Modeling the Electron Transfer Chain in an Artificial Photosynthetic Machine

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ABSTRACT: The development of efficient artificial leaves relies on the subtle combination of molecular assemblies able to absorb sunlight, converting light energy into electrochemical potential energy and finally transducing it into accessible chemical energy. The electronic design of these charge transfer molecular machines is crucial to build a complex supramolecular architecture for the light energy conversion. Here, we present an ab initio simulation of the whole decay pathways of a recently proposed artificial molecular reaction center. A complete structural and energetic characterization has been carried out with methods based on density functional theory, its time-dependent version, and a broken-symmetry approach. On the basis of our findings we provide a revision of the pathway only indirectly postulated from an experimental point of view, along with unprecedented and significant insights on the electronic and nuclear structure of intramolecular charge-separated states, which are fundamental for the application of this molecular assembly in photoelectrochemical cells. Importantly, we unravel the molecular driving forces of the various charge transfer steps, in particular those leading to the proton-coupled electron transfer final product, highlighting key elements for the future design strategies of such molecular assays.

Conversion of light into electric or chemical energy is undoubtedly a very attractive solution for the global energy problem.1−10 Analogously, storage of solar energy into chemical fuels through the development of efficient photoelectrochemical cells (PECs)11−13 opens the route for new and environmentally friendly energy sources. Nevertheless, the development of these devices is not straightforward because several entangled processes have to be finely combined and controlled (i.e., light harvesting, charge separation, and electron transfer). The best inspiration for the design of such devices is definitely provided by nature that developed an extremely efficient molecular machine—the photosystem II (PSII)—able to convert sunlight into chemically accessible energy.5,10,14

PSII uses solar photons to drive the oxidation of water to dioxygen in an amazing way, combining different specialized molecular units (e.g., chlorophyll complex P680, oxygen-evolving center, and redox-active tyrosine−histidine pair).15−16 Therefore, this system is an optimum starting point for the construction of artificial photosynthetic machines. In this perspective, Moore and co-workers proposed a molecular triad (hereafter named BiPhOH-PF10−TCNP and depicted in Figure 1) functionally mimicking the highly efficient initial photoinduced charge-separated state in PSII.17 This system is composed by (i) a functionalized porphyrin moiety (PF10) acting as primary electron donor and mimicking the chlorophyll P680 exciton trap of PSII, (ii) a tetracyanoporphyrin (TCNP) ring that acts as electron acceptor simulating the pheophytin moiety, and (iii) a benzimidazole-phenol group (BiPhOH) that models the tyrosine histidine pair of PSII.

This pair is involved in a proton-coupled electron transfer (PCET) reaction during the photosynthetic cycle. Moore and co-workers provided a detailed spectroscopic and electrochemical characterization of this molecular triad leading to the complex decay pathways reported in the inset of Figure 2.17 Based on experimental data, their hypothesis is that the initial excitation of the PF10 group is followed by singlet energy transfer to the TCNP moiety, whose excited state can relax by a photoinduced electron transfer (PET) toward a charge-separated state giving rise to a Bi-PhOH-PF10 **−TCNP** species. They proposed that this species rapidly undergoes a PCET reaction in which an electron is transferred from the phenol to the PF10 **−** group, while the phenolic proton is transferred toward the benzimidazole group providing the final species, postulated to be the BiH+-PhO−-PF10 **−**-TCNP** molecule. Because time-resolved spectra suggest that this charge-separated state has a long lifetime and a high redox potential, this triad becomes particularly attractive for the development of new PEC devices.17

Nevertheless, for the time being, the nature and the relative energies of all the electronic states involved in this complex mechanism have been only experimentally and indirectly
estimated by combining redox measurements with absorption and emission data of the isolated form of the three molecular fragments composing the triad. At present, no clear direct evidence for the formation of the final PCET product has been obtained from experiments. Indeed, in a recent publication, Moore and co-workers stated that "indirect evidence for PCET comes from reduction potentials of model compounds which indicate that PF10 would not generate sufficient driving force for the formation of the Bi-PhOH-PF10-TCNP− state." In order to tune and control the properties of such a triad as well as to help in the design of new systems, a more detailed knowledge of the electronic structure of all the intermediate states involved in the excited-state evolution is mandatory. Here, for the first time, we provide a complete theoretical structural and energetic characterization of all the crucial species involved in the decay pathway (Bi-PhOH-PF10-TCNP−, Bi-PhOH-PF10-TCNP−, and BiH+-PhO-PF10-TCNP−). By studying the complete triad we show how the final PCET product, BiH+-PhO-PF10-TCNP−, is energetically more stable than the Bi-PhOH-PF10-TCNP− side adduct, highlighting the principal structural differences between them. Furthermore, we investigate the proton-coupled electron transfer reaction reconstructing the reaction path and individuating the structural motifs driving it. Describing the driving force of the various charge transfer steps is one of our principal aims, especially to support the future design strategies of such molecular devices.

The theoretical simulation of the experimentally proposed decay pathways is far from being straightforward because of the necessity of accurately simulating the excited-state evolution of a large system in the presence of a medium—the solvent—which can play an important role in the stabilization of the different states. Density functional theory (DFT) and its time-dependent counterpart (TD-DFT) offer valuable tools for the description of excited-state processes in condensed phase, although this choice makes the accurate simulation of excited states with a net intramolecular charge transfer character far from trivial. For this reason, we complemented the TD-DFT description of such states resorting to the broken-symmetry approach (BS) originally developed by Noodleman and co-workers to describe magnetic coupling and thus open shell singlet states using a single-determinant approach. This kind of approach enables the setup of computationally stable protocols for the description of an excited state dealing with charge transfer processes, which might be of interest in the design of new synthetic models for photoelectrochemical devices.

To simplify the following discussion each excited state of the triad will be labeled as $S_n^X$. The X superscript identifies the diabatic composition of the excited state based on the molecular moiety mostly involved in the excitation (e.g., Bi-PhOH-PF10-TCNP−)}
coupling among them. The PF10 moiety is highly symmetric (principal dihedral angles) suggesting a certain electronic localization on the TCNP unit. The two subunits PF10 and TCNP of BiPhOH-PF10-TCNP are almost perpendicular in S0, while the BiPhOH and PF10 rings are twisted by roughly 67° (Φ2 = −67°, see Figure 1 for the labeling and Table 1 for the values of the other principal dihedral angles) suggesting a certain electronic coupling among them. The PF10 moiety is highly symmetric with the pentfluorenyl phenyl groups similarly oriented with respect to the plane of the porphyrin ring. The TCNP unit assumes a nonplanar structure because of steric interactions between the cyano and phenyl groups, respectively, in the beta and meso positions of the tetrapyrrolic ring. Steric interactions can be found close in energy to S2.

Initially the triad is excited from its ground electronic state (S0). The two subunits PF10 and TCNP of BiPhOH-PF10-TCNP are almost perpendicular in S0, while the BiPhOH and PF10 rings are twisted by roughly 67° (Φ2 = −67°, see Figure 1 for the labeling and Table 1 for the values of the other principal dihedral angles) suggesting a certain electronic coupling among them. The PF10 moiety is highly symmetric with the pentfluorenyl phenyl groups similarly oriented with respect to the plane of the porphyrin ring. The TCNP unit assumes a nonplanar structure because of steric interactions between the cyano and phenyl groups, respectively, in the beta and meso positions of the tetrapyrrolic ring. Steric interactions can be found close in energy to S2.

Figure 2. Simulated decay pathway for BiPhOH-PF10-TCNP. Excitation, internal conversion (IC), energy transfer (EnT), electron transfer (ET), and proton-coupled electron transfer (PCET) steps are represented. Energy levels have been computed at the TD-DFT and broken-symmetry level of theory. The vertically computed excited states are reported in the Franck–Condon region and S2 energy minimum. For comparison, in the inset is reported the experimentally proposed energy level diagram of decay pathways for triad according to ref 17.

Table 1. Characteristic Dihedral Angles (in degrees, refer toFigure 1 for labels) Computed for the Triad in the Relevant Electronic States

| electronic state | Φ1 | Φ2 | Φ3 | Φ4 | Φ5 | Φ6 | Φ7 | Φ8 | Φ9 |
|------------------|----|----|----|----|----|----|----|----|----|
| S0               |     |     |     |     |     |     |     |     |     |
| S2(TCNP)         | −67.14 | −108.88 | 108.38 | −113.75 | −113.45 | −14.55 | −66.54 | −114.48 | −67.64 |
| S2(TCNP)         | −68.15 | −109.58 | 109.02 | −113.38 | −127.11 | −25.03 | −52.79 | −127.37 | −53.64 |
| BiPhOH-PF10**-TCNP** | −54.28 | −111.88 | 107.24 | −121.68 | −117.79 | −17.61 | −62.92 | −117.88 | −63.33 |
| BiPhOHPF10**-PF10-TCNP** | −49.54 | −109.92 | 105.38 | −115.88 | −118.63 | −17.77 | −63.03 | −117.94 | −64.09 |
| BiPhOH**-PF10-TCNP** | −92.11 | −109.33 | 108.68 | −115.81 | −117.99 | −17.54 | −63.49 | −117.49 | −64.21 |

*All parameters are computed on the relative minimum-energy structure.

DFT results show two intense electronic transitions at 3.00 eV (oscillator strength f = 2.966, state S0(TCNP)) and 3.16 eV (f = 2.157, state S2(PF10)) localized respectively on the TCNP and on the PF10 groups. Starting from the absorption event, the simulated pathway can be followed by inspecting Figure 2.

After the excitation to the state S2(PF10), a fast internal conversion to a state still localized on PF10 but at lower energy (state S2(PF10)) can take place (see Figure 2). This is in line with the photochemistry of porphyrin molecules that, following the absorption to higher excited electronic states, give rapid internal conversion to S0 from where emission is observed. The S2(PF10) Franck–Condon region. This state is characterized by an electronic excitation completely localized on the TCNP moiety. The S2(PF10) and S3(TCNP) are the main actors involved in the excitation transfer from the PF10 to the TCNP moieties. Starting from the Franck–Condon region, a change in the S2,
locally excited character from PF$_{10}$ to TCNP can easily occur by coupling to the $S_2$ potential energy surface. In Figure S2 we report energy profiles along a linear synchronous path coordinate linking the $S_{2}^{{\text{PF10}}}$ and $S_{2}^{{\text{TCNP}}}$ minimum energy structures, clearly showing the possible change in the $S_2$ character from PF$_{10}$ to TCNP by a nonadiabatic coupling with the $S_1$ potential surface.

Thus, the global energy minimum in the $S_2$ adiabatic state involves an electronic excitation completely localized on the TCNP unit ($S_{2}^{{\text{TCNP}}}$). This step corresponds to the experimentally hypothesized energy transfer from PF$_{10}$ to TCNP in the triad (first step in the Figure S2 inset).

The TCNP ring distortion is one of the main degrees of freedom involved in the path from $S_{2}^{{\text{PF10}}}$ to $S_{2}^{{\text{TCNP}}}$. Indeed, starting from the Franck–Condon region, the $\Psi_1$ dihedral angle changes by about $4^\circ$ when passing to the $S_{2}^{{\text{TCNP}}}$ excited-state energy minimum.

The fluorescence from the TCNP is experimentally observed at 1.72 eV, and it is computed at 2.02 eV ($f = 0.409$) in the $S_{2}^{{\text{TCNP}}}$ excited-state energy minimum. From an experimental point of view, it has been hypothesized that this state corresponds to the reactant for the first ET process (see inset in Figure 2). Nevertheless, from our calculations it was not possible to individuate a CT character from the PF$_{10}$ to the TCNP unit in structures close to the $S_{2}^{{\text{TCNP}}}$ energy minimum, which would have been a reasonable indication of the possible ET process. Indeed, in this structure another electronic excited state ($S_{1}^{{\text{TCNP}}}$) with energy of 1.63 eV ($f = 0.473$) has been calculated, characterized by an electronic excitation still completely localized on the TCNP group (Figure S1 for the MOs involved in the transition). The main difference between the $S_{2}^{{\text{TCNP}}}$ and $S_{1}^{{\text{TCNP}}}$ states is a significant change of both the electronic and nuclear arrangements during the $S_{1}^{{\text{TCNP}}}$ relaxation. As matter of fact, the charge transfer character of the $S_{1}^{{\text{TCNP}}}$ excitation drastically increases when going from the $S_{2}^{{\text{TCNP}}}$ to the $S_{1}^{{\text{TCNP}}}$ minimum-energy structure: while at the $S_{2}^{{\text{TCNP}}}$ minimum the MOs involved in the $S_{1}^{{\text{TCNP}}}$ transition are completely localized on the TCNP moiety, the character of charge transfer from the PF$_{10}$ to the TCNP unit increases at the $S_{1}^{{\text{TCNP}}}$ minimum-energy structure (see Figure S3 for the MOs involved in the electronic excitation). Considering that the energy difference (0.39 eV) between $S_{1}^{{\text{TCNP}}}$ and $S_{2}^{{\text{TCNP}}}$ corresponds to about 3100 cm$^{-1}$, we propose an internal conversion occurring between the $S_{2}^{{\text{TCNP}}}$ and $S_{1}^{{\text{TCNP}}}$ states and assume the $S_{1}^{{\text{TCNP}}}$ state as the electron-transfer reactant (Figure 2).

The distortion of the TCNP tetrapyrrolic ring is the main degree of freedom involved during the structural relaxation of $S_{1}^{{\text{TCNP}}}$, and it promotes the charge transfer from the PF$_{10}$ to the TCNP unit (see Table 1). Indeed, the $\Psi_1$ dihedral angle, describing the distortion of the porphyrin ring, changes from $-18^\circ$ to $-25^\circ$ during this relaxation, driving the variation in the nature of the MOs involved in the $S_{1}^{{\text{TCNP}}}$ electronic transition. This deformation increases the steric repulsions between the cyano and phenyl groups that, in turn, assume a more planar orientation with respect to the porphyrin ring. The TCNP deformation is, thus, a key structural motif for the charge transfer event. Interestingly, this change in the nature of the excited $S_{1}^{{\text{TCNP}}}$ state was observed only for calculations performed in benzonitrile solution, while it was not reproduced in the analogue $S_{1}^{{\text{TCNP}}}$ optimization in cyclohexane. In this case, the excitation remains localized on the TCNP moiety. This clearly indicates that only polar solvents with high dielectric constant are able to stabilize the electron transfer product, and it is in fair agreement with the experimental evidence indicating that a high quantum yield for the PET reaction is observed only in polar medium (benzonitrile). The energy of the relaxed $S_{3}^{{\text{TCNP}}}$ state is computed at 1.40 eV ($f = 0.565$). Within the TD-DFT framework this is the best picture of the electron transfer product. In order to describe the evolution of this charge-separated state in the ET product, the BS approach was applied. An open shell BS singlet state characterized by a spin density localized on both the PF$_{10}$ and the TCNP groups was computed. The spin density plot and the Mulliken spin density (MSD) integrated for fragments are reported for this structure in Figure 3a, with the fragment definition provided in Figure S4.

![Figure 3](https://dx.doi.org/10.1021/jacslett.0c02766)

Figure 3. (a) Spin density plot for the electron transfer product (Bi-PhOH-PF$_{10}$-TCNP **). In the broken-symmetry approximation. (b) Spin density for the proton-coupled electron transfer product (BiH*-PhO*-PF$_{10}$-TCNP **). (c) Spin density plot for the electron transfer product (Bi-PhOH**-PF$_{10}$-TCNP **). Integration for fragments of the Mulliken spin density is also reported.

Looking at the fragments MSD it is clear that the BS calculated singlet state represents the PET product, namely the Bi-PhOH-PF$_{10}$**-TCNP** adduct. Indeed, two unpaired electrons with opposite spin are localized on the PF$_{10}$ and TCNP moieties, respectively, with negligible contribution on the BiPhOH group. The Mulliken charge analysis for fragments reveals a net positive charge of +1.10 on the PF$_{10}$...
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unit and a net negative charge of \(-0.93\) on the TCNP fragment. This configuration is that expected following an electron transfer from the PF\(_{10}\) to the TCNP group. The Bi-PhOH-PF\(_{10}\)-TCNP** species, in turn, represents the reactant for the next PCET step.

In order to characterize the PCET reaction, we chose the phenol oxygen–hydrogen (O\(_{\text{PhH}}\)-H) distance as the degree of freedom representative of the proton transfer coordinate. We obtained an energy profile by a relaxed scan along this coordinate at the TD-DFT level. The \(S_1\) electronic structure showed only a negligible variation along this coordinate, which means no ET accompanied the PT event.

On the other hand, a BS solution was obtained on the PT product, corresponding to the BiH+-PhO*-PF\(_{10}\)-TCNP** PCET adduct. In Figure 3b we show the spin density plot and the MSD integrated for fragments of this species. This latter analysis shows the electronic holes localized on both the TCNP and phenol (0.78e\(^-\)) units. The O\(_{\text{PhH}}\)-H distance is 1.863 Å in this structure, while the imidazole nitrogen–hydrogen (N\(_{\text{Im}}\)-H) distance is 1.023 Å.

We also observed a small spin polarization on the PF\(_{10}\) moiety. This is principally due to the strong electronic coupling between the BiPhOH and PF\(_{10}\). The transition state (TS) for the PCET step has been also computed (the spin density plot is reported in Figure S5), with an imaginary frequency at \(-1169\) cm\(^{-1}\) (the displacement vectors for the imaginary frequency at the transition state are reported in Figure S6). The O\(_{\text{PhH}}\) and N\(_{\text{Im}}\)-H distance are 1.272 and 1.205 Å, respectively, at the transition state. The integration of the intrinsic reaction coordinate has been also carried out in order to follow the variation of the spin density along the reaction path (Figure 4a). Figure 4a shows that starting from the Bi-PhOH-PF\(_{10}\)-TCNP** species, an electron is transferred from the phenol toward the PF\(_{10}\) group, saturating its electronic hole when the proton is bonded to the imidazole nitrogen. The spin density on the TCNP fragment is constant, revealing the formation of the BiH+-PhO*-PF\(_{10}\)-TCNP** species. In spite of a barrier of 4.44 kcal/mol, the PCET product is slightly favored by about 0.16 kcal/mol.

From a mechanistic point of view, the \(\Phi_1\) dihedral angle is the degree of freedom principally involved in the PCET reaction (see Table 1). This angle defines the relative orientation between the BiPhOH and the PF\(_{10}\) units varying by about 5° during the reaction. \(\Phi_1\) is an important parameter controlling the electronic coupling between the two units, thus modulating the electron transfer among them. To further analyze this point, the variation of the MSD on the PF\(_{10}\) and Ph fragments with respect to the \(\Phi_1\) dihedral angle is reported in Figure 4b. This plot has been obtained scanning the \(\Phi_1\) dihedral angle from \(-45^\circ\) to \(-90^\circ\) on the broken-symmetry BiH+-PhO*-PF\(_{10}\)-TCNP** state. When the two rings are almost perpendicular (\(\Phi_1 = -90^\circ\)), the spin density on the PF\(_{10}\) fragment is zero and that on Ph is about one. When the \(\Phi_1\) angle is varied, the spin density on the PF\(_{10}\) moiety gradually increases, reaching its maximum value (about 0.2) when the two rings become more planar. At the same time the spin density on the Ph fragment decreases, reaching at least the value of about 0.8. This internal mode is crucial to drive the PCET event, and it has to be considered as a critical motif for the future design of these charge transfer molecular machines.

We also computed the alternative BS solution corresponding to the transfer of an electron from the Ph group toward the PF\(_{10}\) one, with no PT between phenol and benzimidazole groups, namely, the Bi-PhOH*-PF\(_{10}\)-TCNP** species (Figure 3c).

This state is found to lie 0.60 eV (13.89 kcal/mol) higher in energy with respect to the Bi-PhOH-PF\(_{10}\)-TCNP** one (Figure 2). Its formation is, thus, energetically unfavorable. Once again Bi-PhOH*-PF\(_{10}\)-TCNP** and Bi-PhOH-PF\(_{10}\)-TCNP** differ principally for the mutual orientation of the BiPh and PF\(_{10}\) moiety, namely for the \(\Phi_1\) dihedral angle (Table 1). Indeed, this degree of freedom changes by about 40° between the two structures, with the Bi-PhOH*-PF\(_{10}\) TCNP** species favored by the perpendicular arrangement between the Ph and PF\(_{10}\) rings.

In conclusion, the complete excited-state cascade of the triad BiPhOH-PF\(_{10}\)-TCNP has been simulated within the TD-DFT and BS frameworks. This combined approach allowed us to

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**Figure 4.** (a) Mulliken spin density (MSD) integrated for fragment along the IRC for the PCET reaction. (b) Mulliken spin density integrated for fragment along the variation of the \(\Phi_1\) dihedral angle on the BiH+-PhO*-PF\(_{10}\)-TCNP** state.

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describe the complexity of the structural and electronic evolution of the charge transfer steps following the electronic excitation of the triad. Furthermore, the internal degrees of freedom involved in the various steps have been successfully analyzed. We individuate the dihedral angles involved in the modulation of the electronic coupling between the BiPhOH and PF10 moieties as crucial parameters for the formation of the various charge transfer species.

The combination of TD-DFT and broken symmetry approaches paves the way to disentangle the complex electronic structure of PSII mimics and for the successful design of charge transfer molecular machines suitable for artificial photosynthesis.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcl.0c02766.

Computational Details; natural transition orbitals involved in the transition leading to $S_1^{PF10}$, $S_2^{TCNP}$, and $S_3^{TCNP}$ excited states; evolution of $S_1^{TCNP}$ and $S_2^{PF10}$ excited states along the linear synchronous path connecting the $S_0^{PF10}$ and $S_1^{TCNP}$ energy minima; natural transition orbitals involved in the transition leading to the relaxed $S_1^{TCNP}$ state; definition of the molecular fragments Bi, Ph, PF$_{10}$ and TCNP; spin density plot for the proton-coupled electron transfer transition state (PDF)

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**Notes**

The authors declare no competing financial interest.

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