

Ab Initio Description of Photoabsorption and Electron Transfer in a Doubly-Linked Porphyrin-Fullerene Dyad

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Abstract: Structure, photoabsorption and excited states of two representative conformations obtained from molecular dynamics (MD) simulations of a doubly-linked porphyrin-fullerene dyad DHD6ee are studied by using both DFT and wavefunction based methods. Charge transfer from the donor (porphyrin) to the acceptor (fullerene) and the relaxation of the excited state are of special interest. The results obtained with LDA, GGA, and hybrid functionals (SVWN, PBE, and B3LYP, respectively) are analyzed with emphasis on the performance of used functionals as well as from the point of view of their comparison with wavefunction based methods (CCS, CIS(D), and CC2). Characteristics of the MD structures are retained in DFT optimization. The relative orientation of porphyrin and fullerene is significantly influencing the MO energies, the charge transfer (CT) in the ground state of the dyad and the excitation of ground state CT complex (g-CTC). At the same time, the excitation to the locally excited state of porphyrin is only little influenced by the orientation or cc distance. TD-DFT underestimates the excitation energy of the CT state, however for some cases (with relatively short donor-acceptor separations), the use of a hybrid functional like B3LYP alleviates the problem. Wavefunction based methods and CC2 in particular appear to overestimate the CT excitation energies but the inclusion of proper solvation models can significantly improve the results.

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Key words: dyad; porphyrin; fullerene; DFT; CC2; charge-transfer

Introduction

Covalently linked porphyrin-fullerene dyads with porphyrin acting as an electron donor (D) and fullerene as an electron acceptor (A) have attracted considerable interest as synthetic photoreaction centers. In the quest for designing molecular ensembles with improved light-induced charge-separation characteristics, one important issue is to understand the steps and mechanisms involved in the photophysics of these systems at quantum chemical level.

In a previous study,¹ we have investigated the ground and excited state properties of a porphyrin-fullerene dyad (H₂P-O34-C₆₀) in which the D-A molecules are connected by a single relatively flexible molecular chain (linker) that allows a substantial degree of conformational flexibility of the molecular geometry. In the present study, we address the same issues in the case of a porphyrin-fullerene dyad (DHD6ee) in which the geometrical freedom of the D-A moieties is significantly restricted by two interconnecting chains (see Fig. 1). In both studies, the conformational behavior of the dyads was investigated by

means of molecular dynamics (MD) simulations performed with the GROMACS MD simulation package. The simulations performed both in vacuum and in solvent environment enabled the identification of the preferred (representative) conformations of the dyad which are investigated here by quantum chemical methods.

Two representative conformations (CA and CB) presented in Figure 2 (2a and 2b, respectively) were selected from our vacuum MD simulations.² The two representative conformations have almost the same center-to-center (cc) distance between porphyrin and fullerene (~6.1 Å) but differ in the relative orientation of porphyrin and fullerene (see Fig. 2). The cc distance represents the distance between the center of fullerene and the center of the porphyrin ring and is mainly determined by the

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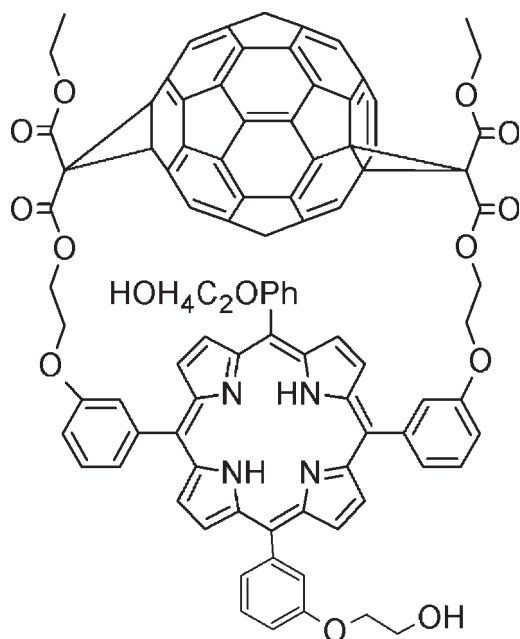


Figure 1. A 2-dimensional view of the DHD6ee dyad. The phenyl substituent is denoted by Ph.

interaction between the porphyrin and fullerene moieties, which includes also the ground state CT interaction, as pointed out for several other D-A molecular complexes.^{3,4}

The two linkers of DHD6ee restrict mainly the cc distance, as shown by our previous molecular dynamics (MD) simulations,² to values which favor an appreciable D-A interaction and a fast electron transfer (ET) between the donor and the acceptor. The strong porphyrin-fullerene interaction is revealed in the absorption spectrum of DHD6ee, which is broader, lower in intensity, and shifted to the red in the Soret band region when compared with the sum-spectrum of porphyrin and fullerene. The absorption spectrum also exhibits in the near-infrared (NIR) region an additional broad weak band, which is assigned to the absorption of a charge-transfer (CT) complex formed at the ground state of the dyad (g-CTC).⁵ The CT absorption band is observed also in the absorption spectrum of H₂P-O34-C₆₀, however its intensity is approximately three times lower.^{6,7} In addition, the ET rate calculated for DHD6ee from spectroscopic measurements is 2–3 orders of magnitude larger than that of H₂P-O34-C₆₀.

Following the photoexcitation of DHD6ee, three intermediate excited states have been identified experimentally prior to the relaxation to the ground state: (a) the locally excited singlet porphyrin state P¹S₁, (b) the excited state charge transfer complex (ex-CTC) or exciplex, and (c) the charge separated state (CS),

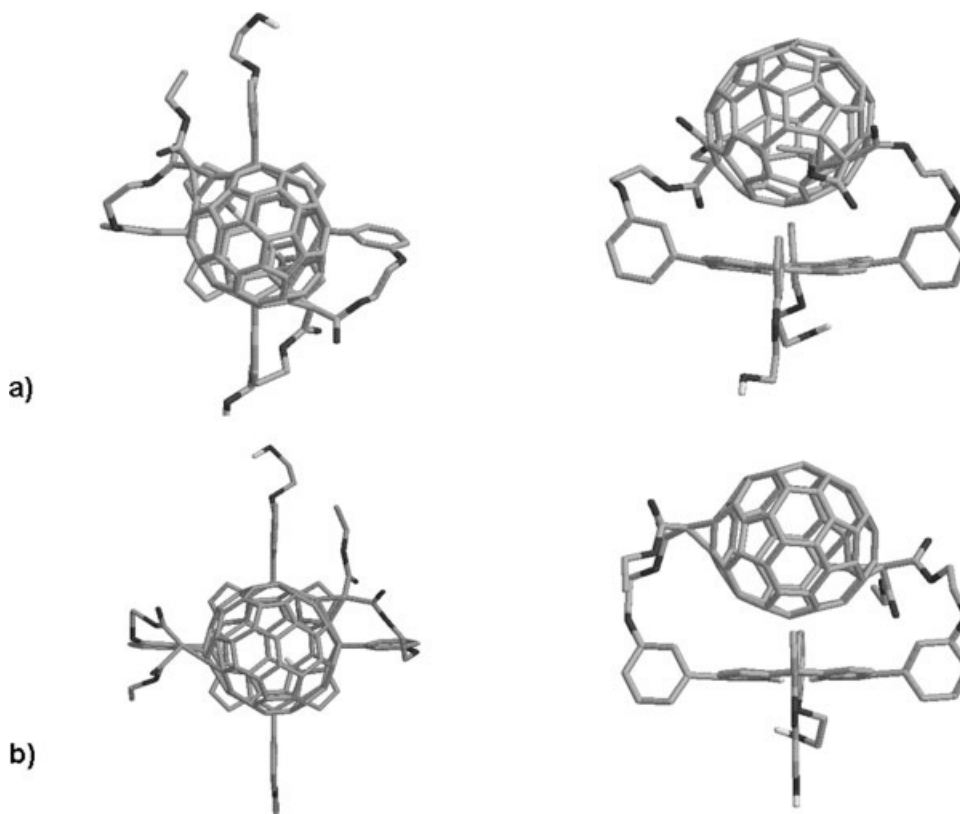


Figure 2. Top and side views of two (a) CA and (b) CB selected representative conformations obtained from MD simulations. Figure adapted from Ref. 2.

which is identified in polar solvents only.^{6,7} The (a) and (c) excited states together with the locally excited singlet and triplet states of fullerene are commonly identified as intermediate states following the photoexcitation of various porphyrin-fullerene dyads described in literature.^{5–10} The exciplex, which represents the conformational relaxed state evolving after the Franck-Condon excitation of the g-CTC, was proven in recent studies to be an important intermediate step in the photophysics of porphyrin-fullerene dyads (and related) systems.^{11–16}

The ultimate challenge in the analysis of ET processes is to gain a detailed understanding of the influence exerted by the molecular and electronic structures of the donors and acceptors on the pathways of the process. Bearing in mind that the ET pathways are mainly dictated by the relative energies of the intermediates and the energy barriers separating them we use DFT and wavefunction based methods in the calculations of both ground and excited state properties of the representative conformations CA and CB of DHD6ee. Several issues related to the ground state and excited states properties of DHD6ee prove to be very interesting from the point of view of both the practical understanding of the phenomena involving DHD6ee and the assessment of the TD-DFT performance and accuracy: (i) interaction of porphyrin and fullerene in the ground state of the dyad and the charge transfer character of the formed ground state; (ii) excitation energies of the dyad, in particular for the electronic transition to the first CT state and for the locally excited singlet porphyrin state; (iii) relaxation of the excited state of the g-CTC to the ex-CTC; (iv) characterization of the ex-CTC; (v) performance of various functionals, as it is known that in general LDA and GGA functionals present a more systematic behavior although hybrid functionals may match better with experiments; (vi) comparison of TD-DFT and wavefunction based methods for the difficult case of CT excitations.

Computational Methods

We compare the results given by LDA, GGA, and hybrid functionals. As representatives of the LDA and GGA the Slater-Vosko-Wilk-Nusair (SVWN)^{17,18} and the Perdew-Burke-Ernzerhof (PBE)¹⁹ functionals were chosen. Becke's three parameter hybrid functional with the Lee-Yang-Parr correlation functional (B3LYP) is used in single point (SP) calculations carried out for properties evaluations.^{20,21}

The basis set used throughout the calculations is the Karlsruhe split-valence basis set augmented with polarization functions (SVP).^{22,23} The SVP basis set consists of two basis functions for H (4s)/[2s], six basis functions for C (7s4p1d)/[3s2p1d], and six basis functions for N (7s4p1d)/[3s2p1d]. The terms in parentheses represent the numbers of primitive functions of each type and the terms in square brackets represent the numbers of contracted basis functions of each type. The resolution of identity approach (RI) is used in the LDA and GGA calculations to reduce the computational effort.²⁴ The TD-DFT excited state geometry optimizations are carried out as described in Ref. 25 and implemented in the Turbomole software package.²⁶

In addition to the various density functionals, the lowest energy transition is calculated at the DFT equilibrium geome-

tries with the approximate coupled-cluster singles and doubles method, CC2.^{27,28} We also investigate the less costly coupled cluster singles (CCS)²⁷ and configuration interaction in the space of all single substitutions with a doubles correction (CIS(D))²⁹ methods. The CIS(D) includes a second-order perturbation correction for dynamical correlation which computationally scales with the fifth power of the molecular size, only, and furthermore, it is size-consistent. CIS(D) can also be considered as a noniterative variant of the CC2 model^{27,30} (and thus is by about a factor of ten times faster). In the correlation treatments, occupied orbitals with orbital energies <1.5 E(HOMO) and high-lying virtual MOs with orbital energies >4 E(LUMO) are excluded. The SVP basis set and the RI approximation are used in the calculations which were all performed with the Turbomole software package.

The solvent stabilization is estimated by the Onsager model,³¹ in which the solvent is treated as a dielectric continuum without a specific structure. The solute is embedded in a spherical cavity with the so-called Onsager radius a . The macroscopic properties of the solvent are considered by the relative permittivity ϵ and the refractive index n . Although it is a very crude model, it nevertheless allows an estimation of the stabilization energy of charge separated states in a polar solvent. It also has to be mentioned that small changes in the cavity radii cause large shifts in the computed stabilization.

The solvation energy for the electronic ground state is calculated using Onsager's formula for a fully relaxed state (E_{sf}), that is, assuming that the solvent relaxes fully about the dipole μ_i :

$$\Delta E_{sf} = -\frac{2\mu_i^2}{4\pi\epsilon_0 a^3} \frac{\epsilon - 1}{2\epsilon + 1}. \quad (1)$$

Excited state solvation energies are calculated using the formula for a partially solvated. If the moment of the solute changes from μ_i to μ_f so fast that the solvent dipoles can not reorient, the solvation energy is calculated using the formula for a partially solvated state:

$$\Delta E_{sp} = -\frac{2\mu_f\mu_i}{4\pi\epsilon_0 a^3} \left(\frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right) - \frac{2\mu_f^2}{4\pi\epsilon_0 a^3} \frac{n^2 - 1}{2n^2 + 1}. \quad (2)$$

Equations (1) and (2) are used to evaluate the vertical excitation energies in solution phase as:

$$E_{ex}^{solv} = E_{ex} + E_{sp} - E_{sf}. \quad (3)$$

Several approaches for evaluating the Onsager cavity radius exist,³² of which the one proposed by Wong and coworkers has been shown to provide reasonable estimates.³³ This approach, which is used also in the present work, specifies the cavity as a sphere whose volume is 1.33 times the volume enclosed by the 0.001 a.u. electron density contour, plus an additional 0.5 Å. The same cavity is assumed for both ground and excited states of the solute. The dipole moments are obtained from TDDFT calculations. The calculations of solvation energies are carried out using toluene as solvent⁵ with $\epsilon = 2.4$ and $n = 1.5$.

Table 1. Ground State Porphyrin-Fullerene Center-to-Center (cc) Distances and rms Deviations of the Porphyrin Ring from the Least-Squares Plane Given in Ångströms (Å) as Obtained from Different Geometry Optimizations.

Functional (conformer)	SVWN (CB)	SVWN (CA)	PBE (CB)	PBE (CA)
cc distance	5.8	6.1	6.7	6.9
rms deviation	0.10	0.19	0.08	0.14

The diameter of fullerene is ~ 7 Å.

Results

Ground State Geometry

Some structural characteristics of the DHD6ee conformers optimized with the SVWN and PBE functionals are presented in Table 1. The cc distances obtained from the total energy minimization with different functionals are listed in the first row of Table 1. The second row of the table represents the root-mean-square (rms) deviation from the least-squares plane calculated for the 24 atoms of the porphyrin ring. The nonplanarity of the porphyrin, which is reflected in the value of the rms deviation, is influencing decreasingly the delocalization of the π electrons in the porphyrin macrocycle.

The general characteristics of the two conformations selected from the MD results, that is, orientation of fullerene with respect to porphyrin and the conformation of the two linkers, are retained after DFT optimization. Independent of the orientation of porphyrin and fullerene, the cc distance is larger by ~ 0.8 Å for the PBE equilibrium geometries than for the SVWN equilibrium geometries. The larger distance corresponds to lower energy conformers.

As observed also for other porphyrin-fullerene dyads,¹ the cc distance is influencing the amount of CT between the donor and acceptor moieties in the ground state of the dyad. The electric dipole moments of both conformers are in all cases oriented from porphyrin to fullerene and can be used as a measure of the amount of CT. The electric dipole moments (see Table 2) of optimized dyad structures in Table 1 are obtained by single point calculations using the SVWN, PW91, and B3LYP functionals. The calculated dipole moments are also given as the fraction of an electron which when transferred over the cc distance results in the computed dipole moment.

The larger dipole moments of CB as compared to CA indicate both a higher amount of CT in CB than in CA and thus a dependence of the CT in the ground state of dyad on the relative orientation of the porphyrin and fullerene. For the same conformer, the dipole moment is increasing with the cc distance. Interestingly, this behavior is opposite to the case of the H₂P-O34-C₆₀ dyad for which we have observed an increase of the dipole moment associated with a decrease in cc distance.¹ The particular variation of the dipole moment in the case of H₂P-O34-C₆₀ was attributed to the increase in CT with decreasing cc distance. However, the cc distances of the equilibrium structures of DHD6ee are generally smaller than in the case of H₂P-O34-C₆₀. It is therefore, possible that a “saturation” of the CT from porphyrin to fullerene is attained at a small cc distance.

Electronic Structure

The energies of some of the highest and lowest occupied molecular orbitals given in Table 3 are obtained by using single point (SP) calculations with SVWN, PBE, and B3LYP on the structures in Table 1. The HOMO and LUMO wavefunctions are presented as isoamplitude surfaces in Figure 3. The same isoamplitude surface value is used for all plots, thus allowing a facile comparison between the localization and delocalization of the same orbitals from calculations with different functionals.

Not surprisingly, due to the part of exact exchange incorporated in the B3LYP functional, calculations with this functional yield always the largest HOMO-LUMO gap, whereas only little variation is seen between the LDA and GGA results obtained for one conformation.^{34–37} At the same level of approximation, the cc distance is exerting an appreciable influence on the energies of the orbitals of the conformers. The results in Table 3 reveal that for a given porphyrin-fullerene orientation the HOMO-LUMO gap is increasing with decreasing distance, which is due to the destabilization of the HOMO and stabilization of the LUMO. However, the amount of stabilization is also orientation dependent. In the case of CB, the HOMO orbital is only slightly destabilized (~ 0.05 eV), whereas the LUMO is experiencing a more pronounced influenced due to the change in cc (~ 0.2 eV). On the contrary, in CA the HOMO is more influenced than the LUMO. It is expected that also the structural differences between CA and CB, and in particular the distortion of the porphyrin ring, contribute appreciably to the molecular orbital energies.

The isoamplitude surfaces in Figure 3 reveal that with the decrease of the cc distance the HOMO and LUMO start to be delocalized over both the porphyrin and the fullerene moieties. The same phenomenon was observed also for the H₂P-O34-C₆₀ dyad.¹ In addition, also the localization of some of the molecular orbitals below and above HOMO and LUMO differ in the shorter and larger cc distance conformers.

Optical Absorption Properties

The TD-DFT method is used to evaluate the excitation energies and the oscillator strengths of the electronic transitions in the visible and the near IR region of the spectrum. Given the clear charge transfer character of the lowest electronic transition and

Table 2. Ground State Electric Dipole Moments Given in Debye (1 Debye = 3.33×10^{-30} Cm), Obtained from Single Point Calculations Using the SVWN, PW91, and B3LYP Functionals for the Geometries Defined in Table 1.

Functional	SVWN		PBE	
	CB (5.8 Å)	CA (6.1 Å)	CB (6.7 Å)	CA (6.9 Å)
SVWN	6.4 (0.23)	3.4 (0.12)	6.9 (0.25)	4.2 (0.13)
PBE	6.2 (0.22)	3.3 (0.11)	6.6 (0.24)	4.1 (0.12)
B3LYP	5.8 (0.21)	4.0 (0.14)	6.3 (0.23)	4.7 (0.14)

The values in parentheses give the fraction of an electron which when transferred over the cc results in the computed dipole moments. The gray shading indicates the local minimum energy conformations.

Table 3. Calculated Orbital Eigenvalue Energies (eV) of the Frontier Molecular Orbitals for the Geometries Defined in Table 1.

Functional for SP calculations	SVWN		PBE		Molecular orbitals
	CB (5.8 Å)	CA (6.1 Å)	CB (6.7 Å)	CA (6.9 Å)	
SVWN	1.28	0.85	0.98	0.64	LUMO+1
	1.10	0.72	0.80	0.48	LUMO
	0.00 (−5.10)	0.00 (−4.75)	0.00 (−4.85)	0.00 (−4.69)	HOMO
	−0.33	−0.41	−0.37	−0.37	HOMO-1
PBE	1.31	0.88	1.02	0.68	LUMO+1
	1.12	0.74	0.83	0.53	LUMO
	0.00 (−4.88)	0.00 (−4.53)	0.00 (−4.65)	0.00 (−4.49)	HOMO
	−0.33	−0.40	−0.36	−0.37	HOMO-1
B3LYP	2.28	1.79	2.00	1.64	LUMO+1
	2.07	1.63	1.79	1.45	LUMO
	0.00 (−5.27)	0.00 (−4.88)	0.00 (−5.04)	0.00 (−4.87)	HOMO
	−0.32	−0.39	−0.31	−0.33	HOMO-1

The HOMO energy is used as reference and its absolute values are given in parentheses. The gray shading indicates the local minimum energy conformations.

the known difficulties of present functionals in describing long-range charge transfer states,³⁸ also CCS, CIS(D), and CC2 calculations are performed. The energy and oscillator strength for the electronic transition to the lowest excited state obtained by TD-DFT with different functionals are given in Table 4 together with the results of the wavefunction calculations. As only toluene absorption spectra are available for DHD6ee compound⁵ the Onsager model is used in estimating the solvent stabilization energies of both ground and excited states.

The values of the TD-DFT lowest excitation energy presented in Table 4 are overall smaller than the experimental absorption maximum of 1.8 eV and they correspond in the case of LDA and GGA functionals more or less to the orbital energy differences. The B3LYP functional on the other hand yields significantly higher energy for the first electronic excitation and comes closest to the experimental value in the case of the dyad having the shortest cc distance. These are clear indications of the underestimation of excitation energies for CT states, which despite the strong interaction in the compact dyad are not fully overcome even by the use of hybrid functionals.

The electronic excitations with energies larger than the first excited singlet are calculated using TD-DFT with LDA and GGA. The results reveal several electronic excitations which involve transitions from orbitals localized on porphyrin or fullerene to orbitals localized on fullerene. An excitation which corresponds to the formation of a locally excited singlet porphyrin state P¹S^C follows, and it involves mainly contributions from transitions between orbitals localized on porphyrin. The calculated excitation energy values range from 1.8 eV to 2.0 eV, when compared with the experimental value of 1.91 eV. The energy of the excitation leading to the first locally excited singlet state of porphyrin, although ca. 0.1 eV lower for CB than for CA, shows little dependence on the structural characteristics such as the cc distance. In addition, the LDA and GGA calculations yield excitation energies which differ only by 0.01. The relatively small influence of the structural characteristics and the functional used in the calculations on the excitation energy of the transition to the locally excited state of porphyrin was also observed for the H₂P-O34-C₆₀ dyad.¹

Table 4. TD-DFT and *ab initio* Transition Energies and Oscillator Strengths of the First Singlet Electronic Excitation of the Dyad (eV).

Method	SVWN		PBE		Properties
	CB (5.8 Å)	CA (6.1 Å)	CB (6.7 Å)	CA (6.9 Å)	
TD-DFT/SVWN	1.12/5.0	0.74/7.4	0.81/0.3	0.48/1.7	Transition energy (eV)/Oscillator strength × 10 ^{−3}
TD-DFT/PBE	1.14/4.7	0.76/7.2	0.84/0.3	0.52/1.3	Transition energy (eV)/Oscillator strength × 10 ^{−3}
TD-DFT/B3LYP	1.60/5.0	1.21/7.9	1.39/0.3	1.06/1.2	Transition energy (eV)/Oscillator strength × 10 ^{−3}
CCS	2.70	2.66	2.61	2.64	Transition energy (eV)
CIS(D)	3.07	2.97	2.88	3.00	Transition energy (eV)
CC2	2.97	2.95	2.86	2.99	Transition energy (eV)

The experimental transition energy measured in benzene solution is ~1.8 eV. The gray shading indicates the local minimum energy conformations.

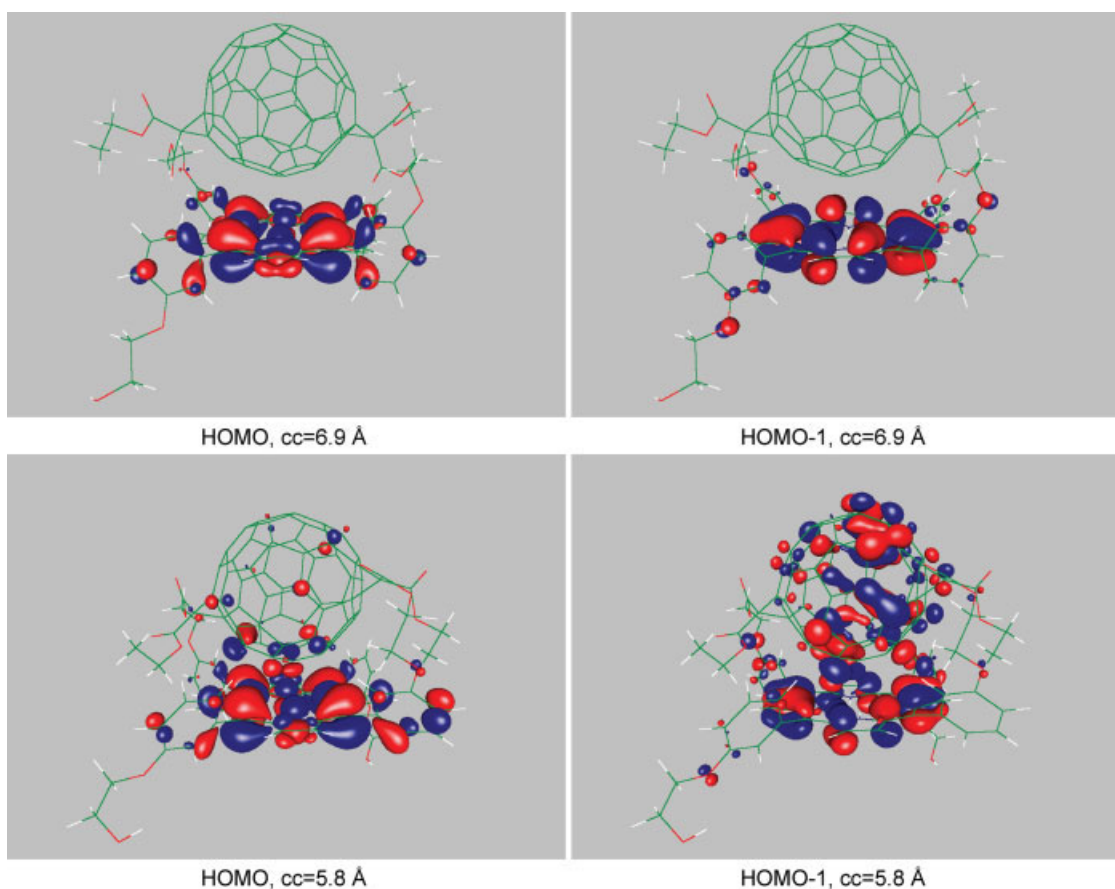


Figure 3. Wavefunctions of HOMO and LUMO presented as isoamplitude surfaces. Relative phases of the wavefunction are indicated by regions of different colors. The cc distances are given in Å.

Considering the pronounced CT character of the first electronic transition, which is posing several problems for present density functionals,³⁸ also CCS, CIS(D), and CC2 calculations are performed for the lowest energy excitation as described under methods. Except for the CCS calculations which can yield relatively larger errors for the excitation energies,³⁹ the results presented in Table 4 show an unexpected large overestimation of the excitation energies by CIS(D) and CC2.^{39,40–46} These are larger by up to 1.3 eV than the experimental value and show little dependence on the cc distance and orientation. The transition is also described as having pronounced CT character, with the HOMOs located mostly on porphyrin and the LUMOs on fullerene. However, while both HOMO and HOMO-1 are involved, only higher LUMOs (LUMO +1, LUMO +2) and not the LUMO orbital contribute to the excitation.

Several possible reasons for the unexpectedly large energy value obtained from the wavefunction based calculations were identified and investigated, that is, multireference character of the ground state, basis set size, excited states dominated by double-excitations and solvent influence. The diagnostic criteria proposed by Janssen and Nielsen⁴⁷ and implemented in the Turbomole program do not indicate a considerable multireference character of the ground state. The obtained values are below or

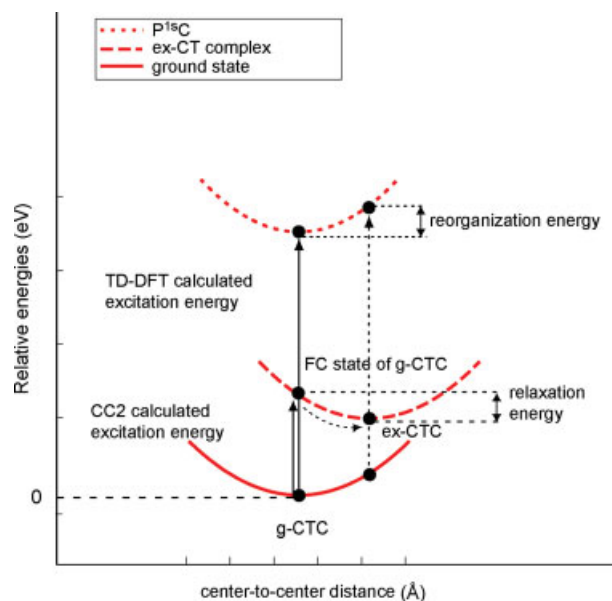


Figure 4. Schematic representations of the ground state and excited state (lowest and P^{1s}C) potential energy curves on the basis of the results obtained by CC2 and TD-DFT calculations.

Table 5. Onsager Cavity Radius, Ground (μ_i) and Excited State (μ_f) Dipole Moments in Debye and Absolute Values for Solvent Stabilization Energies.

	CB (5.8 Å)	CA (6.1 Å)	CB (6.7 Å)	CA (6.9 Å)
a_0 (Å)	8.50	8.63	8.93	9.04
μ_i (D)	6.4	3.4	6.9	4.2
μ_f (D)	18.74	12.45	27.66	17.18
E_{sf} (eV)	1.97×10^{-2}	0.53×10^{-2}	1.97×10^{-2}	0.70×10^{-2}
E_{sp} (eV)	16.26×10^{-2}	6.82×10^{-2}	30.38×10^{-2}	11.29×10^{-2}
E_{ex}^{sol} (eV)	0.16	0.06	0.28	0.11

very close to the optimal accepted values of 0.015 and 0.030 for the D1 (MP2) and D1(CC2) diagnostic criteria, respectively. However, in the limit even larger values are acceptable, that is, 0.040 for D1(MP2) and 0.050 for D1(CC2). Moreover, the authors in reference³⁰ indicate significantly larger values (up to a factor of 5) that are considered acceptable for several excited states calculations. Regarding the basis set size, the SVP basis was chosen so that calculations are cost-effective for larger compounds such as DHD6ee. We expect, based on several results presented in the literature which compare SVP and TZVPP calculations,⁴⁸ that the decrease in excitation energy would be only cca. 0.2 eV when increasing the basis set. Additionally, our calculations reveal that the first excited state is dominated by single-excitations out of the ground state wavefunction, with the double-excitations not exceeding 1%. Finally, the solvent stabilization energies are calculated based on the dipole values and cavity radii given in Table 5 to range between 0.06 and 0.28 eV. Thus, inclusion of solvent stabilization can bring the CC2 values closer to the experimental ones, while at the same time increasing the discrepancy with the TD-DFT. One has to bear in mind that small variations in the Onsager radius will significantly influence the stabilization energy. As such, if the radius is considered as the maximum distance separating charge centres⁴⁹ then the stabilization energy amounts to more than 0.5 eV. Based on these considerations the overestimation of the excitation energies by CC2 can be corrected by the inclusion of solvent effects and a more rigorous solvent description would be needed to obtain quantitative results. This would however escalate the computational demands in the case of very large molecular complexes.

Excited State Structures from TD-DFT Calculations

As mentioned above, the broad and weak absorption band in the near IR region of the DHD6ee absorption spectrum is attributed to the g-CTC absorption. The related Franck-Condon excited state of g-CTC is undergoing conformational relaxation towards the minimum of its PES, that is, the ex-CT complex, see Figure 4. In general, the formation of ex-CTC is considered to have a strong impact on the dynamics of the ET. Thus, the theoretical investigation of the energy and geometric characteristics of ex-CTC is important in elucidating the mechanism and dynamics of ET. In addition, the reorganization energy λ accompanying the formation of ex-CTC from the locally excited singlet state of porphyrin defined in the Marcus theory of electron transfer⁵⁰ is

an important quantity for calculating the rate constants of the ET. Figure 4 presents a schematic representation drawn on the basis of the TD-DFT and CC2 results for the PESs of the ground, ex-CTC, and the P¹S state.

Although TD-DFT underestimates the CT energies, it was shown that properties of intramolecular CT states, such as minimum-energy geometries, are much less effected by the shortcomings of local functional.^{51,52} Consequently, a reasonable compromise for studies of CT states in large molecular systems, such as the present one, is to combine TD-DFT geometries with CC2 single point energy calculations. On the other hand, using CC2 for the study of higher excited states becomes prohibitive and TD-DFT was used for the reorganization energy corresponding to the locally excited state of porphyrin (see Fig. 4). In this case a good performance of the method is expected considering that it is the local excitation of porphyrin that is described, for which TD-DFT has already been shown to yield good results.⁵³

The Franck-Condon state of g-CTC for the SVWN structures in Table 1 is optimized at LDA level for both CA and CB to investigate the geometrical changes accompanying the excited state relaxation. The optimization of the excited state drives the cc distance from 6.1 to 6.3 Å in the case of CA and from 5.8 to 6.0 Å in the case of CB. The increase in the donor-acceptor distance can be explained by a shift of the positions of the ground and excited state PES minima relative to each other. According to the results of the excited state TD-DFT geometry optimizations of CA and CB, the relative shift of PESs is similar to that schematically drawn in Figure 4.

The CC2 single point calculations predict that the relaxation of the excited state of g-CTC from its Franck-Condon state is accompanied by an energy decrease of 0.03 eV and 0.169 eV for CA and CB, respectively. The reorganization energies λ is calculated by using: (a) the results of the TD-DFT/SVWN calculations presented in section 3.3 and in Figure 3 for the transitions leading from the ground state of the dyad to the F-C state of g-CTC and to the P¹S state; (b) the TD-DFT excitation energy of the electronic transition from the ground state structure corresponding to ex-CTC to the PES of the P¹S; (c) the single point DFT energies of the ground state structures marked with big bullets on the PES. The reorganization energy is 0.136 eV for CB and almost three times larger for CA.

Conclusions

Based on the present study, several more general conclusions related to the ground and excited states of porphyrin-fullerene dyads can be drawn. The relative orientation of porphyrin and fullerene is significantly influencing the changes in the MO energies (either HOMO or LUMO are stabilized depending on the orientation), the CT in the ground state of the dyad and the excitation of g-CTC. At the same time the excitation to the locally excited state of porphyrin is only little influenced by the orientation or cc distance. A larger cc distance can be energetically favorable.

TD-DFT (with presently available local functionals) underestimates the excitation energy of the CT state. For some cases (with relatively short donor-acceptor separations), the use of a

hybrid functional like B3LYP, which partially brings back non-local exchange, alleviates this problem. Wavefunction based methods and CC2 in particular appear to overestimate the CT excitation energies but the inclusion of proper solvation models can significantly improve results.

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