



Density functional investigation of the electronic structure and charge transfer excited states of a multichromophoric antenna



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ABSTRACT

We report an electronic structure study of a multichromophoric molecular complex containing two of each borondipyromethane dye, Zn-tetraphenyl-porphyrin, bisphenyl anthracene and a fullerene. 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. The study is performed within density functional formalism using large polarized Gaussian basis sets (12,478 basis functions in total). 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. These differences are also larger than the variations of the ionization potential and electron affinity values observed in non-bonded C₆₀-ZnTPP complexes in co-facial arrangement or end-on orientations. An understanding of the origin of these differences is obtained by a systematic study of the effect of structural strain, the presence of ligands, the effect of orbital delocalization on the ionization energy and the electron affinity. Finally, a few lowest charge transfer energies involving electronic transitions from the porphyrin component to the fullerene subunit of the complex are predicted.

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1. 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 borondipyromethane (BODIPY). Both the BPEA and BODIPY units function by absorbing photons at different wavelength 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 330–430 nm 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. These 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 ($\epsilon = 7.36$) [13].

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The dynamics of the electron and energy transfer in this system makes it very interesting. Using a model two-state hamiltonian, Ghosh et al. [14] have examined the energy and charge transfer rates in the antenna system and found the overall quantum yield to be 95%. The present article reports a density functional theory [15,16] (DFT) based electronic structure study of the heptad in its ground state and the lowest charge transfer state. We systematically study the changes in the frontier energy levels of the complex and its subunits by computing these quantities using the standard delta self consistent method for the complex, subunits, strained subunits, and subunits with ligands. We also examine the intramolecular excitations using the time dependent density functional theory and the charge transfer excitations using our recently developed a perturbative Δ -SCF methodology. We note that the Δ -SCF approach, unlike the TDDFT can describe charge transfer excitation using standard GGA functionals as shown in Ref. 17. In the next section we describe the computational methods followed by results and discussions of our study.

2. Computational method

All calculations reported here are done using the density functional theory using the PBE exchange–correlation functional within the generalized gradient approximation (GGA) [18]. 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 first carried out using PAW pseudopotentials as implemented in the VASP code [19–24]. The VASP optimized structure is subsequently used to derive all the results reported here using the NRLMOL code [25–28]. The NRLMOL code has previously been used to study large light-harvesting systems [29–31]. 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. 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 [32].

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 1. All the contracted basis functions for a given atom are derived from the same set of primitive Gaussians. The mixed basis set contained 12,478 basis functions in total. The all electron NRLMOL (Porezag-Pederson) basis set [33] is specially optimized for the PBE functional used in this work and satisfies the $Z^{10/3}$ (where Z is an atomic number) condition that has been shown to provide accurate description of core binding energies and correct for basis set superposition error. In a similar way, the pseudopotential basis is also optimized for the BHS pseudopotential.

Table 1
The numbers of s-, p-, d-type contracted functions, number of primitive Gaussian and the range of the Gaussian exponents used for each atom.

Atom	s-type	p-type	d-type	Primitives	Exponent range
<i>Pseudo-potential basis</i>					
B	4	4	3	5	4.16–0.069
C	4	4	3	6	5.65–0.077
N	4	4	3	6	8.55–0.104
O	4	4	3	7	$1.05 \times 10^{-0.100}$
F	4	4	3	7	$1.45 \times 10^{-0.131}$
<i>All-electron basis</i>					
C	5	4	3	12	2.22×10^4 –0.077
N	5	4	3	13	5.18×10^4 –0.094
H	4	3	1	6	$7.78 \times 10^{-0.075}$
Zn	7	5	4	20	5.00×10^6 –0.055

The basis set used here is larger than the typical 6-311G basis set used for moderate size molecules. 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 (molecular units) are studied using the time dependent theory as implemented in Gaussian09 [34]. Due to the smaller sizes of these molecular units TDDFT calculations could be performed. The TDDFT calculations proved impractical for the full complex. 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 [17,35] 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 molecular 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 [36,37] and carotene-porphyrin-fullerene triad [35]. Its predictions on C_{70} porphyrin [36] are consistent with recent many-body Green's function GW study [38]. For the details of the method and its performance we refer reader to our recent articles Ref. 17, 35. Since the excited state calculations require larger memory, we have used a hexad cutout of the heptad for the excited state calculations. The calculations on both the ground and excited states of the hexad cutout were 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.

3. 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 $\sim 90^\circ$ 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 energy is marked as a straight line in the plots. The site-decomposed DOS is also presented for 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

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