized on one. This spread may raise the HOMO energy further up thereby reducing the ionization energy. The electron affinity of the (ZnTPP)$_2$-C$_{60}$ is also higher (2.94 eV) than that for an isolated C$_{60}$ molecule (2.68 eV). These changes are much larger than the change seen in non-bonded C$_{60}$-ZnTPP complexes in cofacial arrangement or endon orientations [35, 36]. Furthermore, experimental measurement of reduction potential of a dipyridine C$_{60}$ model reports a change of 10-40 meV only [13]. Similar change was noted for single pyridine connected to a fulleropyrrolidine [44]. Our calculations on a free dipyridine-C$_{60}$ molecule but with same structure as in the heptad shows that the vertical electron affinity increases from free C$_{60}$ by about 0.09 eV. Relaxation of the structure of this dipyridine-C$_{60}$ resulted in decrease of electron affinity to 2.62 eV. A plot of the difference of the density in the neutral and the anionic state shows density distribution both on the C$_{60}$ as well as on the pyridine rings (Cf. Fig. 4). Possible polarization effects on the porphyrin components may lower the energy of the anionic state.

We have used the perturbative $\Delta$-SCF method to determine the lowest charge transfer excitation energy of the heptad which occurs from the porphyrins to the fullerene. In the perturbative $\Delta$-SCF method, the occupied orbitals are expanded in the space of unoccupied orbitals using a perturbative approach. As mentioned earlier, it applications to small donor-acceptor organic conjugates[16] as well as to supramolecular carotenoid-porphyrin-C$_{60}$ triad [34] and porphyrin-fullerene dyads [36] show that the method can be reliably used to determine the charge transfer excitation energies for systems with vanishing transition dipole moments. The method is computationally as expensive for a given excited state as the Kohn-Sham DFT for the ground state. However, the excited state calculations require larger memory since the information about the ground state Hamiltonian is retained. Be-
cause of the large memory requirement for the calculation of the excitation energies, we have used a smaller triad model of the heptad containing only the donor and acceptor moieties as shown in Fig. 2. The geometry of the triad was not optimized to mimic the geometry of that part of the heptad. This part of the heptad will be referred as triad cutout hereafter. The HOMO of the triad cutout is on the porphyrins and the LUMO is on the fullerene. Since this model system is smaller in size, we used an all-electron approach to calculate the excited states. Our calculated CT excitation energy from the HOMO on the Zn-porphyrin to the LUMO of the fullerene in the triad is 1.67 eV. We find that the excited state energies differ only by 0.04 eV if we use a pseudopotential basis instead of an all-electron basis. Experimental estimate of the CT energy on the full heptad molecule is made from the reduction potential of a model C$_{60}$-dipyridine molecule and oxidation potential of pyridined-ZnTPP. This energy is estimated to be 1.37 eV by Gust et al. [13]. On another similar bis-porphyrin-fullerene triad, the experimental value of the CT excitation from porphyrin to C$_{60}$ is found to be 1.46 eV [47]. The linkers connecting the porphyrins to the fullerene in the bis-porphyrin-fullerene triad in Ref. [47] are quite different. The effect due to the axial pyridine ligands is hence missing and therefore a direct comparison between our calculated value and experimental estimate is not possible. We have also calculated the charge transfer excitation from a porphyrin HOMO-1 to fullerene LUMO. Energy of this CT excited state is 2.07 eV. The plots of orbital densities show a low lying virtual bridge state situated on the pyridine linkers. Our calculations show that excitation from HOMO to the pyridine bridge state (Fig. 6) leads to another CT state at 2.82 eV which shows that this state is
FIG. 5: (Color online) The lowest HOMO to LUMO charge transfer state.

unlikely to participate in any charge transfer transition resulting from porphyrin Q-band. The calculated excitation energies do not account for any structural reorganization of the complexes. The ionic relaxation in the triad or heptad is likely to be small due to the highly constrained structures of the complexes. The electrochemical measurements in experiments are carried out in polar solvents such as methyltetrahydrofuran where the solvent reaction field can further stabilize the excited state. The dipole moment of the ground state of the triad cutout is 2.48D and in the CT excited state it increases to 36D. The distance between the Zn ion to nearest fullerene surface distance is about 6.8 Å in this complex which explains the dipole moment of the CT state.

In summary, we have studied the electronic structure using DFT of a multichromophoric molecular heptad that behaves like an antenna. In its ground state, the highest occupied molecular orbital is located mostly on one of the porphyrins and the lowest unoccupied MO is on the fullerene. We find that the BODIPY HOMO lies deep compared to other components of the heptad. In agreement with experimental observation of Gust et al. [13] our calculations indicate that in absence of the fullerene, the electron electron transfer would occur from the Zn-porphyrin to the BODIPY. The ionization potential and electron affinity of the heptad is quite different than that for a ZnTPP or ZnTPP with pyridine ligand. The strain on the porphyrins, presence of the axial pyridine ligands, and the delocalization of the HOMO orbital contributes to the reduction of the ionization potential. The electron
affinity of the haptad also significantly differs for the heptad from an isolated $C_{60}$ or isolated dipyridine-$C_{60}$ molecule possibly due to polarization effects. Our calculated value of the HOMO-LUMO charge transfer energy for a representative bis-porphyrin-fullerene triad cutout is 1.67 eV. The dipole moments of such CT states are high 36D. In this molecule the reorganization of the porphyrins and fullerenes is likely to be small due to the structural constraints. The difference between the calculated value and the experimental energy is likely due to the effects of polar solvents which will stabilize the excited state.

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