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Computational Model of Photocatalytic Water Splitting

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The photochemistry of a supramolecular system consisting of a (truncated) chlorophyll, benzoquinone and water has been explored with ab initio computational methods. It is shown that this photosynthetic model system can split a water molecule upon the absorption of a visible photon via an electron-driven proton-transfer process. It is suggested that the coupled transfer of an electron and a proton in hydrogen-bonded systems is mechanistically superior to electronic charge separation in covalently bonded donor-bridge-acceptor systems.

Oxygenic photosynthesis in green plants is achieved by the cooperation of two reaction centers which are known as photosystems (PS) I and II. In PSII, water is used as an electron donor to neutralize the primary electron donor (chlorophyll) after the initial charge separation. As a byproduct, molecular oxygen is released into the atmosphere[1,2]

The reaction centers PSI and PSII are complex and beautifully organized supramolecular systems which have been optimized through billions of years of evolution. Although the structures of PSI and PSII are nowadays known at 2−4 Å resolution,[3−5] a fully microscopic understanding of the electron-transfer and proton-transfer processes in these reaction centers is still missing.

There have been numerous attempts toward the realization of artificial photosynthesis using bioinspired molecular systems; see refs 6−9 for reviews. The simplified models of the primary charge-separation system that are closest to the prototypes of nature are hydrogen-bonded supramolecular complexes consisting of a porphyrine-type or phthalocyanine-type electron donor and a quinone-type electron acceptor, either in solution or in a fixed position by hydrogen bonding on a suitable substrate.[6−9]

In this work, we have investigated the primary step of photoinduced water splitting in a minimal model system consisting of a truncated chlorophyll (Chl), benzoquinone (BQ) and a water wire. The equilibrium geometries of educt and product have been determined with density functional theory (DFT). The excited states have been characterized with the CC2 method, which is a simplified and computationally efficient variant of coupled-cluster theory. A more detailed description of the computational methods is given in the Supporting Information (SI).

The ground-state equilibrium structure of the supramolecular complex is shown in Figure 1a (the Cartesian coordinates of this structure are given in the SI). To simplify the system, the side chains of Chl have been substituted by hydrogen atoms, with the exception of the methyl ester carbonyl group on the cyclopropanone ring, which can be involved in hydrogen bonding (in the following, Chl refers to this truncated chlorophyll molecule). The BQ is connected to the Chl by a chain of two water molecules. One of these (W_1) is coordinated with its oxygen lone pair to the Mg atom of Chl. The rather short Mg−O distance ($R_{MgO} = 2.048$ Å) indicates a fairly strong Mg−water interaction. A second water molecule (W_2) is hydrogen bonded to W_1 as hydrogen acceptor, and acts as a hydrogen donor to the carbonyl groups of Chl and BQ; see Figure 1a.

The vertical excitation energies of the lowest singlet states, obtained with the CC2 method for the structure of Figure 1a, are given in Table 1 and are shown on the left-hand side of Figure 2. The locally excited (LE) states of the Mg−porphyrin system are denoted as ^1LE_P, those of BQ as ^1LE_Q. In agreement with previous ab initio calculations,[10] we obtain four low-energy excited states of Chl. These excitations (shown in blue in Figure 2) are the well-known weak "$Q_{x,y}$" band at ≈2.3 eV and the stronger "Soret" band at ≈3.4 eV. These results are in good agreement with the excitation energies of Mg−porphyrin (2.14 and 3.22 eV, respectively[11]). Two $^1n\pi^*$ excited states of BQ (shown in green in Figure 2) are located below the Soret band. These states are related to weak bands observed in the gas-phase absorption spectrum of BQ between 2.5 and 3.0 eV.[12]

The two energy levels shown in red in Figure 2 do not have counterparts in the absorption spectra of the molecular components. These excited states, denoted as $^1CT_{PQ}$, are charge-transfer (CT) excitations from the porphyrin system to the quinone. Because the molecular orbitals (MOs) of Chl and BQ do not overlap, the oscillator strength of these transitions is essentially zero. The excited states of water are much higher in energy and are not mixed with the low-lying excited states of the complex.

The frontier MOs of the Chl-$(H_2O)_2$-BQ complex are displayed in Figure 3. The two highest occupied MOs of Chl are shown in (a) and (b) and denoted as π_{1P} and π_{2P}, respectively, the two lowest unoccupied MOs are shown in (d) and (e) and denoted as π_{1P}^* and π_{2P}^*, respectively. These are the π and π^* MOs involved in Gouterman's four-orbital model of porphyrin.[13] The lowest $^1n_{1Q}\pi_Q^*$ and $^1n_{2Q}\pi_Q^*$ excitations in BQ involve the orbitals shown in (c) and (f). In Figure 3 only one of the two (n_{1Q} and n_{2Q}) lone pair

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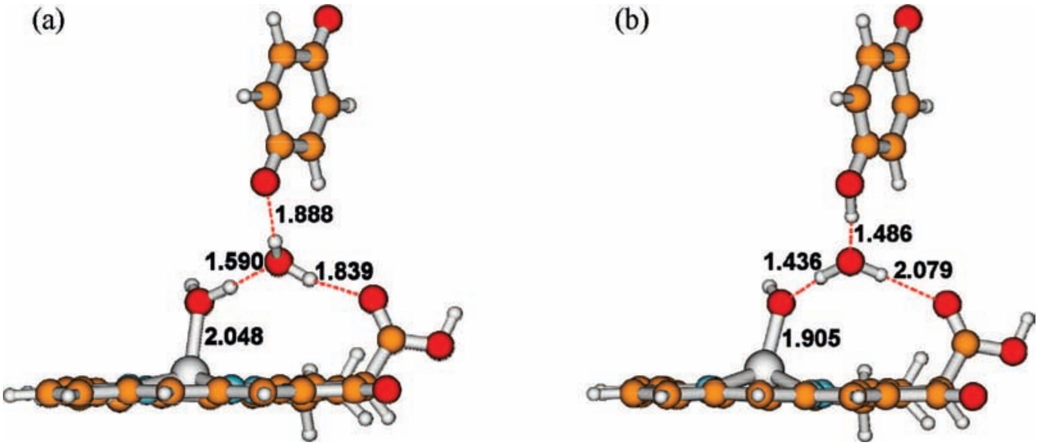

Figure 1. Ground-state equilibrium geometries of the neutral (a) and biradicalic (b) forms of the Chl-$(H_2O)_2$-BQ complex. The numbers denote bond lengths in Ångstroms.

TABLE 1: Vertical Excitation Energies ΔE (in eV) of the Lowest Excited Singlet States of the Chl-$(H_2O)_2$-BQ and Chl-OH(H_2O)-HBQ Complexes, Calculated with the CC2 Method at the DFT-Optimized Geometry of the Ground State[a]

state	ΔE	f
ground-state equilibrium geometry of Chl-$(H_2O)_2$-BQ		
$LE_P(\pi\pi^*)$	2.28 (2.23)	(0.128)
$LE_P(\pi\pi^*)$	2.33 (2.26)	(0.063)
$LE_Q(n\pi^*)$	2.87 (2.43)	(0.3×10^{-5})
$CT_{PQ}(\pi\pi^*)$	2.94	
$CT_{PQ}(\pi\pi^*)$	3.00	
$LE_Q(n\pi^*)$	3.23 (2.83)	(0.2×10^{-4})
$LE_P(\pi\pi^*)$	3.37 (3.22)	(0.239)
$LE_P(\pi\pi^*)$	3.49 (3.31)	(0.352)
equilibrium geometry of Chl-OH(H_2O)-HBQ		
$CT_{PQ}(\pi\pi^*)$	1.62 (1.57)[b]	
S_0	2.51	

[a] The values in parentheses (energies and oscillator strengths) have been calculated with the TDDFT method at the same geometry. [b] Energy of the lowest triplet state of the biradicalic structure calculated at the unrestricted DFT level.

orbitals of BQ is shown. The two low-lying CT states of the complex result from the transfer of an electron from one of the two π orbitals of Chl (a, b) to the π^* orbital of BQ (f).

When the geometry of the lowest CT state is optimized, the structure shown in Figure 1b is obtained (the Cartesian coordinates of this structure are given in the SI). It is seen that a proton has been transferred from W_1 (which is coordinated to Mg) to W_2, whereas a proton of W_2 has been transferred to BQ, reducing the latter to a semiquinone. Overall, a proton has followed the transferred electron from Chl to BQ. The resulting structure (Figure 1b) is a biradical, possessing an unpaired electron on Chl and on BQ. The neutralization of the electronic charge separation by the proton transfer results in a stabilization energy of the two CT states of about 1.4 eV. The energies of the biradical states are lower than the energy of the lowest closed-shell state at this geometry (see Figure 2). The overall enthalpy of the water-splitting process is 1.62 eV (1.57 eV) at the CC2 (DFT) level of theory (cf. Table 1).

The following qualitative picture emerges from the energy diagram and equilibrium structures shown in Figure 2.

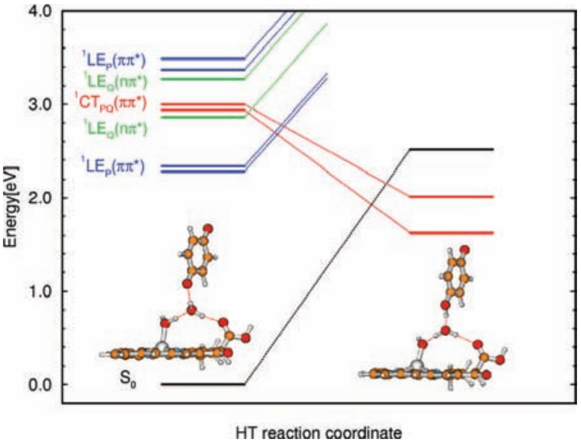

Figure 2. Energy diagram of the ground state and the lowest excited singlet states of the neutral and biradicalic forms of the Chl-$(H_2O)_2$-BQ complex, determined with the CC2 method at DFT equilibrium geometries. Dotted lines denote diabatic correlations of the states.

Excitation of the Chl-$(H_2O)_2$-BQ complex to the Soret band by visible light leads, via a radiationless transition, to the population of the lower-lying optically dark CT states. These radiationless transitions involve the transfer of an electron from a π^* orbital of the porphyrin system to a π^* orbital of BQ. The electron transfer and the ensuing transfer of the proton split W_1 and reduce BQ to a semiquinone (BQH). The energy-level structure in Figure 2 indicates that the water splitting and reduction of BQ is a barrierless process from the Soret band, whereas a small barrier probably has to be overcome from the $Q_{x,y}$ band of Chl.

The excess energy which becomes available by the electron-driven proton-transfer (EDPT) process is sufficient for the breaking of the hydrogen bond between the semiquinone and the Chl-OH-H_2O complex, thus releasing the semiquinone. After the detachment of the semiquinone, a new BQ molecule can attach to the Chl-OH-H_2O radical complex via hydrogen bonding. Because the lowest excited states of the system involve electronic excitations only within (or between) Chl and BQ (H_2O and the OH radical cannot be excited at the wavelengths under consideration), the electronic-energy diagram is largely independent of the stage of water splitting. A detailed discussion of the individual steps of the water-splitting process is beyond the space limits of this communication and will be published elsewhere.[14] After the

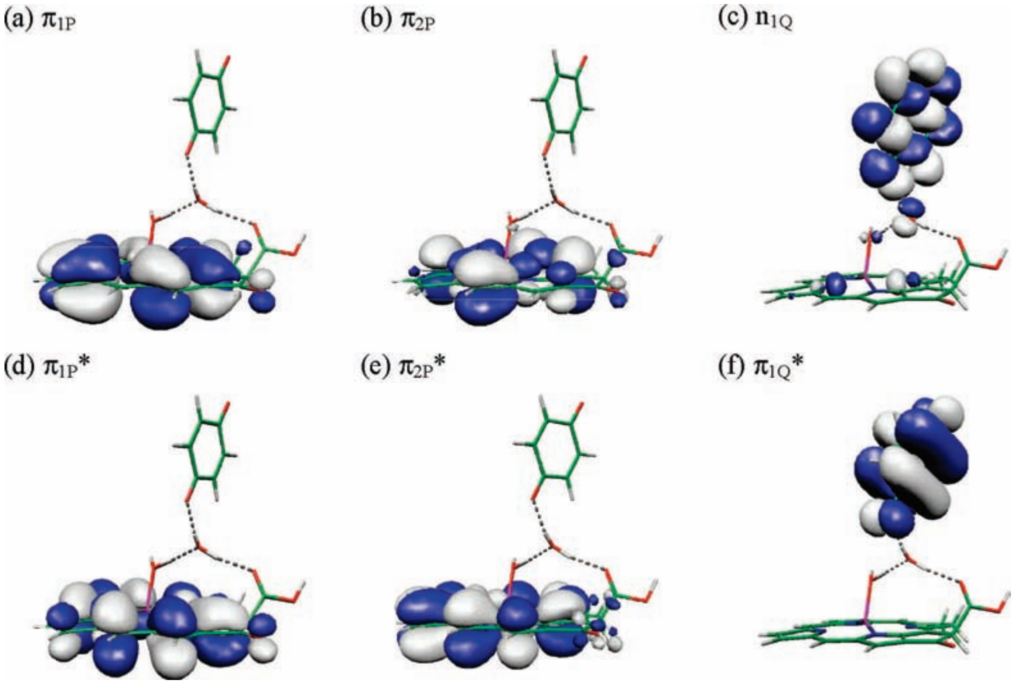

Figure 3. Frontier molecular orbitals of the Chl-$(H_2O)_2$-BQ complex, determined at the equilibrium geometry of the S_0 state; (a)−(c) orbitals occupied in the Hartree−Fock reference; (d)−(f) unoccupied orbitals.

consumption of four visible photons, four BQs have been reduced and O_2 is released according to the overall equation

$$\mathrm{Chl} + 2\mathrm{H_2O} + 4\mathrm{BQ} + 4h\nu \rightarrow \mathrm{Chl} + \mathrm{O_2} + 4\mathrm{BQH} \quad (1)$$

The four hydrogen atoms are still chemically bonded to the benzoquinones. However, their release does not require net enthalpy. The release of H_2 can therefore be accomplished in a dark reaction with a suitable catalyzer.

To summarize, we have shown that a supramolecular system, consisting of Chl, BQ and two (or more) water molecules, can split water with a photon of visible light ($h\nu \approx 3$ eV). The reaction mechanism is an EDPT process.[15] The proton, which immediately (that is, on a time scale of femtoseconds) follows the electron, stabilizes the photoinduced electronic charge-separation process. The forward transfer of the electron and the proton is exoenergetic and barrierless, whereas a barrier presumably has to be overcome on the reaction path of the reverse process (see Figure 2). The mechanistic picture suggested by Figure 2 is quite different from that of covalently bonded donor-bridge-acceptor supramolecular systems.[6–8] The latter are inspired by the Marcus theory of electron transfer.[16] In this picture, the goal is a long-distance electronic charge separation to suppress the losses through charge recombination.[6–8,17] The efficiency of photocatalytic hydrogen production by covalently bonded artificial photosynthetic systems has been found to be rather low because of the charge-recombination losses.[8] In the hydrogen-bonded water-splitting complex, on the other hand, the electronic charge separation is rapidly neutralized by the proton which follows the electron. Therefore, the EDPT process can continue along a hydrogen-bonded chain of acceptor molecules without the creation oflarge electronic dipole moments and long-range polarization effects of the medium.

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Supporting Information Available: Textual presentation of the computational methods. Table of Cartesian coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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