Ultrafast Photoinitiated Long-Range Electron Transfer in Cyclophane-Bridged Zincporphyrin−Quinone Complexes via Conical Intersections

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Upon photoexcitation of the spectroscopically known Q states of cyclophane-bridged zincporphyrin−quinone complexes, an electron is transferred from the porphyrin to the quinone ring on a subpicosecond time scale. The details of the molecular mechanism of this ultrafast process are investigated with modern quantum chemical methods. Two excited-state crossings between the initially excited Q states and an appropriate zincporphyrin-to-quinone charge-transfer state could be identified, which are located in the vicinity of the ground-state equilibrium geometry. One state crossing occurs along a vibrational mode corresponding to a twisting of the cyclophane bridges, the so-called twist mode, while a second crossing appears along a so-called swinging-bridge mode, in which the quinone ring swings versus the porphyrin ring. Arguments are given that these state crossings correspond to conical intersections, which present here a highly efficient pathway for long-range electron transfer. General aspects of the presented mechanism and its relevance for biological electron-transfer processes are discussed.

1. Introduction

Electron transfer (ET) is ubiquitous in biological, physical, inorganic, and organic chemical systems. Understanding and control of ET reactions is one of the most active and widest research fields of physical chemistry today (see for example refs 1−10). The fundamental biological process of primary photosynthesis, for instance, is characterized by a series of subsequent ET events in the reaction center producing long-lived charge-separated states.[11] The initial step in this series of ETs is transfer of an electron from one photoexcited chlorophyll of the so-called "special pair" to the adjacent quinone.[2] In general, such processes in which electrons are transferred upon photoexcitation are referred to as photoinitiated ET (PI-ET). However, a detailed mechanism of how the initial ET step in photosynthesis takes place, i.e., which molecular motion triggers the efficient transfer of the electron, has still to be established.

In contrast, ample data are available on how thermodynamic quantities such as the free energy of reaction ($\Delta G°$), the reorganization energy (λ), or the electronic coupling (H_{AB}) between initial state (A) and charge-separated state (B) influence the efficiency of the ET process (see for example ref 12 and

references herein). In general, most of the ET processes can be interpreted in terms of the quasi-equilibrium picture of nona-diabatic and transition state theories,[1] most prominently Marcus theory.[13−15] Ultrafast ET processes, however, can usually not be described within the framework of such simplified models, since they are generally sensitive to nonequilibrium dynamic effects involving nuclear motion.[1] Nonequilibrium effects can be expected to be of paramount importance when the ET time is of the same order of magnitude as the time scale of vibrational motion, which is usually the femto to picosecond region.

In photochemistry and photophysics, ultrafast processes on that time scale are often found to proceed via so-called conical intersections (CIs), which are regions of coordinate space where two potential energy surfaces meet with a particular topology.[16,17] CIs generally provide an extremely efficient mechanism for interstate crossing[18,19] and are therefore often also called photochemical funnels. Today, a plethora of examples are known from the fields of molecular excitation,[20,21] photoelectron spectroscopy,[18,22] and photochemistry[19,23] and photobiology,[24,25] in which conical intersections are involved in the ultrafast dynamics of large molecular systems. This usually leads to a breakdown of quasi-equilibrium dynamical models and requires a detailed study of the system of interest with modern quantum chemical methods.

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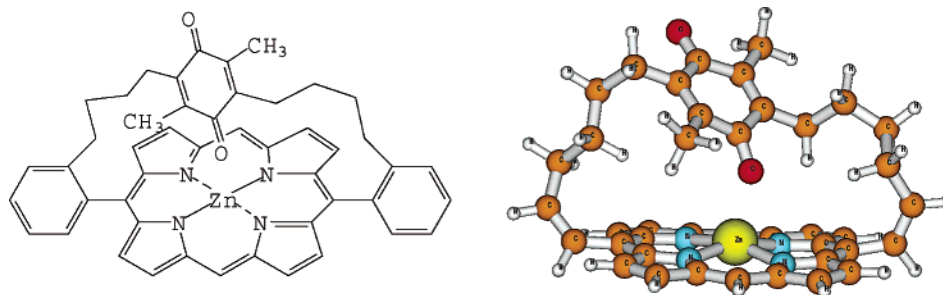
Figure 1. Structure of the original cyclophane-bridged zincporphyrin−quinone complex (ref 27) as well as the model complex used in the calculations, in which the phenyl rings of the cyclophane bridges are replaced by double bonds.

One example for systems exhibiting ultrafast PI-ET is the class of cyclophane-bridged zincporphyrin−quinone complexes (cpb-ZnPQ) synthesized and spectroscopically investigated by Häberle et al.[26] and Staab et al.[27] Since these complexes are structurally related to the architecture of the photosynthetic reaction center, they serve as ideal model systems to study the initial ET step from the chlorophyll to the quinone in the photosynthetic process. Experimentally, when the zincporphyrin of cpb-ZnPQ is locally photoexcited into its energetically lowest π−π^* excited state, the well-known Q_y band, an electron is transferred from the porphyrin ring to the quinone moiety within a few hundred femtoseconds.[26] Furthermore, it has been observed that the efficiency of the PI-ET process in these complexes is essentially independent of the polarity of the solvent, which indicates that nonequilibrium effects are dominant for this process and that quasi-equilibrium theories are not applicable. In fact, the high efficiency and the ultrafast transfer time of this process strongly suggest that a conical intersection between the photoexcited Q_y state and a suitable charge-transfer excited state might be the key factor determining the transfer mechanism.[28] In this case, the conventional view of separate donor and acceptor states interacting via tunneling is not valid, since the states are strongly nonadiabatically coupled, at the intersection seam even infinitely strong, allowing for an ultrafast barrierless transition. Hence, calculations of transfer rates or tunnel splittings via quasi-equilibrium theories as often done in systems in which the transferred electron has to cross or tunnel through a barrier are not possible for ultrafast electron transfer mediated by conical intersections. Recently, it has been pointed out that a conical intersection can trigger intramolecular charge transfer in a retinal protonated Schiff base.[29] In the cpb-ZnPQ complex, however, the PI-ET process should be viewed as an intermolecular ET rather than an intramolecular transfer process, even though the zincporphyrin and the quinone are covalently linked to each other by the cyclophane bridges.

In a previous study,[28] we have made a preliminary investigation of this system using simple model calculations. A cut through the potential energy surfaces for a zincporphyrin and a quinone molecule was calculated, at the configuration interaction with single excitations (CIS) level, keeping the two molecules parallel in a C_{2v} geometry. This showed that there are charge-transfer (CT) states in the same energy region as the porphyrin B and Q states. Furthermore, the geometry dependence of the energy is stronger for the CT states than the porphyrin localized states. As a result, the CT states are very likely to cross the B and Q states and, from symmetry arguments, these crossing points are part of a conical intersection seam.

In this work, we explore the potential energy surface of the cpb-ZnPQ complex in more detail and with more elaborate quantum chemical methods. In particular, we are aiming at identifying the relevant molecular motions of the cpb-ZnPQ complex, which trigger the ultrafast PI-ET process in this system

and along which conical intersections might be located. We focus on two large-scale vibrational motions of the cpb-ZnPQ complex, which are the so-called *twist* and *swinging-bridge* motions,[30] along which the electronic excited states have been calculated. The paper is organized as follows. In section 2, the details of our theoretical calculations will be given. Thereafter, the results of our calculations will be presented (section 3), detailing the potential energy surfaces of the lowest excited electronic states of cpb-ZnPQ along the twist and swinging-bridge modes (sections 3.1 and 3.2). In section 4, the relevance and importance of the presented mechanism of long-range intermolecular electron transfer via conical intersections for biological systems will be discussed. The paper ends with a brief summary and outlook (section 5).

2. Theoretical Methods

Our theoretical investigation of the cpb-ZnPQ complex comprises the optimization of its ground-state equilibrium geometry as well as the calculation of singlet excited electronic states. All calculations reported here have been performed in the framework of the Q-Chem[31] and Gaussian 98[32] packages of programs.

The ground-state structure of the cyclophane-bridged zincporphyrin−quinone complex has been optimized using standard ground-state density-functional theory (DFT) in combination with the gradient-corrected Becke−Lee−Yang−Parr (BLYP)[33] and the hybrid Becke3−Lee−Yang−Parr (B3LYP)[34] exchange-correlation (xc) functional in combination with the 6-31G* basis set. In general, the differences in the geometrical parameters obtained with the different xc-functionals are very small and they agree very favorably with the available crystal structure data.[27] The largest difference between the crystal structure and our optimized geometry occurs for the distance between the Zn of the porphyrin ring and the O atom of the adjacent quinone (Figure 1).

While in the crystal structure this distance is 2.53 Å, it has a value of only 2.33 Å at the level of DFT/BLYP/6-31G*. This is mainly due to two effects. On one hand, we perform a gas-phase calculation which does not include crystal packing effects, which may lead to a decreased tilting angle between the quinone and porphyrin resulting in an increased Zn−O distance, similar to the swinging-bridge motion discussed below. On the other hand, we replaced two phenyl rings of the cyclophane bridges present in the original complex[27] by slightly shorter double bonds for the sake of faster computation times (Figure 1). Although this approximation has essentially no influence on the other geometrical parameters and the relevant singly excited electronic states, it may contribute to the slight shortening of the Zn−O distance. Since the detailed geometrical parameters are only of minor interest in the context of this study, the Cartesian coordinates of the optimized complex are given in

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TABLE 1: Excitation Energies, in eV, of the Experimentally Known Q and B (Soret) States of the Cyclophane-Bridged Zincporphyrin−Quinone Complex Calculated with Various Quantum Chemical Methods[a]

state	CIS	SVWN	BLYP	B3LYP	CASSCF	expt[1]
Q_y	2.40	2.14	2.12	2.26	3.50	2.16
Q_x	2.41	2.15	2.13	2.27	3.52	2.31
B_y	4.29	3.01	3.00	3.22	4.69	3.01[2]
B_x	4.34	3.02	3.02	3.25		

[a] For the CASSCF calculations, a model complex (see the text) has been used.

the Supporting Information. All optimized geometries have been checked by an analysis of the vibrational frequencies, and all have only real values.

For the calculation of the excited singlet states of the cpb-ZnPQ complex, wave function based methods as well as density based methods have been employed. At the equilibrium geometry, we used CIS,[35] the complete active space self-consistent field (CASSCF) approach, and time-dependent DFT (TDDFT)[36,37] to calculate the electronic excitation spectrum of the complex. The standard 6-31G* basis set was used throughout all presented calculations. In the CASSCF calculations, we used a state-averaged reference and an active space of four electrons in five orbitals including the four Gouterman orbitals and the π^* orbital of the quinone.

Since one cannot expect that approximate standard xc-functionals describe all excited states equally well, a crucial step in TDDFT studies is the choice of an appropriate xc-functional for the calculation of the excited states under consideration. In the presented investigation, we are particularly interested in the correct description of the lowest $\pi-\pi^*$ states of the cpb-ZnPQ complex, which are the Q and B states of the zincporphyrin. Therefore, the electronically excited states of the geometrically optimized cpb-ZnPQ have been calculated at the level of TDDFT employing the hybrid B3LYP functional, the gradient-corrected BLYP functional, and the local Slater−Vosko−Wilk−Nusair (SVWN)[38,39] functional and are then compared with the experimental values (Table 1). We have chosen the BLYP xc-functional to be the standard functional in our TDDFT calculations, since it reproduces the experimental energies of the Q and B states of the cpb-ZnPQ complex with an average error of only 0.06 eV. Although the average error of the SVWN functional is smaller, we did not use this functional since severe convergence problems occurred at several steps of our investigation.

It has been pointed out recently that TDDFT employing standard ground-state xc-functionals does not describe CT states correctly[40−44] and most importantly does not give the correct $1/R$ asymptotic behavior of the CT state when R is a distance coordinate between the separated charges of the CT state owing to so-called electron-transfer self-interaction.[41,44] Since the correct description of the asymptotic behavior of the CT states is crucial for our study, we use a hybrid approach combining TDDFT and CIS for the calculation of the excited states along two large-scale vibrational motions of the systems, within which the porphyrin (donor)−quinone (acceptor) distance is strongly varied. The applied approach circumvents the CT problems of TDDFT by using a curve calculated at the level of CIS, which is shifted by a separately calculated ΔDFT value.[41,44] The ΔDFT value is obtained as the difference between the total energies of the ground state and the energetically lowest charge-transfer state and can be calculated only at large intermolecular separations since otherwise the DFT calculation for the desired CT state converges onto the electronic ground state. Following
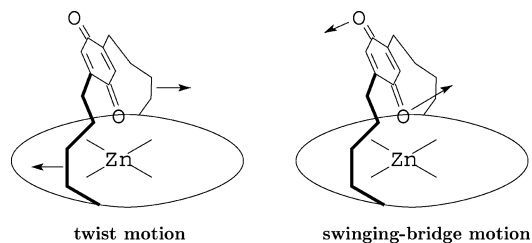

Figure 2. Schematic sketch of two relevant large-scale vibrational motions. The arrows indicate the direction of motion. Both motions result in an increase of the Zn−O distance and simultaneously in an increase of porphyrin−quinone distance.

this procedure, potential energy curves for CT states are obtained that do not suffer from electron-transfer self-interaction and, thus, possess the physically correct $1/R$ asymptotic behavior. The curves for the valence-excited Q and B states calculated with TDDFT can then be used together with the shifted CIS CT curves. By using a constant offset for all distances, one introduces an additional error of approximately 0.1 eV at short distances compared to a complete ΔDFT curve which has been tested for a small ethylen−tetrafluoroethylen complex.[44] The described hybrid approach has already been successfully applied to the calculation of charge-transfer excited states in carotenoid-chlorophyll[45,46] and bacteriochlorin complexes.[44]

3. Ultrafast Photoinitiated Electron Transfer in Cyclophane-Bridged Zincporphyrin−Quinone Complexes

Photoexcitation of the porphyrin ring of cpb-ZnPQ complexes into their well-known Q states results in an ultrafast transfer of an electron from the porphyrin ring to the attached quinone moiety. Essentially independent of the polarity of the environment, the electron transfer occurs within a few hundred femtoseconds.[26] The high efficiency of the observed ET and its short time scale suggest that one or more conical intersections are involved in the process, which may trigger the electron transfer or, in other words, the nonradiative decay of the photoexcited Q states into suitable charge-transfer states. Consequently, state crossings between the Q states and a porphyrin-to-quinone charge-transfer excited state must be present along a suitable nuclear coordinate to permit this scenario. The objective of our study is to identify such state crossings.

One first major problem in our study of the 83 atom asymmetric cpb-ZnPQ complex possessing 243 vibrational degrees of freedom is to find or guess relevant nuclear coordinates along which a state crossing may occur. Here, we are interested in crossings between CT states and $\pi-\pi^*$ excitations purely located at the porphyrin. While the energy of CT states is very sensitive to the donor−acceptor distance due to the strong electrostatic attraction between them, the energy of the latter $\pi-\pi^*$ excitations can be expected to be essentially constant along such a coordinate. Therefore, crossings between CT and $\pi-\pi^*$ excited states should naturally occur along vibrations of the cpb-ZnPQ complex in which the distance between the porphyrin and the quinone ring is strongly varied. In fact, two such large-scale motions have been identified in the cpb-ZnPQ systems by temperature-dependent NMR measurements[30] which are good candidates to be relevant nuclear motions triggering the electron-transfer process. The first vibrational motion is referred to as *twist motion*, in which the cyclophane bridges twist. This results in a relative motion of the porphyrin ring versus the quinone ring (left side of Figure 2). The second motion is a so-called *swinging-bridge* motion,
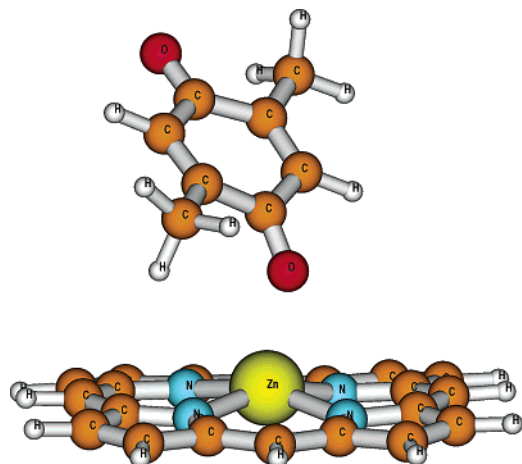
Figure 3. Structure of the model complex used to simulate the twist motion of the cpb-ZnPQ complex. This model has also been used for the CASSCF calculations.

in which the quinone ring seems to swing between two equivalent minimum structures. This motion leads to an increase of the distance between the zinc atom and the quinone O atom similar to the twist mode but also to a decrease of the tilting angle between the rings (right side of Figure 2).

In the following sections, the excited electronic states of cpb-ZnPQ will be investigated along the twist mode (section 3.1) and along the swinging-bridge mode (section 3.2). It will be shown that indeed crossings between a porphyrin-to-quinone charge-transfer excited state and the excited Q states occur in the vicinity of the equilibrium geometry of the ground state. Most likely, these crossings correspond to conical intersections.[47] Previously, conical intersections have been shown to be relevant for ultrafast intramolecular ET, but their role in intermolecular ET is still to be established.

3.1. Electron Transfer along the Twist Vibrational Motion. The twist motion of cpb-ZnPQ (Figure 2) results in a relative motion of the quinone versus the porphyrin. This motion can be simulated by using the model complex displayed in Figure 3 and increasing of the Zn−O distance (R) along the Zn−O direction. The model complex is obtained by replacement of the cyclophane bridges by hydrogen atoms and reoptimization of the corresponding bond lengths. Besides that, the model complex exhibits exactly the same geometrical parameters as the optimized full complex with the cyclophane bridges (compare Figures 1 and 3). Although this approximation seems at first glance rather crude, the cyclophane bridges have only a small influence on the excited electronic states of interest: at the level of TDDFT/BLYP/6-31G*, the four states of the Q and B bands of the cpb-ZnPQ complex have energies of 2.12, 2.13, 3.00, and 3.02 eV, while in the model complex without cyclophane bridges the excitation energies are 2.22, 2.23, 3.02, and 3.09 eV, respectively.

For the calculation of the potential energy curves of cpb-ZnPQ along the Zn−O coordinate R, we used the hybrid approach suggested by Dreuw et al.,[41,44] which combines the benefits of TDDFT and CIS to circumvent the failure of TDDFT for CT states when standard functionals such as BLYP, B3LYP, or SVWN are employed. Following the procedure outlined in section 2, the curves of the Q bands were calculated with TDDFT/BLYP/6-31G*, while the curve of the energetically lowest CT state is obtained via CIS. The CIS curve is then shifted by an offset value of 4.1 eV which is the difference of the total energies of the electronic ground state and the energetically lowest CT state calculated with ground-state DFT/
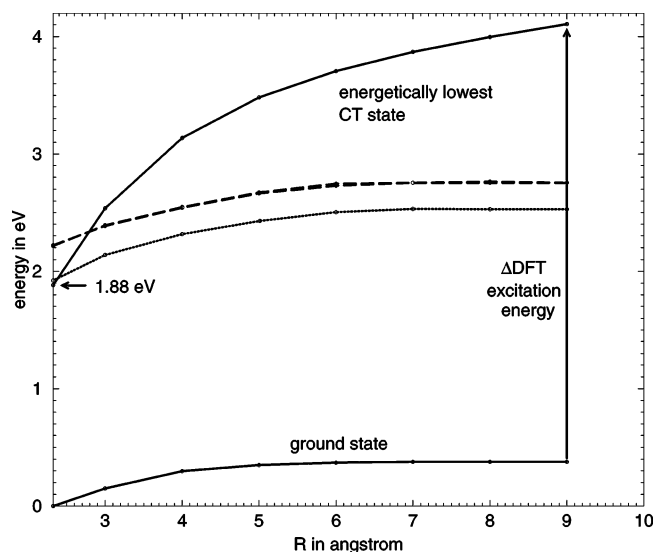

Figure 4. Potential energy curves of the Q states (long-dashed lines), the lowest locally excited quinone $\pi-\pi^*$ state (dotted line), the energetically lowest CT state (solid line), and the ground state (solid line) along the Zn−O distance coordinate R modeling the vibrational twist motion. The curves have been obtained with the hybrid approach by shifting the CIS curve of the energetically lowest CT state such that the calculated ΔDFT excitation energy (vertical arrow) is correct.

BLYP/6-31G* at 9 Å separation. At shorter distances, the ground-state DFT calculation does not converge onto the desired CT state but onto the electronic ground state. In the excited-state calculations along the Zn−O distance coordinate, all other geometrical parameters besides the Zn−O distance were held fixed and were not reoptimized. Following this procedure, the curves displayed in Figure 4 are obtained. These curves reflect only at short distances the potential energy curves of the twist motion of the full cpb-ZnPQ complex with cyclophane bridges (Figure 1), since in the model complex without cyclophane bridges Zn−O distances are possible, which are not accessible in the full system. Nevertheless, we need to do the calculation at large Zn−O separations to obtain a ΔDFT offset value for our applied hybrid approach.

While at large molecular separation the energetically lowest CT state is clearly higher in energy than the Q states of zincporphyrin, the CT state drops rapidly in energy with decreasing Zn−O distance and crosses the Q states at a distance of about 2.85 Å. At the theoretical level of TDDFT/BLYP/6-31G*, another excited state of the cpb-ZnPQ system is also identified to be lower in energy than the Q states of the zincporphyrin, which is the lowest $\pi-\pi^*$ excitation of the quinone molecule. The CT state also crosses this state at a Zn−O distance of 2.5 Å. Consequently, the lowest excited electronic state of cpb-ZnPQ at the equilibrium Zn−O distance of 2.33 Å is a CT state corresponding to a one-electron transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the complex. The HOMO corresponds to the lowest π orbital of zincporphyrin, while the LUMO is the lowest π^* orbital of the quinone (Figure 5).

At the equilibrium geometry, this CT state has an excitation energy of approximately 1.88 eV, as one can see from Figure 4. TDDFT/BLYP/6-31G* yields a value of only 0.53 eV for the excitation energy of this CT state, which corresponds to an error of about 1.4 eV. This dramatic failure of TDDFT for CT excited states is due to the well-known self-interaction as outlined in detail in refs 41, 43, and 44. This demonstrates once more the necessity to use the CIS curves shifted by a ΔDFT
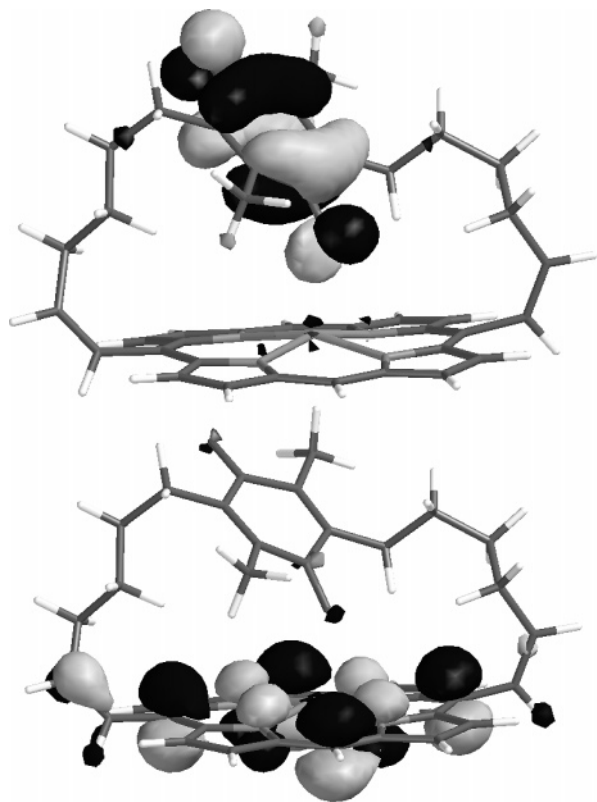
Figure 5. HOMO (lower part) and LUMO (upper part) of the optimized full cpb-ZnPQ complex calculated with DFT/BLYP/6-31G*.

offset to obtain reasonable estimates for CT excited states. CIS/6-31G* alone gives a value of 3.16 eV for the excitation energy of the CT state, which exhibits a similar error of about 1.3 eV. The origin of the overestimation of CIS lies in the limited flexibility of the CIS wave function which does not allow for an appropriate description of the orbital relaxation and correlation effects which occur when an electron is transferred.

To further corroborate our findings, CASSCF calculations for the five energetically lowest excited states have been performed at the equilibrium geometry of the cyclophane-bridged ZnPQ complex, in which the model complex depicted in Figure 3 has been used. The details of the calculation are given in section 2. These calculations qualitatively agree with the results found with the previously applied hybrid approach, because the same energetic order of the relevant states is found. The lowest excited state of the cpb-ZnPQ complex at the equilibrium geometry is according to the CASSCF calculations a zincporphyrin-to-quinone CT state with an excitation energy of 2.86 eV, followed by a second CT state with an energy of 3.28 eV. The Q_y and Q_x states localized at the zincporphyrin are given at 3.50 and 3.52 eV, respectively, at this level of theory (see also Table 1). The optically forbidden low-lying $\pi−\pi^*$ excited state localized at the quinone moiety is not found with the chosen CASSCF approach because the π orbital of the quinone is excluded from the active space of the calculation. As one can see by comparison of the calculated values with the experimental ones for the Q states of this system (Table 1), the excitation energies are overestimated, which explains why the lowest CT state is found at a higher excitation energy than within the DFT framework. The overall situation that a CT state is the lowest excited state at the equilibrium geometry of the cpb-ZnPQ complex and crosses the Q states along the twist motion due to the $1/R$ attraction between the separated charges is the same at both levels of theory.

The excited-state crossings between the CT state and the Q states as well as with the lowest quinone excited state along the twist mode are very important for the ultrafast electron-transfer dynamics in the cpb-ZnPQ complexes. Because we use two independent calculations to obtain the discussed potential energy curves, we cannot distinguish between a real state crossing, which could correspond to a conical intersection, and an avoided crossing. Although we cannot prove that these crossings are conical intersections, it has been shown by Truhlar and Mead[47] that conical intersections are omnipresent in multidimensional systems and whenever two potential energy surfaces of a polyatomic molecule come close to each other, it is very likely that there is a conical intersection close by. The number of degrees of nuclear freedom of such a system is large, and small variations of these essentially constitute "free" parameters to guide the surfaces to a conical intersection. This very intuitive and appealing picture has also been put forward in a mathematical formulation which shows that this is indeed the case.[47] In our example, as is the case for all long-range CT situations, the coupling of the CT state with the one carrying the oscillator strength can a priori be expected to be weak and, hence, the two surfaces will come close to each other along the coordinates discussed here and lead to conical intersections in the vicinity of the avoided crossings obtained. Based on this argument, it is very likely that one will find conical intersections between the Q states and the CT state and between the quinone excited $\pi − \pi^*$ state and the CT state along the twist mode.

3.2. Electron Transfer along the Swinging-Bridge Motion. The swinging-bridge motion is related to the twist motion, since the Zn−O distance is also strongly varied during its motion. On the other hand, the overall porphyrin−quinone distance does not change that strongly since it is compensated by a decreased tilting of the quinone versus the porphyrin as indicated in Figure 2. We have modeled the swinging-bridge motion by increasing the Zn−O distance in the full cpb-ZnPQ complex (right side of Figure 1) and reoptimization of all other geometrical parameters of the electronic ground state at fixed Zn−O distance. The direction of the Zn−O distance is thus also allowed to adjust. By allowing the molecular framework to relax, the cpb-ZnPQ complex automatically follows the swinging-bridge motion, since the induced strain in the cyclophane bridges by increasing the Zn−O distance forces the tilting angle between the porphyrin and quinone ring to decrease.

Along the optimized swinging-bridge motion, the excited electronic states of cpb-ZnPQ have been calculated using the same approach as described above for the twist motion with the difference that the complete cpb-ZnPQ complex including the cyclophane bridges is used here. The valence-excited states of the cpb-ZnPQ complex have thus been calculated with TDDFT/BLYP/6-31G* while the energetically lowest CT excited state has been calculated with CIS/6-31G*. Since in this case it is obviously not possible to calculate a ΔDFT offset at large intermolecular separation, we use the value of 1.88 eV for the excitation energy of the CT state at the equilibrium geometry obtained from the investigation of the twist motion as offset for the CIS curve. The obtained potential energy curves are shown in Figure 6.

At the equilibrium geometry, represented by the vertical line in Figure 6, the lowest state is the porphyrin-to-quinone CT state identified already in the previous section 3.1. Going along the swinging-bridge motion in the direction of longer Zn−O distances, the energy of the CT state increases due to the diminishing electrostatic attraction between the positively charged porphyrin and the negatively charged quinone. At a
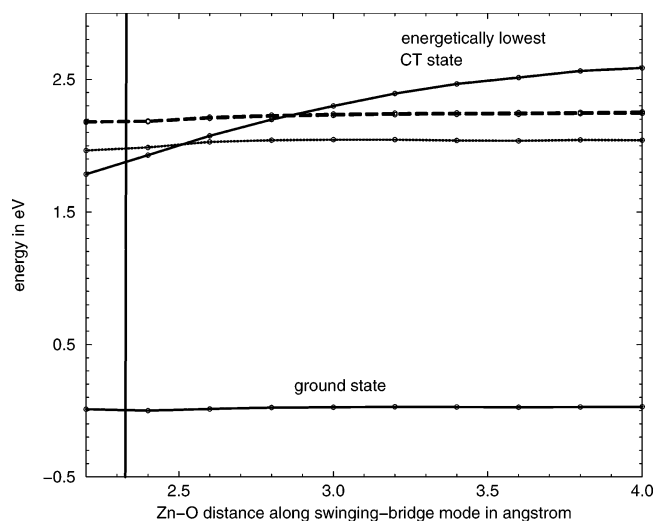
Figure 6. Potential energy curves of the Q states (long-dashed lines), the lowest locally excited quinone $\pi-\pi^*$ state (dotted line), the energetically lowest CT state (solid line), and the ground state (solid line) along the swinging-bridge motion. The vertical line corresponds to the equilibrium geometry of the cpb-ZnPQ complex.

Zn—O distance of 2.45 Å, the CT state crosses first the quinone $\pi-\pi^*$ state, and then at a Zn—O distance of 2.8 Å the Q states of the porphyrin. The potential energy curves along the swinging-bridge motion are similar to the ones obtained for the twist motion at short Zn—O distance, which demonstrates the relation between these motions. Both modes are large-scale motions, in which mainly the Zn—O distance and by that the porphyrin—quinone distance is varied. A difference between the swinging-bridge and twist motion is, though, that the energy of the CT state rises steeper in the twist motion than in the swinging-bridge one. This is due to the fact that the donor—acceptor distance, i.e., the porphyrin—quinone distance, has a closer connection to the Zn—O distance in the twist motion than in the swinging-bridge motion. Furthermore, the ground-state curves of the two motions look different. While the ground state exhibits a pronounced minimum along the twist mode with a well depth of 0.38 eV at the theoretical level of DFT/BLYP/6-31G*, the swinging-bridge motion corresponds only to a very shallow minimum with a well depth of only 0.04 eV. This suggests that the swinging-bridge motion occurs at a lower frequency and that the motion has a larger amplitude. As a consequence, upon photoexcitation the curve crossing between the Q states and the CT state might be reached easier and faster along this motion than along the twist motion.

In analogy to the analysis of the crossings occurring along the twist mode, for the swinging-bridge motion we also cannot determine whether the crossings are real crossings or avoided crossings. Again, based on the arguments given in the previous section and by Truhlar and Mead[47] one can expect that conical intersections are present between the Q states located on the porphyrin ring and the lowest CT state as well as between the quinone excited $\pi-\pi^*$ state and the CT state. Owing to the similarity of the investigated swinging-bridge motion and twist motion, the state crossings occurring along both motions can in principle correspond to the same conical intersection seams. These conical intersections would clearly determine the ultrafast dynamics of the observed photoinitiated electron transfer in cpb-ZnPQ complexes.

One limitation of our calculations reported so far is that we performed gas-phase calculations, i.e., we calculated the excited states of the complex without taking interactions with the environment into account. To include solvent effects into our

calculations, Onsager's continuum solvent model[48] has been employed at the level of DFT/BLYP/6-31G* assuming a solute radius of the complex of 7 Å and a dielectric constant of $\epsilon = 2$ and $\epsilon = 9$. The first corresponds to the dielectric constant of *n*-hexane, while the second is the one of dichloromethane, which both have been used in experiments[26] and which can also be seen as values for a lower and upper bound for a dielectric constant of proteins. In the first case ($\epsilon = 2$), the CT excited state is stabilized by about 0.2 eV compared to the ground state and the other "neutral" excited states, while in the second case ($\epsilon = 9$) the CT state drops by about 0.43 eV. Thus, the charge-transfer states are strongly stabilized in polar media, for instance, solution or protein, which is due to their large static dipole moment of about 21 D compared to the electronic ground state with a static dipole moment of only 1.9 D at the theoretical level of DFT/BLYP/6-31G*. Taking solvent effects into account corroborates the importance of the low-lying charge-transfer excited state for the ultrafast kinetics of the observed long-range electron-transfer process in the cpb-ZnPQ complexes.

4. General Mechanism for Intermolecular Electron Transfer in Biological Systems

Based on our findings, it is very likely that photoinitiated long-range intermolecular electron transfer can be mediated by conical intersections. As we have seen, the energies of CT states are very sensitive to the distance between the electron acceptor and the electron donor owing to the strong electrostatic attraction between the separated charges in the CT state. In contrast, neutral valence-excited states like the $\pi-\pi^*$ excitations in our investigation do not experience this attraction, and are essentially unchanged along a donor—acceptor distance coordinate. Consequently, crossings between CT states and such neutral states occur naturally when the distance between the electron donor and acceptor is varied. This suggests a very general mechanism for ultrafast intermolecular electron transfer, which will be outlined in detail on the basis of the results found for the investigated cpb-ZnPQ complexes.

At the equilibrium geometry of the cpb-ZnPQ complex, the zincporphyrin and the quinone are separated by a sufficiently small intermolecular distance that the lowest porphyrin-to-quinone CT state is the lowest electronically excited state of the system, i.e., the CT state is slightly lower in energy than the Q states. However, even a small increase of the intermolecular separation, due to large-scale vibrational motions, leads to a change in the energetic order of the Q and CT state. Consequently, a crossing between the CT and the Q states must be present in the vicinity of the ground-state equilibrium geometry. In multidimensional systems, such crossings correspond most likely to conical intersections, which act as photochemical funnels and mediate the observed ultrafast ET process.

This scenario can be transferred to the long-range electron transfer in the photosynthetic reaction center, for which the complex without cyclophane bridges (Figure 3) used in section 3.1 may serve as a reasonable model. It can be assumed that the distance between the chlorophyll of the special pair and the adjacent quinones is such that the energy of a relevant CT state is only slightly above the Q states of the chlorophylls. Photoexcitation of the chlorophylls may lead to an excitation of large-scale motions in which the chlorophyll and quinone move toward each other, decreasing the molecular distance and the energy of the CT state relative to the Q state. Consequently, a crossing between Q and CT states occurs along this large-scale motion which ideally is a conical intersection, making

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ultrafast ET possible. In practice, it is difficult to experimentally identify relevant large-scale motions and, concomitantly, conical intersections in the photosynthetic reaction center due to the vast number of degrees of freedom. Our calculated potential energy curves, however, show a negative slope of the Q states along the twist mode (Figure 4), indicating that this large-scale motion will be excited and trigger the electron transfer. Since this outlined mechanism is very efficient and conical intersections are not rare in polyatomic systems, we suspect that they play determining roles for the molecular mechanism of long-range electron transfer in the photosynthetic reactions and other biological photoinitiated ET processes.

5. Brief Summary and Outlook

Upon photoexcitation of the Q states, cyclophane-bridged zincporphyrin−quinone complexes undergo ultrafast electron transfer within a few hundred femtoseconds. Using modern quantum chemical techniques, we have studied the molecular mechanism of this process. Two excited-state crossings between the Q states and an appropriate porphyrin-to-quinone CT state could be identified along two large-scale motions, a twist motion and a swinging-bridge motion. The crossings occur in the vicinity of the equilibrium geometry of the electronic ground state, and arguments are given that these are very likely conical intersections, which would provide very efficient electron-transfer pathways. It is our belief that the mechanism of photoinitiated long-range electron transfer via conical intersections plays important roles in biological photoinitiated ET processes and also for the design of artificial photoelectric devices.

In the future, our findings should be corroborated by further quantum chemical studies and one should aim at proving the occurring crossings to be conical intersections. The obtained potential energy surfaces should also be used in semiclassical and/or quantum dynamical simulations to calculate the kinetics and lifetimes of the ET process.

Supporting Information Available: Cartesian coordinates of the optimized structure of the cyclophane-bridged ZnPQ complex (right side of Figure 1). This material is available free of charge via the Internet at http://pubs.acs.org.

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