

The Role of Polar Functional Groups of the Special Pair on the Excited States in Terms of the Dielectric Environment: Screened Range Separated Time-Dependent Density Functional Theory

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Abstract — We study the role of polar functional groups (PFGs) on the excited states and the changes of net charges on the charge transfer (CT) states in terms of dielectric constant using ab initio theory. It is found that the PFGs play a dielectric medium in which the side PFGs interact strongly with the incoming light, and this interaction contributes to the wave function of excited states. Results reveal that conformer structure due to side groups has more influence on transition dipole moment (TDM) and thus on the electronic excitations. We have also discussed the well-known J- and H- aggregation physical phenomenon for the special pair and shown the excitonic splitting energies of the special pair compared to the monomer's first excited state energies. Excitation energies, oscillator strength, and CT states are obtained by using time-dependent density functional theory (TDDFT) and accompanying screened range-separated hybrid functionals (SRSH) in which comparisons are made with ω B97X-D functional.

Keywords — Range separated hybrid functions, density functional theorem, excited states, charge transfer, dipole moments

1. Introduction

During the last decades, the study of energy and electron transfer processes has been growing rapidly as an interesting technique to understand the naturally light-harvesting antenna and charge separation in photosynthesis reaction centers for biological systems [1]. The bacterial photosynthetic reaction center is the key model to study the energy and electron transfer processes in photosynthesis reactions. In higher organisms, photosynthesis reactions have been influenced by photosystems' key structural and functional features [2]. Bacterial reaction centers (BRCs), especially dimers of special pairs, are crucial in donating electrons in the photosynthesis cascade. Among those special pairs, bacteriochlorophyll is essential to transfer ultrafast electrons during photoexcitation [3]. Those studies aim to understand the electron transfer mechanism, the nature of the photoexcited state, and the extent of the excited state for charge transfer (CT) character in spatial pairs [4].

Bacteriochlorophyll (BChl) molecules are the most efficient pairs in collecting the light near-IR (NIR) region. The special window is due to the partial saturation and raising of both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies [5]. The

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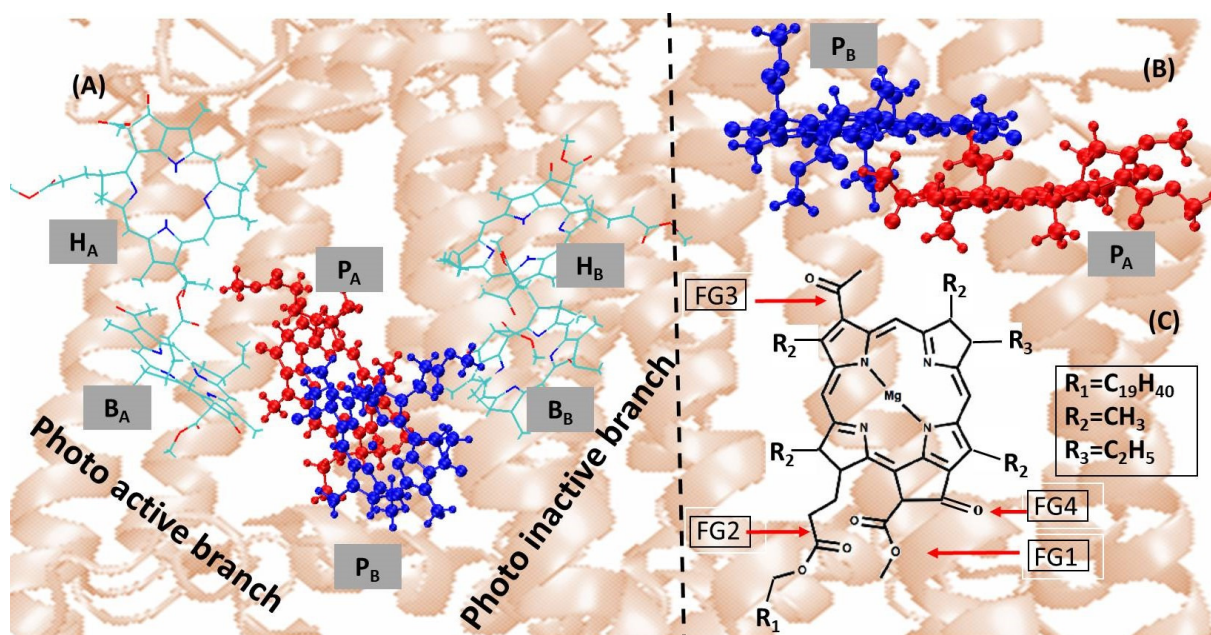


Figure 1. (A) Orientational arrangement of the core pigments in BRCs of *Rhodobacter Sphaeroides*. X-ray nuclear coordinates are taken from Ref. [6]. (B) The explicit orientation of a special consists of two monomers (BChl) labeled P_A and P_B . (C) The chemical structure of a BChl monomer. In our calculations, the residues, R_n ($n=1-3$), are replaced by hydrogens

BChl pairs are easier to oxidize and slightly harder to reduce than their porphyrin congeners. BChl pairs are the potential candidate to represent natural photosynthetic reactions [7]. Those pairs are useful for developing photoelectronic devices by investigating the electronic, optical, photochemical, and redox properties of bacterial photosynthetic reaction centers [8]. Therefore, ongoing research efforts are trying to synthesize symmetric and asymmetric dyads and triads from bacterial photosynthetic reaction centers [9].

The solvent polarity dependence of CT rate processes raises essential questions about the contribution of the photoinduced CT process to the deactivation of the excited state. CT processes involve moving from a locally excited BChl monomer to the following BChl monomer, producing a non-emissive cation, anion, and radical pair stabilized in polar solvents.

Several groups investigated that dyads containing photoexcited bacteriochlorin donate electrons to fullerene, quinone, chlorine, and peryleneimide [10]. The electron transfer can be achieved if CT state energy is lower than the first singlet excited state. The symmetric arrays where electron donor and acceptor are called identical molecules, for example bianthryl, bis(BODIPY), bis(perylenediimide) and bacteriochlorin dyads are reported [11,12]. The intermolecular electron transfer between the Zn-ligated bacteriochlorin complex is also studied [13]. In our recent paper, we have found that the dielectric dependence of the intramolecular CT rate is robust in neutral Zn-ligated dyads, whereas cationic Au-ligated dyads show negligible dielectric dependence of the CT rate [14]. When the CT states mix with excitonic states, the spectroscopy does not detect those states but gives rise to very fast, non-radiative deactivation. Those observations have been seen in symmetrical chlorin and chlorin-porphyrin dyads [15].

The interaction between a plane single molecule and an attached polar functional group has been largely investigated [16–21]. Detailed theoretical analysis shows that the orientation of the polar side chains in single molecules has a recognizable effect on the transition dipole moment (TDM) [21]. They have postulated that the deformation of TDM on single molecules resulted in a change in the number

of single electron excitations responsible for the electronic excited states. Another theoretical study on the singly substituted benzene derivatives shows that the orientation of the TDM depends on the location of the side groups on the plane benzene molecule [17]. In our previous work [22,23], we have investigated that the same pigments (BChl molecules) appearing on both photoactive and inactive sides of the BRC exhibit slightly different excited state energies. This spectral energy difference is mainly attributed to each pigment's distinctly oriented ketonic $-\text{COCH}_3$ group. Additionally, the localized CT state energies differ due to the distinctly oriented PFGs on each BChl monomer in special pair [23].

In light of the aforesaid observables, we have studied the role of the polar functional groups on the BChl ring in special pair in terms of a dielectric constant by the use of novel computational tools based on the polarized continuum model (PCM) with an SRSH scheme [24–27]. A comparison of the excited states of the monomer relative to the dimer was carried out. The well-known H and J aggregation physical phenomenon for shifted and stacked dimer models has been analyzed based on the excited state analyses of TDDFT [28].

2. Methods

The electronic structure of the BChl monomer and all oriented dimers are optimized at $\omega\text{B97X-D}/6\text{-}31\text{G}^*$ level [29,30]. All the range-separated hybrid (RSH) and SRSH functionals based TDDFT calculations with together 6-31G** basis sets, and the continuum media solvent model for the polarization effect of the environment is performed with Q-chem software package unless otherwise noted [31]. SRSH, where the dielectric constant *epsilon* screens the long-range Coulombic interaction: $1/\epsilon$, is a suitable candidate to describe CT accurately states energies using a tunable system-specific range-separation parameters for which we adopted $J^2(\gamma)$ scheme [32,43]. Thus, the SRSH scheme is designed to capture the polarization effect due to the condensed phase accurately [33–35]. Range separated function can be shown as:

$$\frac{1}{r} = \frac{\alpha + \beta \text{erf}(\gamma r)}{r} + \frac{1 - [\alpha + \beta \text{erf}(\gamma r)]}{r} \quad (2.1)$$

where α , β , and γ are the optimally tuned parameters that are explicitly system dependent, and r is the inter-electron distance. The SRSH functional setup follows the generalized exchange-correlation functional formulation, where the energy expression is

$$E_{\text{XC}}^{\text{SRSH}} = \alpha E_{\text{F}_X}^{\text{SR}} + (1 - \alpha) E_{\text{DF}_X}^{\text{SR}} + (\alpha + \beta) E_{\text{F}_X}^{\text{LR}} + (1 - \alpha - \beta) E_{\text{DF}_X}^{\text{LR}} + E_{\text{DF}_C} \quad (2.2)$$

Here, the subscripts ‘X’ and ‘C’ denote exchange and correlation, respectively, while ‘F’ and ‘DF’ refer to Fock exchange and a semilocal density functional for exchange or correlation. In the SRSH exchange-correlation formulation, the parameter α determines the fraction of Fock exchange in the short range (SR), while $\alpha + \beta$ defines the fraction of Fock exchange in the long range (LR) and is constrained to ϵ^{-1} . In this study, we employ the $\omega\text{PBE-h}$ functional [37], as used in previous works [22,27,33,38–40]. This approach ensures a consistent treatment of dielectric screening, wherein the self-consistent reaction field adapts to the dielectric constant, ϵ , within the PCM, while the same constant is used to attenuate the LR exchange in the SRSH functional. In our SRSH-PCM framework, we use the tuned range-separation parameter $\gamma = 0.15 \text{ bohr}^{-1}$ obtained by optimal tuning the special pair in the gas phase based on the $J_2(\gamma)$ scheme, [32,43] followed by resetting the β functional parameter such that $\alpha + \beta$ equals $1/\epsilon$ with α set to 0.2 [27]. In a previous study, we have shown the applicability

of the SRS-PCM scheme not only for the systems exhibiting isotropic dielectric environments but also in anisotropic dielectric environments as in BRCs [41]. Besides, we have also incorporated the SRS-PCM with embedded potential and showed its superiority over the Bethe Salpeter equation (BSE) [42]. Here, the range-separation parameter is obtained by optimal tuning (OT) at the gas phase ($\epsilon = 1.0$) for a given α minimizing the error measure, $J^2(\omega)$, as follows:

$$J^2(\omega) = [\epsilon_{\text{HOMO}}(\omega) + IP(\omega)]^2 + [\epsilon_{\text{LUMO}}(\omega) + EA(\omega)]^2. \quad (2.3)$$

Here, ϵ_{HOMO} and ϵ_{LUMO} are the energies of HOMO and LUMO, respectively. IP and EA represent the system's vertical ionization energies.

We have chosen one very low and one very high value for the dielectric constant to emphasize the environmental effect on the dimer's CT states. We have also chosen other intermediate dielectric constants to see the trends of excitonic and CT state energies. The intermolecular distance between BChl monomers in dimers is preserved to be the same as in the X-ray molecular structure of the special pair, which is close to the realistic case.

3. Results and Discussion

Our analysis begins with the X-ray structural study of the BRC of *Rhodobacter Sphaeroides* [6]. Figure 1(A) depicts the two branches, *A* and *B*, which originate from the special pair, emphasizing the relative orientation of its constituent units within the BRC system. Figure 1(B) presents a schematic representation of the stacking arrangement of these units, where P_A and P_B are designated according to their proximity to their respective branches. Additionally, key orientational differences between the two units are highlighted, as determined from the X-ray-resolved structure. Figure 1(C) illustrates the chemical structure of BChl, along with the functional groups attached to the conjugated porphyrinic system. These functional groups—a keto-ester, a phytol ester with an ethylene linkage, and an acetyl group—are labeled FG1, FG2, and FG3, respectively. Notably, the keto-ester functional group is linked through FG1 and FG4, as shown in Figure 1(C).

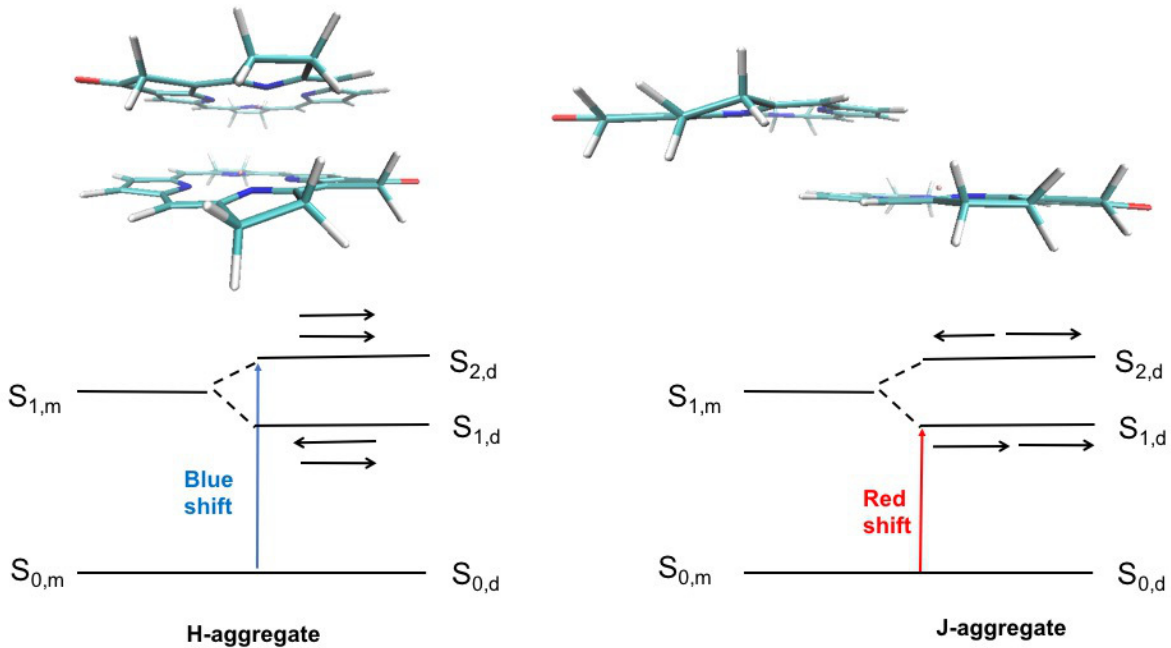


Figure 2. H and J aggregate: Here $S_{0/1,m}$ indicates the ground/excited state energy of monomer and $S_{x,d}$ indicates the excited state energy of the dimer, where $x \in \{0, 1, 2, \dots\}$

Before proceeding with the excited states analysis and the role of the PFGs, we discuss the well-known H- and J-aggregate phenomenon for our dimer model. It is understood that these two types of aggregates are useful tools to define the spectral shift of dimer in monomer [36]. Figure 2 shows two distinct oriented molecular structures (only with FG1) in which the stacked and the shifted, which has indeed the exact orientation of special pair in BRC, dimers exhibit blue and red shifts respectively, concerning that in the monomer. Regardless of the orientation of the dipole moment on each monomer in the dimer model, the TDM would present two types of linings due to the nature of wave-function in TDM: parallel and antiparallel arrangements ($\Rightarrow$ and $\Leftarrow$ or $\rightarrow\rightarrow$ and $\rightarrow\leftarrow$) as it is depicted in Figure 2. In the stacked dimer case (left panel of Figure 2) antiparallel lining lowers the system energetically due to strong interaction of opposite charges on the molecule so one should observe this state in the lowest state in the spectrum. This results in the stacked dimer vanishing oscillator strength (OS) due to the opposite lining of TDM vectors ($\Leftarrow$). On the other hand, the parallel lining of transition dipole moment vectors ($\Rightarrow$) causes repulsive interaction, thus higher the system energetically and present doubling OS. This state is presented as the second lowest state in the spectrum. This type of arranged dimer is called H-aggregate and is characterized by blue-shifted spectra.

Table 1. The stacked and shifted dimers' First and second excited states along with OS are presented; H and J aggregate. First excited state energy and associated OS of the monomer component in the dimer are given in the parenthesis

dimer model	state	excitation energy(eV)	oscillator strength	excitonic splitting energy ¹
stacked	S1	1.9327	0.00	0.129
		(2.0617)	(0.31)	
	S2	2.2097	0.44	0.148
shifted	S1	2.0401	0.62	0.0216
		(2.0617)	(0.31)	
	S2	2.0990	0.02	0.0373

The situation is different when the stacked dimer is shifted to the side, as shown in Figure 2 (right panel), i.e., parallel in-lining TDM ($\rightarrow\rightarrow$) lowers the system energetically. Therefore, this state should be visible in the first lowest excited state in the spectrum, thus doubling OS. On the contrary, antiparallel in-lining TDM ($\rightarrow\leftarrow$) exhibits repulsive interaction, so this state lies in the second lowest excited state and thus vanishes OS. This type of shifted dimer has J-aggregation and presents a red-shift physical phenomenon. Generally speaking, stacked and shifted orientations lead to $J_0 > 0$ and $J_0 < 0$ Coulombic interactions, respectively. Our study found these H and J-aggregate features for the stacked and shifted dimer molecular structures. To support the above-outlined theory, an excited state analysis of these two types of model dimers and their monomers was carried out, and the results are shown in Table 1.

Table 1 shows the first two excited states of both dimers and monomers' first excited state energies with their OS values calculated at the ω B97X-D/6-31G** level. As seen, for the shifted dimer orientation, OS trends are in good agreement compared to the monomer's OS (0.31), i.e., it is doubled compared to the monomer. Here, excitonic state splitting energies indicate the differences between the relevant excited state of the dimer (S1 and S2) and the monomers (in the parenthesis). It is understood that excitonic state splitting energy is small due to weak, but not negative, intermolecular Coulombic

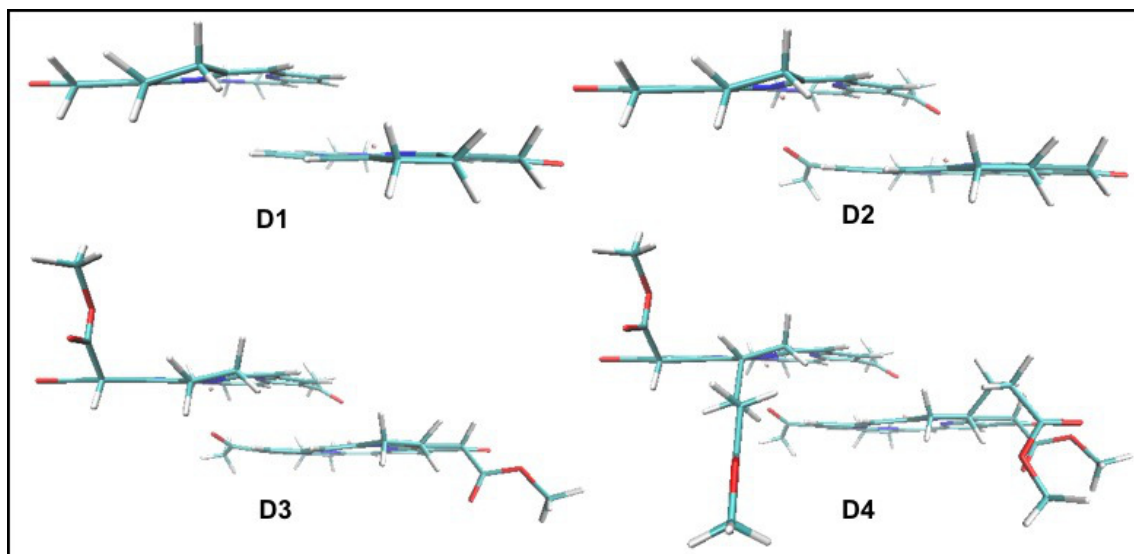


Figure 3. The four cases of dimers present the orientation of the functional groups for each case: D-1 consists of only CO (FG1); D-2 consists of CO+COCH₃ (FG1+FG2) groups; D-3 consists of CO+COCH₃+COOCH₃ (FG1+FG2+FG3) groups; D-4 consists of CO+COCH₃+COOCH₃+C₂H₄COOH₃ (FG1+FG2+FG3+FG4) groups.

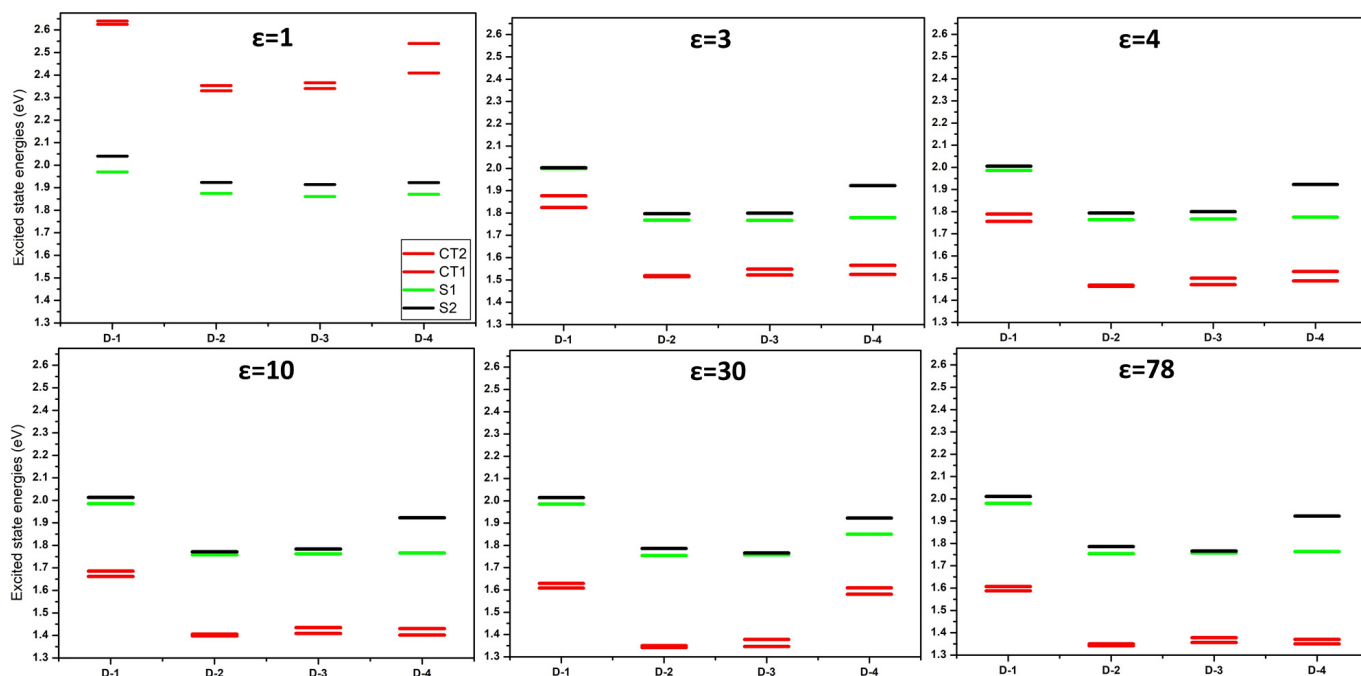


Figure 4. This figure illustrates the role of the functional groups on the bright and CT states of the BChl dimer. Green and black colored bars demonstrate bright and dark states, respectively, and red colored bars demonstrate CT states. See Table 2 in the main text and Table S1 in the SI for the complete numerical values.

interaction ($J_0 < 0$) in the case of shifted dimer. In the case of stacked dimer, OS trends compared to monomer are not as we expected since here intermolecular Coulomb interactions tend to be dominant ($J_0 \gg 0$). We believe this leads to distorted TDM vectors; thus, the expected doubling OS does not appear. This strong Coulombic interaction is also reflected in the excitonic splitting energies caused by large $J_0 \gg 0$. One realizes that in the stacked dimer case, the energy gap between S1 and S2 is larger than in the shifted dimer case.

Table 2. Comparison of the effect of functional groups on the BChl dimer

ε	state	D-1				D-2				D-3				D-4			
		excitation	net charge	oscillator	strength	excitation	net charge	oscillator	strength	excitation	net charge	oscillator	strength	excitation	net charge	oscillator	strength
		energy(eV)				energy(eV)				energy(eV)				energy(eV)			
1 (gas)	S1	1.9700	0.00	0.70		1.8749	0.00	0.77		1.8610	0.00	0.80		1.8709	0.02		0.79
	S2	2.0397	0.00	0.07		1.9238	0.00	0.07		1.9138	0.00	0.01		1.9225	0.02		0.02
	CT1	2.6253	0.38	0.00		2.3307	0.52	0.06		2.3405	-0.28	0.06		2.5439	-0.46		0.00
	CT2	2.6397	-0.38	0.12		2.3536	0.20	0.07		2.3659	0.27	0.07		2.4091	0.65		0.00
	CT1	1.8246	0.22	0.35		1.5144	0.89	0.10		1.5224	0.91	0.08		1.5247	-0.89		0.12
	CT2	1.8774	-0.16	0.01		1.5190	-0.89	0.08		1.5481	-0.88	0.10		1.5651	0.84		0.11
3 (protein)	S1	1.9994	0.09	0.07		1.7675	-0.02	0.86		1.7665	-0.03	0.86		1.7794	-0.06		0.74
	S2	2.0030	-0.15	0.43		1.7971	0.01	0.02		1.7992	0.00	0.01		1.8058	-0.02		0.05
	CT1	1.5879	0.72	0.06		1.3415	0.21	0.00		1.3564	0.89	0.02		1.3500	0.91		0.02
	CT2	1.6070	-0.72	0.01		1.3503	-0.21	0.05		1.3775	-0.88	0.04		1.3697	0.90		0.05
	S1	1.9800	0.00	0.72		1.7544	0.00	0.82		1.7575	0.07	0.76		1.7637	0.09		0.74
	S2	2.0106	0.00	0.00		1.7858	0.00	0.00		1.7658	-0.11	0.06		1.7945	-0.07		0.02
78 (water)	S1	1.9800	0.00	0.72		1.7544	0.00	0.82		1.7575	0.07	0.76		1.7637	0.09		0.74
	S2	2.0106	0.00	0.00		1.7858	0.00	0.00		1.7658	-0.11	0.06		1.7945	-0.07		0.02

We are interested in the spectroscopic properties of shifted BChl dimers shown in Figure 3. Here, the D-4 model in Figure 3 presents the spacial pair orientation in BRC, thus all other dimers are derivative of D-4 dimer. Excited state analyses are shown in Table 2, where one can see that the computed results are dependent on the functional groups. For simplicity, only the relevant bright (or absorption) and CT states are demonstrated in Table 2. In Table 2, we present the potential role of functional groups on the BChl dimer by following their excitation energies and net charges on the CT states as well as their OS values. Here, the dimer geometry (D-4) serves as reference molecular geometry in which other dimer geometries are obtained by removing each distinct functional group one by one (D-4 to D-1) from each monomer symmetrically and re-optimized in a respected dielectric environment. Here, we have indicated two bright states, S1 being bright state (P_-^*) and S2 being dark state (P_+^*) and only relevant two CT states (CT1 and CT2) for each dimer model. As one can see, for all-dielectric environments, in most cases, the net charges on the bright states are almost zero. In some cases, bright states exhibit small charges due to state mixing between relevant bright states and CT states.

One can see from Figure 4 and Table 2 (complementary numerical results are presented in Table S1) that at first glance, CT states present occasionally decreasing charges when each distinct functional group is removed one by one, i.e., D3 and D4 dimers with their COOCH_3 and $\text{COOCH}_3 + \text{C}_2\text{H}_4\text{COOH}_3$ respectively exhibit almost (with some exception) same amount of charges on their CT states whereas having only $\text{COCH}_3 + \text{CO}$ groups as in D2 decreases this net charges on the CT states for the $\varepsilon=78$. Again, removing the COCH_3 group and leaving CO on the monomers of dimer increases the net charges but this time lowered compared to D3 and D4 dimer geometries (For all *epsilon* values). This

observed behavior is more pronounced in higher ε values. This behavior indicates that the existence of long-chain polar functional groups COOCH_3 and $\text{C}_2\text{H}_4\text{COOH}_3$ on the BChl ring plays a medium in which electron transfer is more favorable. The explanation is as follows: oscillating light interacts with the wave functions of charge density in the dimer where these long-chain polar functional groups are also involved, and this strong dipole moment interaction favors an electron to be migrated on either side of the dimer [21].

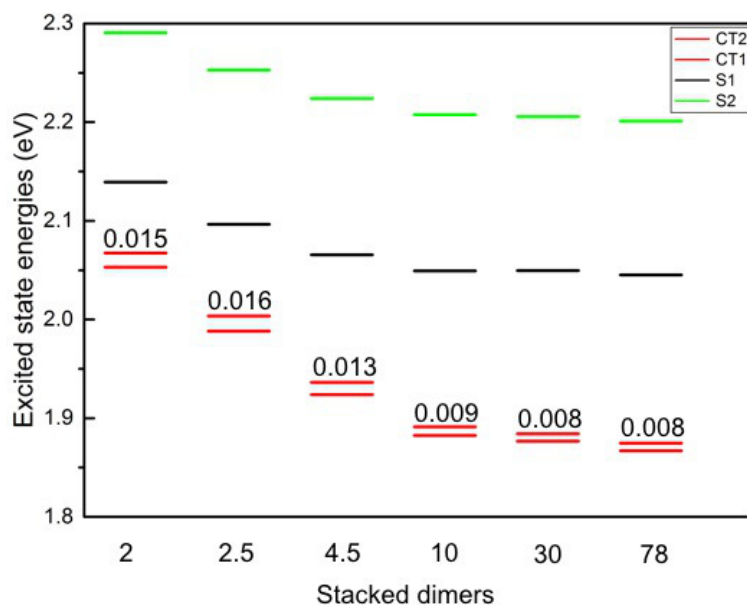


Figure 5. Excited state energies of stacked dimer in terms of dielectric constant. See for the numerical values in Table S2. Black font numbers on the bars demonstrate the differences in CT states energies.

We have demonstrated above outlined results for other intermediate ε values in Figure 4, where green and black colored bars indicate the bright and dark states, respectively, and red colored bars demonstrate the CT states (CT1 and CT2 refer to lower and higher first two energies, respectively). As is seen from Figure 4, CT states appear above the bright states at the low ε values and become more localized (thus stabilized) below the bright states when higher ε values are introduced. The differences appearing on the CT state energies are attributed to the orientation of FGs on each monomer in the dimer model, in which we can say that each CT state is localized on different monomers. In addition, we have also tabulated the bright state energies of monomers appearing in each dimer model.

It is known that TDM depends on the oscillating charge density and a shift of the corresponding charges. Therefore, we have tabulated the total dipole moment values of all shifted dimers in terms of dielectric constants in Table S3 in SI. We assume that the Frenkel bright states dominate the total dipole moment of each shifted dimer (S1). Therefore, we treat all the values in Table S3 as a dipole moment of the S1 state. Dipole moments of D3 and D4 dimers exhibit almost 3 and 2 times higher than the D1 and D2, respectively. This shows that long-chain PFGs contribute to these higher dipole moments. In other words, due to the additional new charge distribution of long-chain PFGs, the magnitude of the dipole moment is increased. Corresponded TDM orientation and HOMO-LUMO orbitals with together orbital energies are demonstrated in Figure 6. We observed that the HOMO-LUMO gap decreased from the D-1 structure to the D-4 structure.

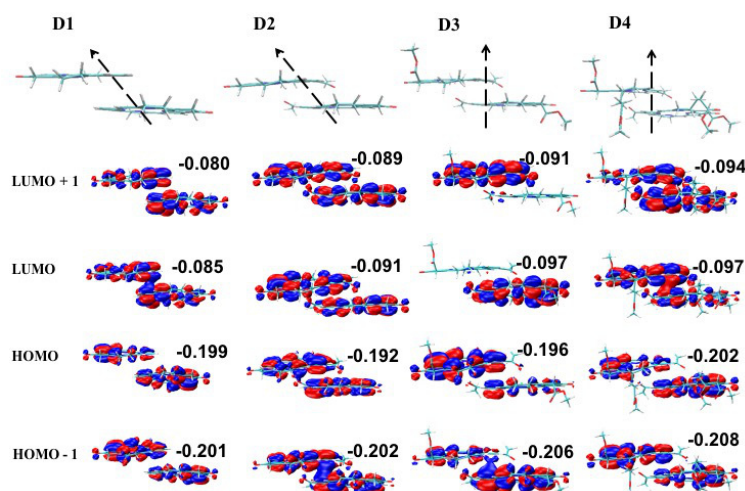


Figure 6. TDM orientation and HOMO-LUMO orbitals. Dashed arrows have been drawn concerning their calculated XYZ values.

Finally, in Figure 5, we have presented the excited state energies of the stacked dimer (see left panel of Figure 2) in terms of the different dielectric environments. Here, it is seen that bright states appear in the S2 state, which is the second bright state and presents H-aggregation regardless of the dielectric environment. As expected, CT states are stabilized even in low ϵ values due to strong coupling between the relevant wave function of the charge densities of two monomers. And this strong coupling leads to higher net charges already in low dielectric environment, see Table S2 in SI for the numerical results.

4. Conclusion

In conclusion, the role of the PFGs on excited states and trends on the net charges have been investigated for the special pair from the BRC of the purple bacterium *Rhodobacter Sphaeroides*. We have found that polar side functional groups play a role as a dielectric medium in which net charges increase by adding corresponding FGs to each plane BChl monomer in a special pair. Dielectric environment dependency on the net charges also shows that an increase in the ϵ value resulted in a minor increase, for some cases, on net charges. Thus, we conclude that the effect of adding PFGs over a dielectric environment (via PCM) dominated the net charges. This can be explained as follows: while the polar side group's electrostatic interactions in the Hamiltonian are taken care of by fully quantum mechanics, the dielectric environment's polarity is treated classically, and the interactions of the point charges are added to the Hamiltonian. Long chain FGs on the D3 and D4 dimer lead to perpendicular TDM concerning the plane of the special pair. It is shown that all special pair-like dimers show J-aggregation regardless of the FGs on it, and this J-aggregation changes to H-aggregation when it is oriented to a stacked dimer.

Author Contributions

The fourth author conceptualized the paper. The first and second authors performed all the necessary calculations and prepared the tables, figures, and the first draft of the paper. They all read and approved the final version of the paper.

Conflicts of Interest

All the authors declare no conflict of interest.

Ethical Review and Approval

No approval from the Board of Ethics is required.

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Supplementary Material

<https://dergipark.org.tr/en/download/journal-file/33463>

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