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Heterogeneous Electron-Transfer Dynamics through Dipole-Bridge Groups

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Abstract

Heterogeneous electron transfer (HET) between photoexcited molecules and colloidal TiO₂ has been investigated for a set of Zn-porphyrin chromophores attached to the semiconductor via linkers that allow to change level alignment by 200 meV by reorientation of the dipole moment. These unique dye molecules have been studied by femtosecond transient absorption spectroscopy in solution and adsorbed on the TiO₂ colloidal film in vacuum. In solution energy transfer from the excited chromophore to the dipole group has been identified as a slow relaxation pathway competing with S₂-S₁ internal conversion. On the film heterogeneous electron transfer occurred in 80 fs, much faster compared to all intramolecular pathways. Despite a difference of 200 meV in level alignment of the excited state with respect to the semiconductor conduction band, identical electron transfer times were measured for different linkers. The measurements are compared to a quantum-mechanical model that accounts for electronic-vibronic coupling and finite band width for the acceptor states. We conclude that HET occurs into a distribution of transition states that differs from regular surface states or bridge mediated states.

Graphical abstract

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Supporting Information Available: Absorption spectrum of the sensitized film. Detailed global fit and amplitude parameters for measurements in solution. Comparison of QY fluorescence measurements and S₁ fluorescence lifetimes. TA measurements of **2** on TiO₂ and expected difference in the TA signal attributed to electron injection. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

Keywords

Porphyrinoids; heterogeneous electron transfer; ultrafast transient absorption; TiO_2

Introduction

Heterogeneous electron transfer (HET) between molecular light-absorbers and semiconductor electrodes is an important process in solar energy conversion, optoelectronics, and photocatalysis. Despite the fact that related systems have been studied for decades, little is known about the details of the reaction and its dependence on the relevant parameters. Nonadiabatic HET depends mainly on two parameters: electronic coupling between donor molecule and acceptor states and the density of acceptor states. The first parameter has been studied by introducing different bridge-anchor groups between the donor molecule and the semiconductor.^{1–4} The second parameter, the Franck-Condon weighted density of states (FCWD) accounts for the accessible acceptor states weighted by Franck-Condon factors. The latter parameter has been investigated by comparing different substrates and different dyemolecules for varying the density of states (DOS) and the level alignment. Experimental results have been mostly discussed in terms of the steady-state density of surface and surface-defect states, level alignment, and Coulomb interaction and led to controversial conclusions. Several studies compared different metal-oxide electrodes and concluded that surface states are important for HET.⁵ The importance of electron-hole Coulomb interaction at the interface has been pointed out by Niemec et al. and Stockwell et al.^{6, 7} Strothkaemper et al. concluded from a multi-technique study that HET proceeds into surface states formed by the anchor group before charge separation occurs. However, the influence of Coulomb interactions could not be observed in this study.⁸ Time-resolved THz studies by Tiwana et al. pointed in the same direction and concluded that local binding, and orbital overlap of the sensitizer on the metal-oxide surface are the prevailing parameters.⁹

In the present study we investigate a unique HET system that comprises a dipole group in the linker and allows to change level alignment by reorientation of the linker. This method only requires minimal changes to the bridge group and no changes to the semiconductor or the anchor group. Previous studies showed that the change in dipole moment alters the level alignment by 200 meV at a ZnO (11–20) surface.^{10, 11} Our time-resolved measurements show that the change in level alignment has no influence on HET rates in contrast to the

general assumption that level alignment is a crucial parameter for HET. We conclude that the distribution of acceptor states cannot simply be extrapolated from the DOS of the electrode and the level alignment. Our results point in the same direction as recently published measurements that showed the formation of a transient electronic configuration that gives rise to a distribution of transition states.¹² They have two implications for applications: first, the transient configuration can present a bottle-neck for HET as discussed by Siefermann et al.¹² Second, it gives the opportunity to independently design a favorable chromophore and adjust the level alignment by introducing dipole groups that shift the donor level just above the conduction band edge and thus optimizes open circuit voltage for the respective chromophore without altering charge separation efficiency. A similar result has been presented recently.¹³

Experimental Section

Apparatus

Steady state absorption was measured with a UV-Vis fiber spectrometer. Steady state fluorescence spectra were recorded with a spectrofluorometer (Jobin-Yvon Fluoromax-4). Nanosecond fluorescence lifetimes were measured with a home-built time resolved fluorometer. The Pump-probe white-light transient absorption setup has been described earlier.¹⁴ Briefly, it employs the output of a home-built NOPA as the pump beam and the supercontinuum generated in a sapphire plate as the probe beam. The cross correlation of pump and probe beam was taken as the instrument response function (IRF) and was kept below 30 fs by means of prism pulse compressors. Pump and probe beams were respectively focused to 300 μm and 100 μm spot diameters resulting in a fluence of 320 $\mu\text{J cm}^{-2}$ for the pump beam. Polarization between pump and probe beam was set to magic angle and parallel for measurements in solution and on the film, respectively. Finally, single wavelength detection was performed using a monochromator and a lock-in amplifier. A detailed description of the setup and measurement procedure can be found in a previous publication.¹⁴

Sample Preparation

Structures of the studied compounds are shown in Figure 1a. All three are composed of a Zntetraphenyl-porphyrin (Zn-TPP) chromophore, a bridge group, and an anchor group. The bridge group in **2** is a phenyl ring, whereas in **1** and **3** it is a N,N-dimethyl-4-nitroaniline group. The three dyes are terminated by an isophthalic acid group (Ipa) as anchor. Recent publications have discussed the synthesis,¹⁰ as well as the electrochemical and steady state spectral properties of these dyes.¹⁵ Our experiments in solution were performed in spectroscopy grade solvents: diethyl ether (ether) and tetrahydrofuran (THF) from Fisher Scientific. Measurements on the semiconductor were done on nanoporous anatase TiO_2 films. To prepare the films, a colloidal TiO_2 solution was synthesized by a sol-gel technique described elsewhere.¹⁶ The solution was then cast onto 50 μm thin AF45 glass (Schott Displayglass) via the doctor-blade technique. For the sensitization, the TiO_2 films were first annealed in a furnace. Then, they were immersed in a 100 μM solution of the desired compound in THF. We minimized the sensitization time to 20 min and applied a thorough rinsing process to remove any unbound dye. This process was validated by measuring the

decrease of fluorescence from the film and the disappearance of fluorescence from the supernatant. After rinsing, the films were dried under Ar before being placed in a vacuum chamber. The chamber has a pair of 0.5 mm fused silica windows and was kept to 10^{-7} mbar. A detailed description of the procedure was previously reported.¹⁴ Minimizing the sensitization time prevents aggregation of Zn-porphyrin (Zn-P) derivatives on TiO_2 .¹⁷

Signal Analysis

Transient absorption signals at a specific wavelength (σ_λ) were fitted to the expression

$$\sigma_\lambda = \sum_{i=0}^n A_i^\lambda N_i(t), \quad (1)$$

where A_i^λ is the independent amplitude at each wavelength, and $N_i(t)$ is the population of each state. The n terms involved in equation (1) represent the states involved in the relaxation process. This parameter was kept at the minimum that allows fitting the signals at all wavelengths, using the same number of states, without a systematic deviation of the residuals. Thus, the signal at a given wavelength has a weighted contribution from the population of each state. The time dependent population of each state was obtained by solving a set of linear rate equations that allow parallel and sequential decays and represent the imposed relaxation model, i.e.

$$\dot{N}_0(t) = -Bg(t) + \sum_j \frac{1}{\tau_j} N_j(t), \quad (2)$$

$$\dot{N}_1(t) = Bg(t) - \sum_k \frac{1}{\tau_k} N_1(t), \quad (3)$$

$$\dot{N}_i(t) = \sum_j \frac{1}{\tau_j} N_j(t) - \sum_k \frac{1}{\tau_k} N_i(t). \quad (4)$$

In the last set of equations τ_j are the time constants associated to the $N_j \rightarrow N_i$ population transitions, whereas τ_k represent the $N \rightarrow N_k$ depopulation constants. The term $Bg(t)$ in (2) and (3) acts as a source term that represents the pump pulse and is composed of the amplitude B and the Gaussian envelope

$$g(t) = \exp \left[-4 \ln(2) \left(\frac{t - t_0}{W_{\text{IRF}}} \right)^2 \right]. \quad (5)$$

This function takes into account W_{IRF} as the width at half maximum of the IRF. Therefore, the main objective of the fitting procedure is to find a set of parameters $\{A_i^\lambda, \tau_i\}$ that produce the best global fit.

Results and Discussions

Steady state measurements

Steady-state absorption and fluorescence spectra at 10^{-5} M in THF together with the structure of the Zn-P compounds are shown in Figure 1. Absorption and emission of the compounds can be explained by the standard interpretation for porphyrin UV-vis absorption by a two-fold degenerate S_2 state (423 nm in THF), known as the Soret or B band, and weaker Q_1 (555 nm) and Q_0 (595 nm) bands.¹⁸ Except for a small shift that has been attributed to the phenyl linkers,^{19, 20} the spectra resemble those of Zn-tetraphenyl-porphyrin (Zn-TPP).^{21–23} Upon the addition of the N,N- dimethyl-4-nitroaniline group absorption and emission spectra changed slightly in the range of the Soret band. Absorption spectra on the film did not show any charge transfer band and only a small redshift and broadening by 3 nm and 5 nm for the Soret band (Figure S1), respectively, indicating moderate electronic coupling.³ No signatures of aggregate formation were observed in absorption spectra from solution or from the film.²⁴

UPS measurements by the Bartynski group showed that the nitroaniline group introduces a strong dipole moment that shifts the energy level alignment by 200 meV depending on its orientation where **1** is 100 meV higher in energy than **2** and 200 meV higher than **3** on a ZnO (11–20) surface.¹¹

Transient absorption measurements in solution

Knowledge of intramolecular photo-dynamics is a prerequisite for studying HET dynamics. Photodynamics of the Zn-TPP chromophore has been extensively investigated.^{21–23, 25–29} For comparison, we applied femtosecond transient absorption spectroscopy (TA) to reproduce the reported dynamics for commercial Zn-TPP.

The different relaxation processes are illustrated in the Jablonski diagram in Figure 2. Time constants are given in Table 1. Figure 3 shows TA traces for compounds **1–3** at the indicated probe wavelength after excitation of the Soret band at 420 nm. Transients have been measured at three different wavelength that contain signals from S_2 and S_1 excited state absorption (ESA), stimulated emission (SE) and from ground state bleach (GSB). Global fitting to an appropriate rate model at these wavelength allows to extract lifetimes for the individual states as has been reported earlier.¹⁴ Briefly, after Soret excitation the negative signal at 550 nm appears within our IRF; it is attributed to GSB in accordance with the steady state spectrum. The positive signals at 520 nm and 655 nm show rise times between 100 fs and 120 fs. These time constants are considered to originate from vibrational or higher excited state relaxation within S_2 . However, this assignment is still under debate and is subject to ongoing research.^{22, 30} The blue dashed line in Figure 3 includes relaxation processes in the S_2 state. The femtosecond relaxation is followed by internal conversion (IC) from S_2 to S_1 with about $\tau_2 = 1.5 \pm 0.1$ ps. This process appears as a positive contribution at

all wavelengths assigned to ESA (red dashed line in Figure 3). At 655 nm a 10 ps relaxation component followed by a slow relaxation (>500 ps) is observed. Measurements at 550 nm show a 100 ps component followed by a >500 ps process. At 520 nm only the slow process (>500 ps) is observed. The 10 ps and 100 ps processes have been assigned to vibrational relaxation (VR) within the S_1 state and are the subject of ongoing research.^{22, 31} The slowest component in our model was set to 1.8 ns, corresponding to the fluorescence lifetime. Relaxation processes within the S_1 band are combined in the red dotted line Figure 3. A detailed fit and corresponding fit parameters can be found in the supporting informations (SI).

Compared to Zn-TPP, **2** differs by the additional phenyl linker group and shows overall the same dynamics (Table 1). The time constant τ_2 is slightly faster compared to Zn-TPP in agreement with other meso-substituted Zn-TTPs.³² Previous measurements on similar substituted Zn-Ps showed that the photo-physics were not affected by functionalization of one of the mesophenyl groups.^{33, 34} On the other hand, compounds **1** and **3** showed different dynamics at 520 nm and 550 nm (Figure 3 blue shaded area at 520 nm) while the dynamics at 655 nm was almost identical to **2**. The wavelength dependence indicates that the respective process is coupled to the S_2 excited state since at 655 nm predominantly S_2 population is probed. This is also supported by TA measurements in solution after Q-band excitation that show identical dynamics for all three compounds at 520 nm (Figure 4). The UV-vis spectrum indicates that direct excitation of the nitroaniline group is very weak and not likely to be the reason for the change in dynamics. To confirm this we performed TA measurements under identical conditions on the bridge group alone (diphenyl-N,N-dimethyl-4-nitroaniline). The very weak absorption around 420 nm (Figure 5) required a 15 times higher concentration for achieving a comparable TA signal at 550 nm probe wavelength.

Therefore, direct excitation cannot account for the additional signal from **1** and **3** in Figure 3. As a side note, the dynamics of the weak TA signal from the nitroaniline group is similar to dynamics reported earlier for p-nitroanilin.³⁵ The next possible explanation is energy transfer from the Zn-P chromophore S_2 state to the excited state of the nitroaniline group. The spectral overlap shown in Figure 5 is favorable for energy transfer. Energy transfer from Zn-P should result in quenching of the fluorescence from the S_1 state. Steady-state fluorescence quantum yield (QY) measurements comparing QY from the three compounds showed that fluorescence is indeed quenched by 20% in **1** and **3** when compared to **2** (Figure S3). Fluorescence lifetime measurements confirmed that the lifetime of the S_1 state was not affected by the nitroaniline group. At the same time no difference in QY was detected after Q-band excitation. The 20% loss in QY corresponds to an energy transfer time of around 6 ps from the S_2 state to the bridge group. Energy transfer adds another pathway for de-exciting the S_2 state that is indicated as τ_D in Figure 6. By applying the corresponding model, the photodynamics of **1** and **3** can be fit globally by assuming an energy transfer time constant $\tau_D=3.5$ ps, a value that is in overall agreement with the fluorescence QY measurements. For the fit all time constants were kept constant while small adjustments to the amplitudes were necessary to account for changes in spectral weight. Fit parameters are summarized in Table S1 in the SI. This confirms that energy transfer accounts for the

difference in intramolecular photodynamics. To distinguish between Förster and Dexter energy transfer we calculated the expected Förster energy transfer time from the distance between chromophore and semiconductor surface and the overlap integral.³⁶ The resulting 200 ps are much longer than the observed 3–6 ps and indicate that Dexter energy transfer is the prevailing mechanism.

Transient absorption measurements on colloidal TiO₂ films in UHV

HET in the film can in principle occur from the S₁ and S₂ state. Energy transfer to the nitroaniline group is not expected to influence HET from the S₁ state. UPS measurements of the ground state level alignment combined with UV-Vis spectra indicated that the S₁ excited state is located around the Fermi level about 100 meV below the conduction band edge when absorbed on ZnO. Intrinsically n-doped ZnO single crystals and TiO₂ nanoparticles have similar band gap energies and Fermi level alignment. Hence, a similar molecular level alignment can be expected. Accordingly, no signature of fast HET can be observed in TA measurements after excitation of the Q-band. The fastest time constant for the decay of the S₁ state is around 9 ps (Figure 7a). This is at least one order of magnitude slower than expected when compared to systems with similar bridge groups.^{37–39} Therefore, we conclude that the S₁ excited state is located below the conduction band edge at the TiO₂ interface and the slow decay is likely governed by injection into defect trap states.⁴⁰ Several TA measurements on similar systems found fast HET by evaluating the rise time of the probe signal around 600 nm.^{38, 39} This assumption appears to be unreasonable in our case because the rise time resembles our instrument response function of 28 fs (Figure 7b). Sub-20 fs ET would be very fast considering the length of the linker group.¹ It should be noted that the previously published measurements were performed in a solvent environment while our measurements were performed in vacuum. Energy level alignment deduced from electrochemical measurements in solvent environment was different for these measurements when compared to level alignment measured by the Bartynski group via UPS in UHV.¹¹

Comparison between the three compounds on the TiO₂ film after Soret excitation is complicated by the interaction between the Zn-TPP chromophore and the nitroaniline group because it cannot be excluded that the excited state of the nitroaniline group is involved in the HET process for **1** and **3**. Indeed, TA traces for the three compounds at 520 nm and 620 nm when attached to colloidal anatase TiO₂ show that the dynamics of **2** differs slightly from that of **1** and **3** (Figure S5, and Figure S6) while **1** and **3** show almost identical dynamics. A fit with a model that includes the HET process shown in Figure 8 results in an initial decay of 80 ± 7 fs for all three compounds (Figure 9, S5, S6). Fit parameters for **1** and **3** are given in Table S2 in the SI. We assign the fast decay of the excited state absorption to electron injection into TiO₂. This is also supported by photocurrent measurements that clearly show electron injection from **1**, **2**, and **3** into TiO₂,¹⁵ and by efficient fluorescence quenching.³⁴ This injection time agrees well with measurements on similar systems.^{37,39} It is clearly faster than the 1.5 ps S₂-S₁ IC measured in solution (cf. Figure 3). The decaying signal on the ps time scale has previously been attributed to transient absorption from the cation for compounds similar to **2** and can be fitted with similar time constants that have been reported previously.^{38, 39} The difference in the ps dynamics between **1/3** and **2** is not

easy to explain. The energy transfer on the 3.5 ps time scale should be negligible when competing with 80 fs HET. On the other hand, the LUMO of the nitroaniline group is near resonance with the excited state and can influence coupling to the electrode. The cation spectrum and dynamics of the di-phenyl nitroaniline group are not known and are hard to measure because of the weak transition dipole moment and since the concentration of the chromophore in the film can not easily be increased. Therefore, we will focus our discussion on the comparison between the compounds **1** and **3** that show the largest difference in level alignment (200 meV) and at the same time identical HET dynamics. It should be noted that the dipole induced level shift of 200 meV was measured on a ZnO single crystal surface while our time-resolved measurements were performed on colloidal TiO₂. The binding geometry of the molecule on the surface is another important aspect that can influence the injection pathway and the projection of the dipole moment. IR-spectroscopy suggests a chelating or bidentate bond of the anchor group to TiO₂ that would support an upright binding geometry.³⁴ In addition, previous measurements showed that through-space electron injection in general is slow and does not compete with through-bond injection in systems with injection times below 100 fs.^{37, 41, 42} Therefore, we assume that electron transfer occurs predominantly through the bond. Under this assumption the relevant parameter is the dipole moment projected onto the molecular axis which is independent of the binding angle of the molecule.

The independence of HET dynamics on level alignment is the main result of this paper. A simple approximation for non-adiabatic HET rates k_{ET} is given by a Fermi-Golden rule expression:

$$k_{ET} = \frac{2\pi}{\hbar} |V_{ke}|^2 FCWD \quad (6)$$

The Frank-Condon weighted density of states *FCWD* is a sum over all possible donor/acceptor combinations weighted by the respective Franck-Condon factor. In the so called wide-band-limit the band of acceptor states in the semiconductor is wide enough and the donor level is sufficiently above the lower band edge such that the whole ET spectrum can be accommodated. In this case the FCWD is reduced to a pure DOS. Ramakrishna, Willig, and May developed a parametrized fully quantum mechanical model for HET that includes an electronic-vibrational quasi continuum and allows to compare HET dynamics function of crucial parameters like level alignment, reorganization energy, and electronic coupling V_{ke} .⁴³ Two of the cases that were compared in their work used parameters that are very close to systems **1** and **3** investigated here. The excited states were located 0.5 eV and 0.7 eV above the edge of a 1.4 eV wide band of acceptor states with constant DOS. A reorganization energy of 200 meV and a constant electronic coupling that gave rise to an electron transfer time of 84 fs in the wide band limit were assumed. The calculations showed that even in case of constant DOS and constant coupling strength HET times differ by about 18 fs, between 90 fs for 0.7 eV and 108 fs for 0.5 eV (fits to Figure 3 in Ref. 43). Comparison of fits with fixed injection times (62 fs and 98 fs) show that even in this case an energy dependent injection time can be resolved by our measurement (Figure S7). This difference would increase if one of the parameters showed energy dependence. It is known

that the DOS of the TiO₂ anatase (101) surface shows a steep rise close to the CB edge.² On the other hand, calculations suggest that the coupling strength does not depend strongly on the energy.⁴ The special case where the energy dependence of the coupling is assumed to compensate the change in DOS exactly can not be excluded. However, considering our previous results this situation is not very likely.¹⁴

The fact that our measurements show identical HET times for both molecules can be explained by assuming a strong modulation of electronic coupling that favors acceptor states in resonance with the donor state or a strongly modulated transient DOS that is much narrower than the steady-state surface density of states. Both cases result in the same situation where the donor state only couples to a narrow band of acceptor states that makes HET virtually independent of level alignment. The distribution or density of these “active” acceptor states has not been observed in any steady-state measurements or calculations. It can be assumed to be governed by the formation of the excited state that leads to a transient electronic configuration. This electronic configuration determines the density of active acceptor states. However, restricting the donor acceptor coupling to only a few states contradicts the non-adiabatic picture of HET because narrowing the band of acceptor states would require increasing the electronic coupling in order to keep the HET time constant. The electronic coupling in the above mentioned example was already around 8 meV. A considerably narrower band would require a much stronger electronic coupling, leading to a higher Landau-Zenner transition probability and, consequently, render the application of a non-adiabatic model questionable. It is interesting to note that our result coincides with recent measurements of inter- and intra-molecular photoinduced charge transfer reactions in molecular systems that show ET rates that are independent of the driving force in the inverted region.^{44, 45}

From our measurements we conclude that the distribution of acceptor states cannot be deduced from parameters like the surface density of states and the electronic coupling alone. The discrepancy can be explained by the formation of a transient transition state during the first tens of femtosecond of the reaction that is different from permanent surface or defect states found from equilibrium calculations. This short lived configuration is generated by the strong perturbation due to the excitation of the electron, and governs the density of acceptor states and consequently HET dynamics. Our conclusions are supported by previous measurements from our group,¹⁴ and by other recent experiments. For example, Racke et al. found a new hybridized interfacial density of states that fundamentally alters carrier dynamics and changes the electronic structure.⁴⁶ While, Siefermann et al. used femtosecond XPS to study HET and found strong indications for the formation of a transient electronic configuration.¹²

Conclusions

We have investigated photo-dynamics and electron transfer dynamics of a set of Zn-TPP derivatives with variable dipole moment in the bridge group. Intramolecular photo-dynamics resembled the well known dynamics of the Zn-TPP chromophore. The dipole carrying nitroaniline group gave rise to Dexter energy transfer from the excited state of the Zn-P chromophore. Surprisingly, on the film the two derivatives with opposite dipole moments

that resulted in a shift of 200 meV in level alignment showed identical HET dynamics. We compared the dynamics with a previously published quantum mechanical model for non-adiabatic HET and find strong indications that the dye molecules couple to a much smaller subset of acceptor states than expected from the electrode's surface density of states. Future work involving different chromophores, different dipole groups with possibly stronger dipole moments, and different semiconductor substrates will show if this is a general property of HET systems or specific to the combination that was under investigation.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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References

- Ernstorfer R, Gundlach L, Felber S, Storck W, Eichberger R, Willig F. Role of Molecular Anchor Groups in Molecule-to-Semiconductor Electron Transfer. *J. Phys. Chem. B.* 2006; 110:25383–25391. PMID: 17165985. [PubMed: 17165985]
- Persson P, Lundqvist MJ, Ernstorfer R, Goddard WA III, Willig F. Quantum Chemical Calculations of the Influence of Anchor-Cum-Spacer Groups on Femtosecond Electron Transfer Times in Dye-Sensitized Semiconductor Nanocrystals. *J. Chem. Theory Comput.* 2006; 2:441. [PubMed: 26626531]
- Wang L, Ernstorfer R, Willig F, May V. Absorption Spectra Related to Heterogeneous Electron Transfer Reactions: The Perylene TiO₂ System. *J. Phys. Chem. B.* 2005; 109:9589–9595. PMID: 16852154. [PubMed: 16852154]
- Li J, Wang H, Persson P, Thoss M. Photoinduced Electron Transfer Processes in Dye-Semiconductor Systems with Different Spacer Groups. *J. Chem. Phys.* 2012; 137:22A529.
- Katoh R, Furube A, Yoshihara T, Hara K, Fujihashi G, Takano S, Murata S, Arakawa H, Tachiya M. Efficiencies of Electron Injection from Excited N3 Dye into Nanocrystalline Semiconductor (ZrO₂, TiO₂, ZnO, Nb₂O₅, SnO₂, In₂O₃) Films. *J. Phys. Chem. B.* 2004; 108:4818–4822.
- Niemec H, Rochford J, Taratula O, Galoppini E, Kužel P, Polívka T, Yartsev A, Sundström V. Influence of the Electron-Cation Interaction on Electron Mobility in Dye-Sensitized ZnO and TiO₂ Nanocrystals: A Study Using Ultrafast Terahertz Spectroscopy. *Phys. Rev. Lett.* 2010; 104:197401. [PubMed: 20866996]
- Stockwell D, Yang Y, Huang J, Anuso C, Huang Z, Lian T. Comparison of Electron-Transfer Dynamics from Coumarin 343 to TiO₂, SnO₂, and ZnO Nanocrystalline Thin Films: Role of Interface-Bound Charge-Separated Pairs. *J. Phys. Chem. C.* 2010; 114:6560–6566.
- Strothkämper C, Bartelt A, Sippel P, Hannappel T, Schütz R, Eichberger R. Delayed Electron Transfer through Interface States in Hybrid ZnO/Organic-Dye Nanostructures. *J. Phys. Chem. C.* 2013; 117:17901–17908.
- Tiwana P, Docampo P, Johnston MB, Snaith HJ, Herz LM. Electron Mobility and Injection Dynamics in Mesoporous ZnO, SnO₂, and TiO₂ Films Used in Dye-Sensitized Solar Cells. *ACS Nano.* 2011; 5:5158–5166. PMID: 21595483. [PubMed: 21595483]
- Chitre K, Batarseh A, Kopecky A, Fan H, Tang H, Lalancette R, Bartynski RA, Galoppini E. Synthesis of Zinc Tetraphenylporphyrin Rigid Rods with a Built-In Dipole. *J. Phys. Chem. B.* 2015; 119:7522–7530. PMID: 25626725.

11. Rangan S, Batarseh A, Chitre KP, Kopecky A, Galoppini E, Bartynski RA. Tuning Energy Level Alignment At Organic/Semiconductor Interfaces Using a Built-In Dipole in Chromophore-BridgeAnchor Compounds. *J. Phys. Chem. C*. 2014; 118:12923–12928.
12. Siefermann KR, Pemmaraju CD, Nepl S, Shavorskiy A, Cordones AA, Vura-Weis J, Slaughter DS, Sturm FP, Weise F, Bluhm H, et al. Atomic-Scale Perspective of Ultrafast Charge Transfer at a Dye-Semiconductor Interface. *J. Phys. Chem. Lett.* 2014; 5:2753–2759. [PubMed: 26277975]
13. Hu K, Robson KCD, Beauvilliers EE, Schott E, Zarate X, Arratia-Perez R, Berlinguette CP, Meyer GJ. Intramolecular and Lateral Intermolecular Hole Transfer at the Sensitized TiO₂ Interface. *J. Am. Chem. Soc.* 2014; 136:1034–1046. PMID: 24367914. [PubMed: 24367914]
14. Nieto-Pescador J, Abraham B, Pistner AJ, Rosenthal J, Gundlach L. Electronic State Dependence of Heterogeneous Electron Transfer: Injection from the S₁ and S₂ State of Phlorin into TiO₂. *Phys. Chem. Chem. Phys.* 2015; 17:7914–7923. [PubMed: 25721314]
15. Ngo KT, Rochford J, Fan H, Batarseh A, Chitre K, Rangan S, Bartynski RA, Galoppini E. Photo-electrochemical Properties of Porphyrin Dyes with a Molecular Dipole in the Linker. *Farad. Discuss.* 2015
16. Rochford J, Chu D, Hagfeldt A, Galoppini E. Tetrachelate Porphyrin Chromophores for Metal Oxide Semiconductor Sensitization: Effect of the Spacer Length and Anchoring Group Position. *J. Am. Chem. Soc.* 2007; 129:4655–4665. PMID: 17385856. [PubMed: 17385856]
17. Ye S, Kathiravan A, Hayashi H, Tong Y, Infahsaeng Y, Chabera P, Pascher T, Yartsev AP, Isoda S, Imahori H, et al. Role of Adsorption Structures of Zn-Porphyrin on TiO₂ in Dye-Sensitized Solar Cells Studied by Sum Frequency Generation Vibrational Spectroscopy and Ultrafast Spectroscopy. *J. Phys. Chem. C*. 2013; 117:6066–6080.
18. Baerends E, Ricciardi G, Rosa A, van Gisbergen S. A DFT/TDDFT Interpretation of the Ground and Excited States of Porphyrin and Porphyrazine Complexes. *Coord. Chem. Rev.* 2002; 230:5–27.
19. Rochford J, Galoppini E. Zinc(II) Tetraarylporphyrins Anchored to TiO₂, ZnO, and ZrO₂ Nanoparticle Films through Rigid-Rod Linkers. *Langmuir*. 2008; 24:5366–5374. PMID: 18410135. [PubMed: 18410135]
20. Lin C-Y, Lo C-F, Luo L, Lu H-P, Hung C-S, Diao EW-G. Design and Characterization of Novel Porphyrins with Oligo(phenylethynyl) Links of Varied Length for Dye-Sensitized Solar Cells: Synthesis and Optical, Electrochemical, and Photovoltaic Investigation. *J. Phys. Chem. C*. 2009; 113:755–764.
21. Yu H-Z, Baskin JS, Zewail AH. Ultrafast Dynamics of Porphyrins in the Condensed Phase: II. Zinc Tetraphenylporphyrin. *J. Phys. Chem. A*. 2002; 106:9845–9854.
22. Kullmann M, Hipke A, Nuernberger P, Bruhn T, Gotz DCG, Sekita M, Guldi DM, Bringmann G, Brixner T. Ultrafast Exciton Dynamics after Soret- or Q-band Excitation of a Directly β,β' -linked Bisporphyrin. *Phys. Chem. Chem. Phys.* 2012; 14:8038–8050. [PubMed: 22549252]
23. Lukaszewicz A, Karolczak J, Kowalska D, Maciejewski A, Ziolek M, Steer RP. Photophysical Processes in Electronic States of Zinc Tetraphenyl Porphyrin Accessed on One- and Two-Photon Excitation in the Soret Region. *Chem. Phys.* 2007; 331:359–372.
24. Li Y, Steer RP. Kinetics of Disaggregation of a Non-Covalent Zinc Tetraphenylporphyrin Dimer in Solution. *Chem. Phys. Lett.* 2003; 373:94–99.
25. Chosrowjan H, Taniguchi S, Okada T, Takagi S, Arai T, Tokumam K. Electron Transfer Quenching of S₂ State Fluorescence of Zn-Tetraphenylporphyrin. *Chem. Phys. Lett.* 1995; 242:644–649.
26. Andersson M, Davidsson J, Hammarstrom L, Korppi-Tommola J, Peltola T. Photoinduced Electron Transfer Reactions in a PorphyrinViologen Complex: Observation of S₂ to S₁ Relaxation and Electron Transfer from the S₂ State. *J. Phys. Chem. B*. 1999; 103:3258–3262.
27. Kumble R, Palese S, Lin VS-Y, Therien MJ, Hochstrasser RM. Ultrafast Dynamics of Highly Conjugated Porphyrin Arrays. *J. Am. Chem. Soc.* 1998; 120:11489–11498.
28. Gurzadyan GG, Tran-Thi T-H, Gustavsson T. Time-resolved Fluorescence Spectroscopy of High-Lying Electronic States of Zn-tetraphenylporphyrin. *J. Chem. Phys.* 1998; 108:385–388.
29. Enescu M, Steenkeste K, Tfibel F, Fontaine-Aupart M-P. Femtosecond Relaxation Processes from Upper Excited States of Tetrakis(N-methyl-4-pyridyl) Porphyrins Studied by Transient Absorption Spectroscopy. *Phys. Chem. Chem. Phys.* 2002; 4:6092–6099.

30. Liang Y, Bradler M, Klinger M, Schalk O, Balaban MC, Balaban TS, Riedle E, Unterreiner A-N. Ultrafast Dynamics of meso-Tetraphenylmetalloporphyrins: The Role of Dark States. *ChemPlusChem*. 2013; 78:1244–1251.
31. Moravec DB, Lovaasen BM, Hopkins MD. Near-infrared Transient-absorption Spectroscopy of Zinc Tetraphenylporphyrin and Related Compounds. Observation of Bands that Selectively Probe the S_1 Excited State. *J. Photochem. Photobiol. A*. 2013; 254:20–24.
32. Lin C-Y, Lo C-F, Luo L, Lu H-P, Hung C-S, Diao EW-G. Design and Characterization of Novel Porphyrins with Oligo(phenylethynyl) Links of Varied Length for Dye-Sensitized Solar Cells: Synthesis and Optical, Electrochemical, and Photovoltaic Investigation. *J. Phys. Chem. C*. 2009; 113:755–764.
33. Rangan S, Coh S, Bartynski RA, Chitre KP, Galoppini E, Jaye C, Fischer D. Energy Alignment, Molecular Packing, and Electronic Pathways: Zinc(II) Tetraphenylporphyrin Derivatives Adsorbed on $TiO_2(110)$ and $ZnO(110)$ Surfaces. *J. Phys. Chem. C*. 2012; 116:23921–23930.
34. Rochford J, Galoppini E. Zinc(II) Tetraarylporphyrins Anchored to TiO_2 , ZnO , and ZrO_2 Nanoparticle Films through Rigid-Rod Linkers. *Langmuir*. 2008; 24:5366–5374. PMID: 18410135. [PubMed: 18410135]
35. Thomsen CL, Thøgersen J, Keiding SR. Ultrafast Charge-Transfer Dynamics: Studies of p-Nitroaniline in Water and Dioxane. *J. Phys. Chem. A*. 1998; 102:1062–1067.
36. Langlois A, Harvey PD. Maple-assisted Calculations of the J-integral: a Key Parameter for the Understanding of Excited State Energy Transfer in Porphyrins and other Chromophores. *JPP*. 2014; 18:666–674.
37. Gundlach L, Ernstorfer R, Willig F. Pathway-Dependent Electron Transfer for Rod-Shaped Perylene-Derived Molecules Adsorbed in Nanometer-Size TiO_2 Cavities. *J. Phys. Chem. C*. 2007; 111:13586–13594.
38. Imahori H, Kang S, Hayashi H, Haruta M, Kurata H, Isoda S, Canton SE, Infahsaeng Y, Kathiravan A, Pascher T, et al. Photoinduced Charge Carrier Dynamics of ZnPorphyrin/ TiO_2 Electrodes: The Key Role of Charge Recombination for Solar Cell Performance. *J. Phys. Chem. A*. 2011; 115:3679–3690. [PubMed: 20961148]
39. Chang C-W, Luo L, Chou C-K, Lo C-F, Lin C-Y, Hung C-S, Lee Y-P, Diao EW-G. Femtosecond Transient Absorption of Zinc Porphyrins with Oligo(phenylethynyl) Linkers in Solution and on TiO_2 Films. *J. Phys. Chem. C*. 2009; 113:11524–11531.
40. Myahkostupov M, Pagba CV, Gundlach L, Piotrowiak P. Vibrational State Dependence of Interfacial Electron Transfer: Hot Electron Injection from the S_1 State of Azulene into TiO_2 Nanoparticles. *J. Phys. Chem. C*. 2013; 117:20485–20493.
41. Gundlach L, Ernstorfer R, Willig F. Ultrafast Interfacial Electron Transfer from the Excited State of Anchored Molecules into a Semiconductor. *Prog. Surf. Sci.* 2007; 82:355–377.
42. Imahori H, Kang S, Hayashi H, Haruta M, Kurata H, Isoda S, Canton SE, Infahsaeng Y, Kathiravan A, Pascher T, et al. Photoinduced Charge Carrier Dynamics of Zn-Porphyrin- TiO_2 Electrodes: The Key Role of Charge Recombination for Solar Cell Performance. *J. Phys. Chem. A*. 2011; 115:3679–3690. [PubMed: 20961148]
43. Ramakrishna S, Willig F, May V. Theory of Ultrafast Photoinduced Heterogeneous Electron Transfer: Decay of Vibrational Coherence into a Finite Electron-icvibrational Quasicontinuum. *J. Chem. Phys.* 2001; 115:2743–2756.
44. Koch M, Rosspeintner A, Adamczyk K, Lang B, Dreyer J, Nibbering ETJ, Vauthey E. Real-Time Observation of the Formation of Excited Radical Ions in Bimolecular Photoinduced Charge Separation: Absence of the Marcus Inverted Region Explained. *J. Am. Chem. Soc.* 2013; 135:9843–9848. PMID: 23750737. [PubMed: 23750737]
45. Petersson J, Hammarström L. Ultrafast Electron Transfer Dynamics in a Series of Porphyrin/Viologen Complexes: Involvement of Electronically Excited Radical Pair Products. *J. Phys. Chem. B*. 2015; 119:7531–7540. PMID: 25766332. [PubMed: 25766332]
46. Racke DA, Kelly LL, Kim H, Schulz P, Sigdel A, Berry JJ, Graham S, Nordlund D, Monti OLA. Disrupted Attosecond Charge Carrier Delocalization at a Hybrid Organic/Inorganic Semiconductor Interface. *J. Phys. Chem. Lett.* 2015; 6:1935–1941. [PubMed: 26263273]

Figure 1.
UV-Vis spectrum and structure of the three Zn-porphyrin derivatives.

Figure 2.
Jablonski diagram showing the well-known intramolecular photodynamics of Zn-TTP.
Values for Zn-TTP and **2** are given in Table 1

Figure 3.

Transient absorption at the indicated wavelength of the three compounds in ether after Soret excitation. The global fit and its decomposition into contributions from individual states is indicated. The difference in dynamics between the compounds **1** and **3** and compound **2** is indicated for 520 nm probe wavelength by the blue shaded area.

Figure 4.
Transient absorption of the studied compounds after Q band excitation.

Figure 5.
Molar absorptivity of the nitroaniline linker and S₂ fluorescence of Zn-TPP.

Figure 6. Jablonski diagram including energy transfer from the S_2 state of Zn-TTP to the nitroaniline group.

Figure 7.

Transient absorption signal from solution (a) offset for visibility and from the film for compound 2 (b) after Q-band excitation. The 9 ps fit to the decay is included in (a). Rising edge of the signal together with the instrument response function (IRF) and a fit with 20 fs rise time.

Figure 8. Jablonski diagram for **1** and **3** on the TiO_2 film including HET. The energy axis is not to scale.

Figure 9.

Transient absorption signal from the film after Soret-band excitation for two different time intervals.

Summary of time constants (τ_i) of the absorption kinetics of the studied compounds. Amplitudes are given in the supplementary documentation (Table SI).

Table 1

System	τ_1 (fs)	τ_2 (ps)	τ_3 (ps)	τ_4 (ps)	τ_5 (ns)
Zn-TTPP	120	—	1.8	10	100
2	120	—	1.5	10	100
1/3	110	3.5	1.5	10	100

^aThe energy transfer process (τ_D) is present only in **1** and **3**, cf. Figure 5.