SINGLE-MOLECULE INTERFACIAL ELECTRON TRANSFER DYNAMICS IN SOLAR ENERGY CONVERSION

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A Dissertation

Submitted to the Graduate College of Bowling Green State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

December 2016

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This dissertation work investigated the parameters affecting the interfacial electron transfer (ET) dynamics in dye–semiconductor nanoparticles (NPs) system by using single-molecule fluorescence spectroscopy and imaging combined with electrochemistry. The influence of the molecule–substrate electronic coupling, the molecular structure, binding geometry on the surface and the molecule-attachment surface chemistry on interfacial charge transfer processes was studied on zinc porphyrin–TiO$_2$ NP systems. The fluorescence blinking measurement on TiO$_2$ NP demonstrated that electronic coupling regulates dynamics of charge transfer processes at the interface depending on the conformation of molecule on the surface. Moreover, semiconductor surface charge induced electronic coupling of molecule which is electrostatically adsorbed on the semiconductor surface also predominantly alters the ET dynamics.

Furthermore, interfacial electric field and electron accepting state density dependent ET dynamics has been dissected in zinc porphyrin–TiO$_2$ NP system by observing the single-molecule fluorescence blinking dynamics and fluorescence lifetime with and without applied bias. The significant difference in fluorescence fluctuation and lifetime suggested the modulation of charge transfer dynamics at the interface with external electric field perturbation. Quasi-continuous distribution of fluorescence intensity with applied negative potential was attributed to the faster charge recombination due to reduced density of electron accepting states.
The driving force and electron accepting state density ET dependent dynamics has also been probed in zinc porphyrin–TiO$_2$ NP and zinc porphyrin–indium tin oxide (ITO) systems. Study of a molecule adsorbed on two different semiconductors (ITO and TiO$_2$), with large difference in electron densities and distinct driving forces, allows us to observe the changes in rates of back electron transfer process reflected by the suppressed fluorescence blinking of molecule on ITO surface.

Finally, the electric field effect on the interface properties has been probed by using surface-enhanced Raman spectroscopy and supported by density functional theory calculations in alizarin–TiO$_2$ system. The perturbation, created by the external potential, has been observed to cause a shift and/or splitting interfacial bond vibrational mode, typical indicator of the coupling energy changes between alizarin and TiO$_2$. Such splitting provides evidence for electric field-dependent electronic coupling changes that have a significant impact on the interfacial electron transfer dynamics.
To my beloved family and friends
ACKNOWLEDGMENTS

To all who have made this work possible and enjoyable, I express my deepest gratitude:

Dr. H. Peter Lu, my research advisor, for being a constant source of ideas, support, and inspiration, a generous PI and a caring person throughout all these years.

The Bowling Green State University (BGSU) Department of Chemistry and Center for Photochemical Sciences and the Office of Basic Energy Sciences within the Office of Science of the U.S. Department of Energy (DOE) for funding.

Dr. Ksenija D. Glusac, Dr. Alexey T. Zayak, and Dr. Yu Zhou, my dissertation committee members, for their valuable time. I also thank Prof. Zayak for stimulating discussions on computational modeling.

Dr. Wilson Ho, Professor at University of California, Irvine Department of Physics and Chemistry for the collaboration. Thanks to Shaowei Li and Arthur Yu for experimental support.

Dr. Vishal Govind Rao for all the techniques, ideas, and everything he taught me about research and life. Thank you isn’t enough for all that Dr. Rao has done for me.

All the present and past group members; especially Dr. Yufan He for his helpfulness and teaching; Dr. Papatya C. Sevinç for initial training, Min Gu, Dr. Dibeyndu K. Sasmal, Dr. Nibedita Pal, Dr. Rajeev Yadav, Dr. Maolin Lu, Achut Silwal, Meiling Wu, and Susovan Roy Chowdhury for their friendship and support.

Nora Cassidy, Alita Frater and Hilda E. Miranda (Administration), Charles Codding (Machine shop), and Doug Martin (Electronic shop) for help.

All the Bowling Green Nepalese community; especially Usha Pandey Kadel, Dr. Gokul Kadel and Vijaya Shrestha for helping and caring me like a family member.
My doctoral work and its culmination would not have been possible without the encouragement, love and support from my family.
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CHAPTER 1. INTRODUCTION

This chapter is dedicated to the basic concepts and theories of electron transfer processes and the factors affecting electron dynamics in the molecule–semiconductor systems.

1.1. Electron Transfer

Electron transfer (ET) is defined as a rapid process in which an electron transfers from one chemical species (electron donor) to another (electron acceptor) mostly without breaking and forming the bond.\textsuperscript{1-3} It is ubiquitous in biological, physical, inorganic, and organic chemical systems.\textsuperscript{4-15}

Electron transfer process can initiate both from the ground state and the excited state of the molecule. The driving force for the ground state ET process is basically the decrease in the electrical potential of the electron donor (D) and acceptor (A) molecules. Electron transfer from excited state involves the absorption of light and subsequent promotion of an electron from the ground state, most likely singlet state (S\textsubscript{0}), to the singlet excited states (the spin selection rule). The photoexcitation process gives rise to an unstable molecule with the absorption of a photon. The excited molecule then follows various radiative and non-radiative relaxation pathways. The energy levels involved in excitation and relaxation processes are usually depicted in a Jablonsky diagram. In Figure 1.1, the electronic ground state and first and second excited singlet states are designated as S\textsubscript{0}, S\textsubscript{1}, and S\textsubscript{2}, respectively. The thin horizontal lines represent vibronic levels, involving in addition to electronic and vibrational excitation. Transitions between the levels are depicted as vertical arrows, straight ones involving radiative transitions, wavy ones involving nonradiative transitions. From the ground state S\textsubscript{0} a molecule can absorb a photon, leading to an excited state, for example S\textsubscript{2}. Usually, excitation from a higher vibronic state is followed by fast
(typical time scale: $\sim 10^{-12}$ s) nonradiative relaxation to the lowest vibrational level of $S_1$, a process called internal conversion (IC), leading to the generation of heat.

**Figure 1.1.** The simplified Jablonski diagram representing the photophysical processes that an excited molecule can undergo. D, donor; A, acceptor; Abs, absorption; ET, electron transfer; Fl, fluorescence; IC, internal conversion; ISC, intersystem crossing; Ph, phosphorescence.

From $S_1$, the excited molecule can usually relax to the ground state in one of the various ways. (1) The molecule can return to the ground state while emitting a photon, fluorescence (fl, $\sim 10^{-9}$ s). (2) The molecule can lose its excitation energy via internal conversion, without emitting a photon (IC, $\sim 10^{-8}$ s). (3) The molecule can transfer an electron (ET, $\sim 10^{-15}$ s). Finally, (4) the electrons in the molecule can undergo a spin conversion to a triplet state, a process called intersystem crossing (ISC, $\sim 10^{-8}$ s). The resulting triplet state ($T_1$) can decay to the ground state in a radiationless way via internal conversion or while emitting a photon, phosphorescence, which usually takes place on a much longer time scale than fluorescence ($\sim 10^{-6}$ s), since it involves a spin-forbidden transition. The time scales mentioned are typical values and vary substantially among different molecules and can also depend on the molecular environment.
However, in order for ET to take place, it should compete with the other radiative and non-radiative deactivation processes including radiative decay to the fluorescence, non-radiative internal conversion (IC), and inter-system crossing (ISC).\textsuperscript{16}

Both ground and the excited state ET can be explained using Marcus theory.\textsuperscript{1,2,6,9,17-26}

1.1.1. Marcus Theory of Electron Transfer

According to classical Marcus theory, ET rate between a discrete donor and acceptor states in solution can be described in terms of standard Arrhenius relationship:\textsuperscript{2,27-29}

\[
k_{ET} = \nu_N \kappa_E \exp \left( -\frac{\Delta G^\ddagger}{k_B T} \right)
\]

(1.1)

where \(\nu_N\) is the nuclear frequency factor, \(\kappa_E\) is the electronic transmission factor, \(k_B\) is the Boltzmann constant, and \(T\) is the temperature. The activation barrier (\(\Delta G^\ddagger\)) is related to the free energy change for the ET event or reaction driving force, \(\Delta G^0\), and the total nuclear reorganization energy, \(\lambda\), which is the sum of both inner (molecular) and the outer (solvent) reorganization energy, as:\textsuperscript{15}

\[
\Delta G^\ddagger = \frac{1}{4\lambda} (\Delta G^0 + \lambda)^2
\]

(1.2)

This equation suggests that for a reaction with the constant nuclear reorganization energy and the electronic transmission coefficient, the plot is a bell-shaped curve with the features as shown in Figure 1.2:

a) When \(\lambda > -\Delta G^0\), the process is thermally activated and the ET rate increases with the increasing driving force. This is known as normal region.

b) When \(\lambda = -\Delta G^0\) implies for the barrierless ET, meaning that the change in the driving force does not affect the ET rate, so called as optimal region. In this case, maximum value of rate constant of ET is obtained.
c) When $\lambda < -\Delta G^0$, the ET rate decreases with the increasing driving force, which is termed as the inverted region.\textsuperscript{15,30}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{The schematic representation of the normal, barrierless, and inverted Marcus regions in terms of potential energy surfaces of donor (D) and acceptor (A). $\lambda$, reorganization energy; $\Delta G^\ddagger$, activation energy; $\Delta G^0$, free energy of reaction.}
\end{figure}

The electronic transmission factor, $\kappa_E$, is related to the probability of ET to occur and is given by Landau-Zener coefficient for curve crossing:\textsuperscript{2,27,31}

\begin{equation}
\kappa_E = \frac{2P_0}{1 + P_0} \quad P_0 = -\exp \left[ -\frac{|H_{if}|^2}{\hbar \nu N \sqrt{\lambda k_B T}} \right] \tag{1.3}
\end{equation}

where $|H_{if}|$ is the electronic coupling matrix element which decreases exponentially with the increasing distance between D and A. Additionally, in the case of bridging ligand, this term can be written as a second order perturbation expression including the donor-bridge and bridge-acceptor couplings.\textsuperscript{32} Depending on the electronic coupling strength between the donor and acceptor states, the ET can occur either adiabatically or non-adiabatically (Figure 1.3).
Figure 1.3. The schematic representation of non-adiabatic and adiabatic potential energy surfaces.

(a) In an adiabatic process (strong coupling limit), $|H_{if}|$ is large, thus, $\kappa_E \cong 1$;

$$k_{ET} = \nu_N \exp \left( - \frac{\Delta G^\pm}{k_B T} \right)$$

(1.4)

In this limit, the activation barrier may be largely modified by coupling. In the case of a small barrier ($\Delta G^\pm \ll k_B T$), the reaction rate may be directly determined by the effective nuclear frequency $\nu_N$, which in some cases can be the solvation time. The curves of the two states form a continuum which allows electron to cross barrier smoothly.$^{2,15,33}$

(b) In a non-adiabatic process (weak coupling limit), $|H_{if}|$ is small, the exponential function in the above expression 1.3 can be expanded and truncated, leading to the familiar expression for non-adiabatic electron transfer rate:

$$k_{ET} = \frac{2\pi}{h} \frac{|H|^2}{\sqrt{4\pi \lambda k_B T}} \exp \left[ - \frac{(\lambda + \Delta G^0)^2}{4\lambda k_B T} \right]$$

(1.5)

In the case of non-adiabatic ET, the process can be assumed as a jump of an electron in between the states.$^{2,8,15,27,34}$
It should also be noted that in the case of excited state involved ET process, the Gibbs free energy change should be replaced with the redox potential of the excited state.\textsuperscript{1,30}

1.2. Interfacial Electron Transfer at Molecule–Semiconductor Interfaces

In general, electron transfer between a solid and a molecule adsorbed on it is referred as an interfacial ET. In molecule–substrate systems, a molecule acts as an electron donor and a substrate may serve as an electron acceptor. The disparate sets of properties between the two components of the interface: molecules and solid-state materials create the challenges for the study of the organic–inorganic interface. For example, molecules exhibit discrete, localized electronic states, unique vibrational frequencies, and well-defined directional bonds. Conversely, solid-state materials possess continuum of delocalized electronic and vibrational states, form defects that disrupt the regular bonding patterns, show different properties at the surface and bulk, and exhibit quantum confinement effect.\textsuperscript{35} The Interfacial ET is the key step for many processes and the understanding of the factors affecting the dynamics of this process, such as at semiconductor–molecule or metal–molecule interfaces, is significant for many applications, including photovoltaic devices, molecular electronics, and photocatalysis.\textsuperscript{6,9,11-14,36-38}

Between the semiconductor and the molecule, two different interfacial ET processes can take place (Figure 1.4): forward electron transfer (FET) and back electron transfer (FET). It should be noted that the hole injection process between semiconductor and the molecule is also possible in certain systems.\textsuperscript{39-42} For applications like solar energy conversion, the electron injection from the lowest unoccupied molecular orbital (LUMO) of the molecule (typically referred as dye) to the continuum of the states of the conduction band of the semiconductor and subsequent recombination of the electron in semiconductor with oxidized molecule are the main phenomena, and therefore, are of particular interest.
Figure 1.4. The schematic representation of the interfacial ET processes that can take place at the dye–semiconductor interface. VB, valence band of the semiconductor; CB, conduction band of the semiconductor; S, ground state sensitizer; S*, excited-state sensitizer.

1.2.1. Forward Electron Transfer

Electron transfer from the photoexcited state of an adsorbate molecule to the conduction band of a semiconductor nanocrystalline thin film is termed as forward electron transfer. In this case, the reactant state corresponds to the electron in the molecular excited state, and the product states correspond to the electron in the semiconductor conduction band and oxidized molecule. In other words, electron injection occurs from a discrete molecular excited state to the continuum of semiconductor energy states, as shown in Figure 1.5. However, semiconductor states also become discrete once the particle size reaches the quantum-confined regime.\(^{43}\)

The mathematical expressions for non-adiabatic ET between two discrete electronic states have to be modified to apply for interfacial ET because one needs to take account the continuous bands as well as the distribution of trap states in semiconductor. For instance, the expression for non-adiabatic ET from metal to molecules in solution, a common case for electrochemical study, can be derived by including the population distribution for an electron.
near the Fermi level and the density of states in the solid.\textsuperscript{8,25,26} Detailed theoretical discussion of ET including classical and quantum mechanical approaches was provided by Marcus, Hush, Gerischer, Levich, and Jortner.\textsuperscript{1,17,44-46} According to non-adiabatic ET theory, the total ET rate from adsorbate excited state to semiconductor can be expressed as the sum of ET rates to all possible accepting states in the semiconductor. Adopting an approach similar to that of Marcus theory,\textsuperscript{25,26} we can write down an expression for the total ET rate from adsorbate to semiconductor:

$$
k_{ET} = \frac{2\pi}{\hbar} \int_{-\infty}^{+\infty} dE \rho(E) (1 - f(E, E_F)) |\overline{H}(E)|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp \left[ -\frac{(\lambda + \Delta G^0 - E)^2}{4\lambda k_B T} \right]
$$

where $\Delta G^0 = E_{CB} - E_{ox}$ is the energy difference between conduction band edge and the redox potential of adsorbate excited state which is also termed as driving force for FET; $\rho(E)$ is the density of state at energy $E$ from the conduction band edge, which can contain both the bulk state and surface states; $\overline{H}(E)$ is the average electronic coupling between the adsorbate excited state and different accepting states in the semiconductor at the same energy $E$; $f(E, E_F)$ is Fermi occupancy factor; and $\lambda$ is the total reorganization energy. However, for the system involving a dye molecule and semiconductor with a broad CB having a large number of acceptor states, like TiO$_2$, the energy-level matching mechanism via molecular vibrations is not required and the rate constant for interfacial ET is essentially independent of nuclear factors. For such cases, the rate constant of ET, $k_{ET}$, has also been approximated as the product of a Franck–Condon weighted density of states (FCWD), which depends on the interaction between the acceptor and donor vibrational wave functions and an electronic term proportional to $|H|^2$, the electronic coupling matrix element squared.\textsuperscript{47,48}
\[ k_{ET} = |H|^2 FCWD \] (1.7)

**Figure 1.5.** Schematic diagram of potential energy as a function of nuclear configuration for electron injection from an adsorbate excited state (S*) to a continuum of product states. Driving force and barrier of ET varies with the energy of acceptor states. Orange colored curve shows the barrierless ET pathway at \( \lambda \) below the adsorbate potential.

Electron transfer to conduction band states at \( \lambda \) below the adsorbate excited-state oxidation potential has the lowest barrier, as indicated by the orange curve in Figure 1.5, and whose density of states is expected to dictate the nonadiabatic ET rate.

Assuming injection is the only pathway for deactivation of excited state molecules and an inhomogeneous distribution of adsorbate/semiconductor interactions exists, the total change of injected electron population, \( N_e(t) \), is given by the integration over the distribution of electronic coupling matrix elements, \( H \).
\[ N_e(t) = N_0 \left[ 1 - \int_0^\infty g(H)e^{k_{\text{ET}}t} dH \right] \]  

(1.8)

where \( N_0 \) is the total number of excited molecules, and \( g(H) \) is a distribution function. Thus, this equation predicts the injection rates are distributed giving rise to non-single-exponential process.\(^8\)

Electron transfer dynamics at semiconductor–molecule interface and the factors affecting it have been investigated extensively due to its key role on the efficiency of the systems, such as photovoltaic devices,\(^9,11\) molecular electronics,\(^14\) photocatalysis,\(^49\) photoelectrolysis, and photolithography.\(^35\) In these studies, wide band gap metal-oxide semiconductors, such as TiO\(_2\) (~3.2 eV),\(^29,49-56\) ZnO (~3.2 eV),\(^8,57-60\) SnO\(_2\) (~3.6 eV),\(^61-64\) In\(_2\)O\(_3\) (~3.0 eV),\(^65\) and SrTiO\(_3\) (~3.2 eV),\(^65\) either single-crystals or nanoparticles are loaded with various organic dyes.\(^66\) Interfacial ET from the excited molecule to the CB or to the energetically accessible surface states of the semiconductor typically takes place in the time scale ranging from tens of femtoseconds to several hundred picoseconds and exhibits complex inhomogeneous dynamics due to the spatial heterogeneities of the nanoscale environments and the inhomogeneous distribution of vibronic coupling between the absorbed molecules and the rough surface.\(^8,9,67-69\) Generally, the ET process at the interface exhibits exponential dependence to the distance between the semiconductor and the ET center and very weak dependence on the temperature.\(^10,70\)

Additionally, FET process is also known to be affected from properties of semiconductor nanoparticle, molecular adsorbate, surface binding properties, and interfacial environment.\(^9\)

Details of these parameters and their influence in interfacial ET rate is discussed in section 1.2.3.

**1.2.2. Back Electron Transfer**

For back electron transfer from the semiconductor to the oxidized adsorbate, the donor state corresponds to the electron in the semiconductor and the acceptor state corresponds to the
electron in the ground state of the dye. In contrast with FET process, in BET, the donor state connects with only one acceptor state. However, there is a distribution of semiconductor reactant states, each corresponding to electrons trapped at different trap sites. ET rates from different trap sites vary because of the difference in electronic coupling and driving force. The total back ET rate is the average of the ET rates of all injected electrons recombine with oxidized dyes. Quantitative description of back ET process can be achieved by accounting the energy and distance distribution of trapped electrons, electron diffusion time between trap sites, and inhomogeneous distribution of adsorbate/semiconductor interaction giving rise to a distribution of electronic coupling. Total BET time involves the electron diffusion time between the trap states and interfacial BET time to the oxidized dye. When electron diffusion between trap sites is much slower than interfacial BET (trap-limited kinetics), the BET kinetics can be described by

\[ N_e(t) = N_0 \int_0^{r_0} dr P(r) \exp \left[ - \int_0^t k(r, t) dt \right] \]  

(1.9)

where \( P(r) \) is the initial spatial distribution of trapped electrons and \( r_0 \) is their maximum distance from the adsorbate. \( k(r, t) \) is the electron-transfer rate for electrons trapped at distance \( r \) from adsorbate and its time dependence accounts for the change in trap energy. This model also predicts a highly non-single-exponential process due to the distribution of trap energy and distance. However, the validity of this model questioned by recent BET studies in dye-sensitized nanocrystalline thin films which indicate diffusion processes can play a dominating role.

As discussed above, the BET kinetics are generally complex. Following photoexcitation and electron injection, the neutral ground state dye is recovered by (i) instantaneous recombination of electron in a single trap site with oxidized dye, and (ii) a more complicated process requiring additional time and likely involving deep or shallow trap sites.
after the electron injection into the semiconductor in a dye-sensitized solar cell, the electron can either diffuse away to the metal electrode becoming a part of photovoltaic energy or can undergo Levy type non-Brownian motion, such as trapping, de-trapping, and scattering especially due to the additional pathway provided by the surface states inside the bandgap, and recombine with the oxidized molecule. As a result of these complex processes in semiconductor, BET occurs in a longer time scale, sub-nanoseconds to several milliseconds and exhibits single exponential, multiexponential, and stretched exponential dynamics.\textsuperscript{76,78-80} It is evident in literature that the back ET rate is susceptible to the various factors such as reaction driving force, electronic coupling, and density of accepting states. Furthermore, in consideration to the device efficiency, the BET, electron recombination with the parent oxidized molecule, is critical phenomenon which should be taken into consideration.\textsuperscript{9,56,74,75,81}

1.2.3. Factors Affecting Interfacial Electron Transfer at Semiconductor–Molecule Interface

1.2.3.1. Relaxation Pathways

As briefly discussed in section 1.1, the electron injection is not the only relaxation pathway for the excited molecule (donor); hence, this process should compete with the other radiative and non-radiative relaxation pathways. It is quite common to have electron injection on the timescale of vibrational relaxation and internal vibrational energy redistribution. As a result, competition between ET and intramolecular relaxation pathways will also need to be taken into account. Previously it has been reported that in molecule-TiO\textsubscript{2} complexes, it is likely to observe biphasic ET dynamics with an ultrafast component in femtosecond time-domain and slower component(s) in the picoseconds or slower time-domains due to ET and the intra-molecular vibrational relaxation being in the similar timescale (Figure\textsuperscript{1.6}). It has also been suggested that the ET from the initially “hot” excited state in combination with the non-radiative relaxation are
responsible from the fast component while the ET from the relaxed state corresponds to the slower component. Even though the biphasic rates are not common for organic molecules, they still possess multi-exponential behavior.\(^8\)

**Figure 1.6.** Overview of excited state relaxation pathways and typical time scales of the processes in dye-sensitized TiO\(_2\) system.

The origin of fast and slow component of FET rate has been rationalized by a two-state model of competing electron injection and intramolecular relaxation pathways. In this model, the vibrationally hot excited state above the CB edge can either inject an electron into TiO\(_2\) with a rate constant \(k_1\) or relax to the vibrationally relaxed states with a rate constant of \(k_2\). Assuming the electron injection from lower state is significantly slow, the integrated rate equation describing the formation kinetics of injected electrons is:

\[
N_e(t) = N^*(0) \left[ \frac{k_1}{k_1 + k_2} \left( 1 - e^{-(k_1+k_2)t} \right) \right]
\]

where \(N_e(t)\) is the number of injected electrons at time \(t\) and \(N^*(0)\) is the number of initially populated excited states.\(^8,9\) Biphasic injection occurs when the injection rate is competitive with intramolecular relaxation and there is a large rate difference between injection from the initially excited Franck-Condon state and the relaxed excited state. However, biphasic kinetic model has been obsolete because organic chromophores that have been used as sensitizers have generally
not been able to undergo such a significant relaxation in the excited state manifold. As a result, FET kinetics are less distinctly biphasic, although they are still multiexponential.\(^9\)

In addition to the intra-molecular relaxation, excited molecule can also experience the relaxation by transferring energy, e.g. Forster energy transfer, electrostatic coupling of the transition dipole moments of donor and acceptor, to another molecule or to the semiconductor which would result in the quenching of ET.\(^82\) Even though energy transfer from the excited molecule to semiconductor is highly unlikely due to energy considerations (uphill process), it might cause the excitation of the electrons from the trap states to the CB.

1.2.3.2. Semiconductor

Interfacial ET is sensitive to semiconductors because of the differences in conduction band electronic structures and band edge position. These semiconductor properties affect the ET rate regulating parameters such as electronic coupling strength to the adsorbate and the density of the electron accepting states in the conduction band.

The ET dynamics at different semiconductor, such as TiO\(_2\), ZnO, Nb\(_2\)O\(_5\), SnO\(_2\), interfaces have been investigated in recent years. Comparative studies of ET dynamics on TiO\(_2\), ZnO, and SnO\(_2\) suggest that the faster dynamics is observed for TiO\(_2\) in comparison to ZnO and SnO\(_2\).\(^9,62,83\) Electronic structure calculations suggested that d-orbitals characteristic of the CB of TiO\(_2\) in comparison to s and p characteristic of ZnO and SnO\(_2\), respectively, can give rise to faster dynamics. Even though the d-states are narrower, their density of electron accepting states are substantially higher than s and p states.\(^84,85\) Additionally, different crystal facets of TiO\(_2\) (001) exhibit differences in ET rates arose from the differences in the structure of the surfaces.\(^86\)
1.2.3.3. Electronic Coupling

The proximity of the excited molecule to the semiconductor or coupling is another factor affecting the ET dynamics. Electronic coupling strength is determined by the extent of electronic overlap between donor and acceptor orbitals which may depend on the spatial separation of donor and acceptor electronic orbitals. Donor-acceptor electronic coupling varies exponentially with distance and can be expressed as:

\[ H_{DA} = H_{DA}^0 \exp(-\beta(R - R^0)/2) \]  

(1.11)

where \( H_{DA}^0 \) is the value of \( H_{DA} \) at the van der Waals separation \( R^0 \) and \( \beta \) is a constant that scales the distance dependence.\(^87\) Generally, shorter distance between donor and acceptor indicates strong electronic coupling and vice versa. However, the deviation from exponential dependence has been observed for shorter and longer separation distance between donor and acceptor.\(^88,89\)

Coupling between molecular excited states and semiconductor can be altered by using a bridge between the chromophore and the binding group, an insulating layer such as Al\(_2\)O\(_3\), and different binding groups.\(^64,90\)

The length of the bridging unit influences the coupling properties. Studies suggested that the ET rate more likely to decay exponentially with the increasing bridge length suggesting that the electron tunnels through the bridge.\(^91\) From various bridge-length dependent ET dynamics studies, it has been found that the flexibility of the bridge and surface binding complicates the quantitative investigation of electron injection through bridges.\(^70,92-94\) It should be noted that if the molecule has the flexibility on the surface after the adsorption; due to the free rotation of the molecule, the coupling properties are subjected to change in time. Recent findings suggest that when the rigid bridges and multi-connection points used to restrict the movement of the molecule, fast electron injection rates can be observed even through the long bridges.\(^92\)
Additional to the bridge, variation of anchoring or binding group alters the electronic coupling strength. Previous reports suggested that the molecules that are not chemisorbed on the semiconductor surface do not contribute or weakly contribute to the ET process.\textsuperscript{95} So far, many different anchoring groups such as hydroxyl, carboxylate, thiol and so on have been used.\textsuperscript{9,93,96,97} The change in the anchoring group alters the electronic properties of the molecule which changes the degree of electronic coupling at the interface causing the variation in the ET dynamics.

Willig et al. reported the interfacial ET dynamics by using carboxylic acid and phosphonic acid as the anchoring groups.\textsuperscript{68,70} The difference in the respective rate constant values was suggested to originate from the different degree of the coupling at the interface due to the change in the binding group. Furthermore, the binding mode of the same anchoring group can exhibit different behavior at the interface depending on the molecule, surface, and pH. Several computational and experimental studies showed that the binding of COOH to TiO$_2$ can occur through variety of binding modes under different conditions.\textsuperscript{9,93,96,97} However, the dependency of ET rate on electronic coupling is more complicated because there exists an inhomogeneous distribution of molecule/semiconductor interactions (crystal surfaces, adsorption site, adsorption geometry, etc.), giving rise to a distribution of electronic coupling, resulting in the non-single-exponential kinetics.\textsuperscript{8,98,99}

\subsection{1.2.3.4. Defects and Trap States}

In general, the defects can be oxygen vacancies, interstitial atoms, impurities, and step edges. In the case of both nanoparticles and the crystal surfaces, the density and type of the defect states are susceptible to the preparation conditions which makes them hard to characterize, control, and fully understand the influence of the defects to the interfacial ET dynamics.\textsuperscript{73,100}
Intrinsic semiconductor surface states play an important role in both electron injection and recombination process, both as electron traps and intermediate states for electron transfer to oxidized molecules. The defects sites significantly alter the electronic configuration, resulting in the localized surface states both in the band gap and within the band structure of the semiconductor. The created surface states can act as an additional relaxation pathway for the electrons by trapping, de-trapping, or scattering. The trapping might take place either by direct electron injection to the trap state or as a result of the electron relaxation from the CB. Previously, Aydil et al. reported that even though the ET rate in a single-crystal rutile TiO$_2$ nanowire is expected to be faster, it exhibits similar dynamics with the ET in TiO$_2$ nanoparticles and suggested that this phenomenon arises a consequence of the trapping and de-trapping due to the existence of the surface states in the semiconductor. The origin of the nonexponential recombination was attributed to the spatial and energetic distribution of trap states for the injected electrons in the nanoparticles. In addition to the spatial distribution, these traps sites may also have very different energies, leading to a distribution of driving force and therefore the back ET rates. Increase in the number of filled trap states decreases the electron trapping/detrapping time inside the semiconductor and significantly increasing the recombination time. However, lack of knowledge of the extent and nature of the trap states in most nanomaterials complicates to study its role in ET dynamics.

1.2.3.5. Density of the Electron Accepting States and Driving Force

Interfacial ET rate depends on the electron accepting state density in semiconductor, determined by energy difference between the CB edge of the semiconductor and the excited state of the molecule or driving force. The increase in the energy difference between the CB edge and the excited state of the molecule increases the injection probability. Especially close to the CB
edge, this phenomenon shows exponential dependence, although high above the band edge, the variation is slow.\textsuperscript{8,73,107} For instance, the density of states (DOS) in TiO\textsubscript{2} is often modeled as an exponential tail extending below the CB edge as shown in Figure 1.7.

To obtain some insight into the qualitative behavior of ET rate dependence on the DOS assuming the case of defect-free semiconductor, the DOS near the CB edge is described by:

\[
\rho(E)dE = \frac{(2m^*)^{3/2}\sqrt{E}dE}{2\pi^2\hbar^3} \tag{1.12}
\]

where \(m^*\) is the effective mass of electrons in the conduction band. Assuming the effective electronic coupling is independent of the energy, we can calculate the injection rate, \(k_{ET}\), as a function of DOS using equation 1.6. The injection rate increases with the increase in DOS. This results from the increase in the density of accepting states in the solid at higher energy above the conduction band edge. A larger total nuclear reorganization energy leads to a smaller ET rate in the region of small driving force, because of a higher activation barrier for ET. This trend can also be understood in terms of Gerischer’s theory of ET.\textsuperscript{8,108,109}

The dependence on density of states is much more complicated than one to imagine. The ET rate depends not only on the total density of states but also on the density of states coupled to the adsorbate electron-donating state. Furthermore, the quantitative details of the dependency will change if the density of states does not follow the simple relationship shown in equation 1.8 or if the average electronic coupling varies with the energy of the adsorbate.
Figure 1.7. Schematic representation of the molecule–semiconductor nanoparticle interface and the energetic/kinetics scheme determining the injection yield. The density of defect states is often modeled as an exponential tail extending below the band edge as shown by shaded area.

Although, the maximum driving force (lowest energy barrier) arises at the optimal Marcus region where the reorganization energy is equal to the Gibbs free energy, its density of states is expected to dominate ET rate. Previously, various methods have been employed for the investigation of accepting state density dependent ET dynamics. For example, a systematic study of molecules with different excited state energetics and their ET rates at the same semiconductor material has indicated the trend of ET rates with DOS as indicated by equation 1.6. However, this method has weakness due to the fact that the electronic coupling properties of different molecules can be different, leading to variation in the ET rates.\textsuperscript{110}

Effect of pH: The CB edge position in semiconductor can be tuned by varying pH or potential determining ions in solution (Figure 1.8). Changing the sample pH affects a Nernstian-type change in the semiconductor band energies for metal-oxide semiconductors.\textsuperscript{111}
\[ E_{CB}(pH) = E_{CB}(pH = 0) - 0.06 \text{ eV} \times pH \] 

(1.13)

Higher pH value moves the CB to more negative potentials and lowers the density of the electron accepting states. Equation 1.13 predicts the CB edge offsets by 0.06 eV with unit pH change.

**Figure 1.8.** Schematic of TiO\(_2\) Particles following acid (Positive) or base (Negative) treatment.

Assuming the adsorbate redox potential remains unchanged, the electron injection rate is predicted to decrease at higher pH because of a reduced density of semiconductor accepting states at the injection energy level\(^\text{110}\). However, the energy levels of the molecule can also be influenced by the pH value and additionally, as mentioned before, it can alter the coupling between the molecule and the semiconductor\(^\text{112,113}\).

The density of accepting states in semiconductor can also be modified by applying potential to an electrochemical cell. Application of a more negative potential primarily raises the Fermi level in the conduction band, decreasing the density of accepting states. Studies have observed potential-dependent ET rates consistent with the change in density of accepting states. The drawback for this method is that the applied potential can also alter the interfacial properties between molecule and the semiconductor\(^\text{107,114}\).

Even though all methods have limitations, the similar trend observed evidences the significance of density of electron accepting states in determining ET rate.

Conduction band edge of semiconductor depends on surface charge and chemical species adsorbed on the surface. These chemical additives alters the driving force for ET by offsetting
the CB edge position and hence changes the ET dynamics (Figure 1.9). For example, Lian and co-workers found the pH dependence on ET rates.\textsuperscript{115} Electron injection yield decreases with higher pH. This occurs because the deprotonation of oxide surface shifts the CB edge to a higher energy level.

**Figure 1.9.** Effect of chemical additives on the energetics of the density of TiO\textsubscript{2} conduction band acceptor states and driving force. DOS is density of states. The density of CB/trap states (shaded areas) is represented as an exponential distribution.\textsuperscript{116}

1.2.3.6. **Semiconductor Size and Crystallinity**

The particle size of the semiconductor plays an important role in determining the energetics of the semiconductor. The origin of the quantum size effect has been proposed to be the quantum confinement of the electrons. Previously, it has been suggested that for bands to be continuous, at least one of the dimensions of the semiconductor should be macroscopic in size, otherwise, the energy levels become discrete.\textsuperscript{117} Furthermore, Yamamoto et al. reported that the energy gap of the TiO\textsubscript{2} nanoparticles increases with the decreasing nanoparticle size, which is known as a quantum size effect. The surface structure or crystallinity of the semiconductor particle determines the efficiency of the dye adsorption. A heterogeneous surface structure, resulting from, e.g., dislocations and abrupt termination of the crystal lattice at the surface, will lead to a variation in the interaction between the dye and semiconductor. For example, the
binding of the dye to various particle surfaces results in a variety of anchoring geometries for the
dye that may influence the kinetics of interfacial electron injection between the molecule and
semiconductor.\textsuperscript{118}

1.2.3.7. Interfacial Geometry

The geometric structure of the chromophore–semiconductor interface governs its
electronic properties and ET dynamics. For instance, water adsorbs on TiO\textsubscript{2} both dissociatively
and in the molecular form depending on the type of the surface, the presence of defects, the
surface coverage, the temperature, and other factors. Chromophore molecules that has multiple
binding groups can be expected to have complex surface geometry which is difficult to predict.\textsuperscript{35}
For the carboxylic acid anchoring group, six major types of possible anchoring modes have been
identified.\textsuperscript{119} Moreover, the mode of attachment and the position of the anchoring groups in a
dye molecule also affect the coupling strength between the excited states of the dye molecule and
the semiconductor.

1.3. Semiconductor–Electrolyte Interface

When two materials are brought in contact there is a formation of space charge region
because of changes in charge carrier concentration at the interface resulting into band bending.
Band bending refers to the local imbalance in charge neutrality or space charge which results in
the continuous energy shift of a semiconductor’s energy band edge near the interface. Band
bending in semiconductor can be induced by metal contact, electric field, surface states, and
surface adsorption.\textsuperscript{120,121}

1.3.1. Field-Effect-Induced Band Bending

An electric field can induce band bending near the semiconductor surface. Figure 1.10
gives a schematic diagram of a field-effect induced band bending on an n-type semiconductor
with no surface states by assuming the same work functions of the conductive electrode and the semiconductor. The energy band is flat when the bias voltage between conductive electrode and semiconductor is zero ($V = 0$). When a bias voltage is applied to the electrode, an electric field is set up between the conductive surface and the semiconductor. The electric field can penetrate into the near surface region of the semiconductor due to the insufficient screening by the charge carriers of low concentration in the semiconductor. When $V > 0$, the electric field causes electron accumulation near the surface and bends the band downward, and vice versa.

**Figure 1.10.** Schematic diagram of electric field effect induced band bending on semiconductor. CB, conduction band; VB, valence band; $E_{F,s}$, Fermi level of semiconductor; $E_{F,m}$, Fermi level of metal electrode. Blue line indicates the space charge regions.

It should be noted that the magnitude of band bending depends on the particle size, dopant concentration, and dielectric constant. The band bending will decrease with decrease in particle size.\textsuperscript{104,120}

### 1.4. Interfacial Electron Transfer from Single Molecules

One application based on photoinduced ET process is the dye-sensitized solar cell (DSSC), which is believed to be a low-cost solar energy conversion device.\textsuperscript{122,123} TiO\textsubscript{2} is the most commonly used semiconductor film in DSSCs and the solar cells based on TiO\textsubscript{2} have shown promising efficiencies.\textsuperscript{47,51,124,125} Although the ensemble-averaged ET dynamics from dye...
molecules to various semiconductors such as TiO$_2$, SnO$_2$, ZnO, and In$_2$O$_3$ have been extensively investigated, the single molecule ET dynamics of these dye molecules are still poorly understood.\textsuperscript{126-130} Studying interfacial ET dynamics from single molecules has been an appealing and challenging effort since the first work in single molecule ET dynamics by Lu and Xie.\textsuperscript{131} Their pioneering work demonstrated the capability to detect single molecule ET dynamics using single-molecule fluorescence spectroscopy. A wide distribution of ET rates caused by the inhomogeneity of molecular interactions on the semiconductor surface was observed in their experiments and was used to explain the physical origin of the multiexponential kinetics of ET. The details of the single-molecule spectroscopic techniques applied to interfacial ET dynamics study in this dissertation and its current status will be discussed in Chapter 2.

1.5. References


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CHAPTER 2. EXPERIMENTAL SECTION

The samples used in this dissertation work are based on TiO$_2$ nanocrystalline thin films which are sensitized by organic dye molecules (mostly porphyrins). The synthesis of TiO$_2$ colloid and the preparation of nanocrystalline surface are based on the published procedures, but also modified slightly for single-molecule study. The single-molecule studies are conducted by single-molecule fluorescence imaging and spectroscopy which consists of laser source, confocal microscope and time-correlated single photon counting (TCSPC). This chapter introduces the experimental setup, summarizes the procedures for sample preparations, and basis of statistical data analyses for single-molecule measurements.

2.1. Single-Molecule Studies and Its Significance

In ensemble measurements, the properties of bulk or huge numbers of molecules are investigated to yield the average value of a parameter for a large number of (presumably identical) copies of the molecule under study. Signals from ensemble level are usually strong, however, the individual behavior cannot be distinguished, and only average characteristics can be measured. Additionally, single-molecule techniques studying one molecule at a time can reach the dynamic views of molecules in action. In typical single-molecule measurements, first, molecular properties are measured one molecule at a time. After recording the parameters from a number of individual molecules, the distribution of the parameter can be made that contains more information than the average value alone, especially in complex dynamical systems.$^{1,2}$

*History of Single-Molecule Studies:* The optical detection of single molecules was first achieved at cryogenic temperature by absorption in 1989 (Moerner and Kador) followed by emission or fluorescence in 1990 (Orrit and Bernard).$^{3,4}$ In 1990, Keller and coworkers were able to detect single Rhodamine-6G (R6G) molecules flowing through a small detection volume.$^5$
This discovery paved the way for the new advancements in single-molecule methods that have made single-molecule fluorescence microscopy to a successful tool to study molecular structures, properties and functions.\textsuperscript{6} Although the early experiments were performed at liquid helium temperature, Betzig and Chichester were able to record the first room-temperature single molecule images immobilized on a surface in 1993 using near-field optical microscopy. Soon after, a new technique called single molecule spectroscopy (SMS) was established and quickly developed.\textsuperscript{7-9} In 1997, Lu and Xie further applied single-molecule studies to interfacial ET kinetics and later to enzymatic dynamics.\textsuperscript{10,11} These pioneer works in single-molecule studies have made significant contributions to open up possibilities for studying chemical and biological processes with imaging and spectroscopic approaches.

Following the invention of single-molecule technique, there were various single molecule studies established, but the optical detection of the single molecules has become the most common technique today because of its practical applicability to a wide range of samples.\textsuperscript{1,5,12-14} Nevertheless the first detection of single molecules is achieved by absorption techniques, the most common technique today is the detection of emitting fluorescence (Figure 2.1). Single-molecule fluorescence imaging and spectroscopy have become powerful tools to study the excited state structure and dynamics of single molecules.\textsuperscript{15,16} Fluorescence imaging exploits the accurate location of the molecules and the spectroscopy extracts the emission properties and many more of single molecules.\textsuperscript{9}
Figure 2.1. Schematic diagram of the energy flow (Jablonski diagram) in the fluorescence. The colored circles represent the energy states of the fluorophore, where green shows the ground state energy level and red the excited state energy level. Yellow represents the fluorophore in the lowest vibrational level of first excited state.

2.2. Single-Molecule Fluorescence Imaging and Spectroscopy

To accomplish single-molecule fluorescence spectroscopy by using optical irradiation to detect a single molecule on a surface, several strategies are needed. Only one probed molecule should be in the volume under study, and the light emitted by the molecule should be detectable from the background noise. The first condition is generally achieved by focusing an excitation laser beam into a small volume of very dilute solution. For example, at room temperature a concentration of roughly $10^{-10}$ M and a volume of 10 μm$^3$ is required to achieve the limit of one molecule in detection volume.\textsuperscript{1,17} Also, the probe molecules should have large absorption cross section and high fluorescence quantum yield.

The fluorescence detection of single-molecule sensitivity can be achieved using the efficient fluorophore and appropriate instrumentation at ambient conditions. The reason for the molecular-level fluorescence sensitivity is the Stokes’ shift, emission of longer wavelength photons while absorbing photons of shorter wavelength, allows, after proper filtering, detection of the fluorescence signal against a background. Single-molecule fluorescence microscopy at
ambient conditions relies on the accurate detection of photons emitted by one or more fluorophores while, at the same time, limiting the background signal using advanced microscopy technique. The higher the signal-to-background (S/B) ratio, the more detailed and clear the information is that can be obtained. Optimization of the S/B ratio is therefore an essential element in single-molecule fluorescence microscopy. In general, two approaches can be distinguished: (1) Increasing the signal, by creating the optimal conditions for the fluorophore to emit photons and by increasing the sensitivity and efficiency of photon collection and detection. (2) Decreasing the background, using advanced microscopy techniques that probe only small volumes around the molecule of interest. Second approach is more important for the visualization of single-molecule which is often achieved by using confocal microscope. The main components of such a microscope are an illumination source for excitation of the fluorophores, filters to extract light of wanted colors and suppress unwanted light, an objective to direct the excitation light and efficiently collect the emission light, and a detector. Since much of the emitted light is lost in the detection pathway and the total number of photons that a fluorophore can emit is restricted due to photobleaching, it is imperative in single-molecule fluorescence studies to use optimal components in each part of the instrument.

2.2.1. Confocal Microscopy

Confocal microscopy is an optical imaging technique offering higher optical resolution and better contrast over conventional optical microscopy by eliminating out-of-focus light in specimens that is not from the microscope’s focal plane. In a conventional wide-field optical microscopy, the image of specimens in the area of interest is often influenced by fluorescence emitted from out-of-focus region. In contrast, a confocal microscope, which uses a pinhole in an optically conjugate plane in front of the fluorescence detector to eliminate the out-of-focus signal
(the name "confocal" stems from this configuration), provides significant improvements in both axial (z-direction, or depth of field) and lateral resolution. As shown in Figure 2.2, only the emitted fluorescence by specimens very close to the focal plane can reach the detector after pinhole and the out-of-focus fluorescence is excluded. Higher z-resolution and reduced out-of-focus blur make confocal images better than conventional wide-field images.\textsuperscript{1,18,20-23}

**Figure 2.2.** Confocal microscopy geometry including the light pathways. APD, avalanche photodiode.

Figure 2.3 shows the confocal fluorescence image of single polymer beads. Each spot represents the diffraction-limited fluorescence image of a single polymer bead.
Figure 2.3. A representative fluorescence image (10×10 µm$^2$) of fluorescent beads obtained using inverted confocal microscope used in this work (for imaging calibration).

Furthermore, combining the confocal microscope with time-correlated single photon counting (TCSPC) makes a powerful tool to investigate temporally and spatially resolved information about materials.$^{12,13,15}$

2.2.2. Photon-Stamping Spectroscopy

Photon counting is an intensity measurement technique based on the quantum nature of light. TCSPC technique detects and count individual photons from the signal rather than measuring. The advantages of single photon counting (SPC) over traditional analog method of measurements are: (1) SPC is insensitive to the drift and noise associated with the instrument. (2) Digital nature of SPC simplifies both the acquisition as well as analysis of the data. Figure 2.4 shows the major components and data acquisition process of a TCSPC system in reverse start-stop mode.
Figure 2.4. Photon counting method of TCSPC technique. (A) Block diagram of TCSPC in reverse start-stop mode (B) Photon counting module monitors the photon arrival time and the time interval between laser pulse and detected photon (delay time). The output of a TCSPC measurement are (C) a histogram of delay times and (D) fluorescence intensity trajectory (number of photons per integration time). CFD, constant fraction discriminator; TAC, time-to-amplitude converter; ADC, analog-to-digital converter.

A brief description of the functions of the components is discussed below:

**Laser:** The light source used for the excitation of the chromophore is a pulsed laser. In reverse start-stop mode, every excitation pulse also sends a ‘stop’ signal (“sync” signal) for the time-to-amplitude converter (TAC), which measures time interval between excitation pulse and the detected photon.

**Detector:** Fluorescence from the sample is collected by the confocal microscope and focused to the detector. In our case the detector used is an avalanche photodiode (APD). APD converts the photon counts to voltage. However, the output of APD includes the electronic noise as well. The resulting ‘signal + noise’ is being sent to the constant fraction discriminator (CFD) and then directed to TAC as a “start” signal.
**Constant Fraction Discriminator (CFD):** The electric pulses from APD is sent through a CFD to accurately measure the arrival time of each photon. This unit differentiates the signal from the detector. If the signal level is below the given threshold, it will be completely ignored while the signal level above the threshold will be recognized. The threshold level is decided by the noise level of the detector. However, there is a finite probability of detecting multiple photons at the same time. This problem can be resolved electronically by setting an upper limit. CFD generates a TAC “start” signal only if the signal level is between upper and lower limit.

**Time-to-Amplitude Converter (TAC):** When TAC receives the “stop” signal from laser, it generates an analog output voltage whose amplitude very precisely represents the time that has elapsed between “start” and “stop” signals (delay time).

**Analog-to-Digital Converter (ADC):** ADC is used to resolve the signal from TAC into thousands of time channels and write into the corresponding address of memory. The histogram of occurrence of each time delay is constructed and the lifetime of the single molecule is achieved by fitting the decay curve, as shown in Figure 2.4C.

In this dissertation work, the photon by photon recording is carried out by similar TCSPC technique described above which is referred as photon-stamping.\textsuperscript{12,13,24} Photon-stamping detection technique of single molecule fluorescence using single photon counting has been widely applied and demonstrated recently in a number of studies.\textsuperscript{25-27} In general, two parameters are recorded for each detected photon: the chronic detection time, i.e., photon detection recording real time, of the photon and the specific photon emission time delay from the molecule’s excited state (Figure 2.5). For binning in chronic arrival time from the single-molecule photon-stamping trajectories, one can have the conventional single-molecule intensity trajectories (Figure 2.4D), and from each photon time delay, one can build histogram to measure
the excited state lifetime (Figure 2.5C). The name of the single-molecule photon-stamping spectroscopy originated from an analogy to the mails receiving with two stamps: one marking the time the mail is sent out from the sending post office and other the time the mail arrived at the receiving post office.\textsuperscript{16,24,27-29} Photon-stamping recording can be done using a continuous-wave (CW) laser as well as a pulsed-laser. CW laser based approach is used only for measuring the time trajectory of the single-molecule fluorescence intensity fluctuation by detecting each photon and stamping (recording) its arrival time with highest time resolution. The time resolution is only limited by the photon flux, excitation saturation, photobleaching, and detector counting rate. In a pulsed-laser based approach, each emitted photon is detected and its delay time stamped from the pump laser pulse. The delay time is the duration from the time of excitation of the single molecule to the emission by the same molecule, which is a one-event measurement of the fluorescence lifetime of the molecule that is corresponding to a single exponential decay as a Poisson process or a nonexponential decay as a nonPoisson process. One advantage of this approach is single-molecule excited-state lifetime can be studied by averaging only hundreds of photons instead of fitting the histogram to exponential decay, making it possible to study the fluctuations in the decay time with adequate time resolution.\textsuperscript{27} Therefore, this technique combined with confocal imaging demonstrates powerful and exquisitely sensitive that permits one to investigate spatially heterogeneous samples one molecule at a time, thereby eliminating the ensemble averaging intrinsic to most optical measurements. In addition to elucidating photophysical differences between spatially resolved molecules, the technique also provides complementary temporal information on single fluorophores, such as the evolution of excited- and trapped-state populations, fluorescence lifetimes, nonradiative relaxation, and intersystem crossing rates.
Figure 2.5. Photon-stamping spectroscopy concept and definition of the parameters: (A) scheme of a train of laser excitation pulses and detected emission photons; (B) scheme of the time-stamped photon sequence. Each data point represents a detected photon event with two physical parameters recorded, the delay time $\tau_p$ and the real time $t_p$ of detection. The sorted distribution along the y-axis of $\tau_p$ gives the conventional time-correlated photon counting lifetime decay curve, and the binning along the x-axis of $t_p$ gives the conventional single-molecule photon counting intensity trajectory.
2.2.3. Single-Molecule Detection

Single-molecule detection is carried out with a home-built inverted scanning confocal microscope. The working principle of the experimental setup is depicted in Figure 2.6. The excitation source used is either from a femtosecond Ti:sapphire laser (Coherent Mira 900 D; 1.6 W; 200 fs pulse width; operated at 850–1000 nm)-optical parametric oscillator (APE-OPO, Coherent Inc.) system or from a picosecond pulsed laser (532 nm, Coherent Antares, YAG) at 76 MHz repetition rate. The 1064 nm output signal from OPO is frequency doubled to generate 532 nm laser pulses by using lithium triborate (LBO) nonlinear optical crystal. The sample placed on a piezo scanner is illuminated by the laser beam focused through a 100 × 1.3 numerical aperture (NA) oil immersion objective (Zeiss FLUAR). The information about the specimen (e.g. fluorescence) is obtained by point by point scanning of the laser beam across the specimen. Scanning of the sample and moving the sample to a particular position with respect to laser focus is done with a nanoscale-precision x-y piezoelectric closed-loop position scanning stage (Physik Instrumente, Germany). The laser beam is focused to a diffraction-limited spot (λ/2 diameter) to excite dye molecules on the upper surface of a glass cover slip (Fisher Scientific, 0.17 mm thick) or a nanocrystalline thin film. The illuminated area and its image lie in conjugate planes. A pinhole in the image plane transmits signal only from the focal plane of the objective. This is called confocal ray path. Signal from out of the focal area are obstructed by the pinhole and do not contribute to the image formation. Signal from the sample is collected by the same objective and focused to the avalanche photodiode (APD) (PerkinElmer SPCMAQR-14; pinhole size of APD is 170 μm). Photon by photon counting is achieved with the TSCPC system (SPC-830, Becker & Hickl GmbH) in a FIFO (first-in first-out) mode.
Figure 2.6. Schematic of a single-molecule confocal microscope combined with photon-stamping spectroscopy. APD, avalanche photodiode; SPC, single photon counting.

The instrument response function (Figure 2.7) for the fluorescence lifetime measurement had a full-width-at-half-maximum of ~500 ps.

Figure 2.7. Instrument response function (IRF).
2.2.4. Electrochemical Cell Configuration and Spectroelectrochemistry

We used a home-built electrochemical cell (Figure 2.8) with three-electrode configuration (working electrode: indium tin oxide (ITO)-coated surface; counter electrode: platinum wire; quasi-reference electrode: silver wire) for all the electrochemical measurements. The electrode calibration was reported using the Ru$^{3+/2+}$ redox-couple of [Ru(bpy)$_3$] (PF$_6$) and it was found that the quasi-reference electrode is offset from the normal hydrogen electrode (NHE) by 0.31 ± 0.01 V.\textsuperscript{30} It is also important to note that the specific applied potential does not always guarantee the same potential sensed by all single molecules owing to the inhomogeneous potential distributions in the semiconductor and at the semiconductor–electrolyte interfaces. This inhomogeneity in potential distributions arises due to the inherent roughness of the TiO$_2$ NP surface, nanoscale gradient of dielectric constants and electric conductivity, and inhomogeneous surface electric work functions.\textsuperscript{31} Electrochemical experiments were performed by a CHI 600C electrochemical analyzer (CH Instruments, Inc.), equipped with a three-electrode system connected to the home-built cell. For correlated electrochemical measurement with photon-stamping measurements the home-built cell was incorporated in the sample stage of same optical setup described above (Figure 2.6).

Figure 2.8. The schematic representation of the home-made electrochemical cell where platinum wire (red) is the counter electrode, silver wire (black) is the reference electrode, and ITO (green) is the working electrode.
2.3. Sample Preparation

2.3.1. Preparation of Semiconductor Substrate Surfaces

TiO$_2$ nanoparticles (NPs) have been prepared according to the literature procedure.$^{32}$ 20 mL of pure-water (Barnstead, EASYpure II) was acidified by hydrochloric acid (EMD Chemicals) to pH 1.5. After that, 500 mg of titanium isopropoxide (Ti(OCH-(CH$_3$)$_2$)$_4$) (Aldrich, 99.999%) was dissolved in 20 mL of 2-propanol and 2 mL of this solution was added to the acidified pure-water dropwise under vigorous stirring. A transparent solution of colloidal TiO$_2$ NP was obtained and used as they were unless indicated otherwise. Cover glasses (Fisher, 18 mm × 18 mm, thickness ~170 µm) were thoroughly cleaned by sonication in deionized water, ethanol, acetone, and deionized water, respectively, each for 20 min and then dried using a nitrogen gas before their use. The colloidal solution was spin coated on clean glass cover slips to form nanocrystalline thin films. The AFM image of the TiO$_2$ NP-coated cover glass is shown in Figure 2.9, demonstrating a homogenous coverage of TiO$_2$ nanoparticles (size range, 5-15 nm) on the glass cover slip.

![AFM image of TiO$_2$ nanoparticles on the glass cover slip. (A) Topography; (B) height profile; (C) 3D view of topography.](image)

Charged TiO$_2$ NPs are prepared using simple acid-base chemistry. The negatively charged TiO$_2$ NPs are prepared by adding aqueous sodium hydroxide to the prepared colloidal
solution and final pH is maintained $\sim 9$. At this pH, deprotonation of all surface hydroxyl group occurs and the TiO$_2$ NPs become negatively charged.

Indium tin oxide (ITO)-coated transparent coverslips (SPI Supplies; 18 mm $\times$ 18 mm; 8-12 ohms; thickness $\sim 170$ $\mu$m) were thoroughly cleaned by sonication in deionized water, acetone, isopropyl alcohol and deionized water, each for 15 minutes, and dried in a jet of nitrogen gas before their use. The AFM topographic image is shown in Figure 2.10.

![Image](image1)

**Figure 2.10.** AFM image of ITO surface. (A) Topography and (B) height profile.

For spectroelectrochemistry experiment, the transparent ITO-coated coverslip was first spin-coated with TiO$_2$ NP solution (25 $\mu$L, 0.62 $\mu$M) at 3000 rpm followed by overlaying 25 $\mu$L of 0.1 nM $m$-ZnTCPP in ethanol. The morphology of the sample surface is shown in Figure 2.11.
Figure 2.11. AFM images of 0.62 μM colloidal TiO$_2$ nanoparticles solution spin-coated on ITO-coated coverslip: (a) before washing with water and (b) after washing with water, showing no morphological change of the sample surface after washing with water. (c) and (d) are topographic profiles along the line indicated in (a) and (b). (e) and (f) are 3D views of images (a) and (b), respectively. All the images are obtained by tapping mode in air.

2.3.2. Dyes and Solvents

Zn(II)-5,10,15,20-tetra (4-carboxyphenyl) porphyrin ($p$-ZnTCPP), Zn(II)-5,10,15,20-tetra (3-carboxyphenyl) porphyrin ($m$-ZnTCPP), and Zn(II) meso-Tetra (N-methyl-4-pyridyl) Porphine Tetrachloride (ZnTMPyP) were purchased from Frontier Scientific, Inc. (R & D purpose only). Dye structures are shown in Figure 2.12.

Figure 2.12. Structures of zinc porphyrin sensitizers used in this dissertation work.
Ethanol (200 proof, anhydrous ≥ 99.5 %), acetone (CHROMASOLV® Plus, for HPLC, ≥ 99.5 %, Aldrich), and poly(methylmethacrylate) (PMMA) (MW 15000 gmol\(^{-1}\)) were purchased from Aldrich. All the reagents were used as received.

The porphyrin dyes are selected because they have high fluorescence quantum yield and the molecular extinction coefficient which are essential requirements for single-molecule detection. Also, dyes absorption and emission wavelengths are appropriate for the excitation source and emission detectors used in this work. The UV-vis absorption and emission spectra of \(m\)-ZnTCPP in ethanol and in TiO\(_2\) NPs solution are shown in Figure 2.13. The absorption band consists of soret band (\(S_0\)–\(S_2\) transition) at ∼420 nm and Q bands (\(S_0\)–\(S_1\) transition) over the range of 520–650 nm, typical for porphyrin solutions. The emission spectrum covers the wavelength range from 570 to 750 nm with emission maximum at 620 nm. It should be also noted that the absorption and emission features for \(p\)-ZnTCPP and \(m\)-ZnTCPP were similar because they have same constituents and differ only in the position of –COOH group in phenyl ring which is orthogonal to the porphyrin ring plane.

![Figure 2.13. UV-vis absorption and fluorescence emission spectra of m-ZnTCPP and m-ZnTCPP bound to TiO\(_2\) in ethanol.](image)
The UV-vis absorption and emission spectra of ZnTMPyP in water and in TiO₂ NPs solution are shown in Figure 2.14. The absorption band consists of soret band (S₀–S₂ transition) at ~435 nm and Q bands (S₀–S₁ transition) over the range of 500–650 nm, typical for porphyrin solutions. The emission spectrum covers the wavelength range from 550 to 700 nm with emission maximum at 630 nm.

Figure 2.14. UV-vis absorption of ZnTMPyP (A) and ZnTMPyP adsorbed to TiO₂ in water (B). Fluorescence spectra of ZnTMPyP (C) in water and (D) in TiO₂ NPs aqueous solution. Emission is quenched in TiO₂ solution because of electron transfer from ZnTMPyP to TiO₂ NPs.

2.3.3. Sample Preparation for Single-Molecule Experiment

For the single-molecule experiments, we prepared the sample following earlier reported works. For a control experiment, 25 µL of 0.1 nM dye dissolved in suitable solvent was first spin coated on a clean cover glass at 3000 rpm and covered by spin coating 50 µL PMMA (in CH₂Cl₂, 1 mg/mL) to form a thin film to protect the dye molecules from singlet O₂ photobleaching. The sample of dye on TiO₂ NPs for interfacial ET study, was prepared by spin coating of 25 µL of 0.1 nM dye on TiO₂ NP-coated cover glass at 3000 rpm followed by overlaying 50 µL PMMA (in CH₂Cl₂, 1 mg/mL) by spin coating at 3000 rpm. p-ZnTCPP and m-ZnTCPP were dissolved in ethanol whereas ZnTMPyP was dissolved in water. To consider
purity of the reagents used and their effect on spectroscopic measurements, a confocal image from a control experiment is shown (Figure 2.15), where a blank solvent solution is spin coated on a clean cover glass followed by spin coating 50 µL PMMA (in CH₂Cl₂, 1 mg/mL) to form a thin film.

![Confocal fluorescence images](image)

**Figure 2.15.** The Confocal fluorescence image of a blank ethanol solution spin coated on a clean cover glass followed by spin coating 50 µL PMMA (in CH₂Cl₂, 1 mg/mL) to form a thin film is displayed in (A). The Confocal fluorescence image of \( m \)-ZnTCPP on bare cover glass is displayed in (B) for comparison (Image Size: 20 × 20 µm²).

### 2.4. Correlation between Fluorescence Blinking and Interfacial Electron Transfer Dynamics

In photoinduced interfacial ET, the dye molecules are electronically excited through light absorption, permitting ET to the conduction band (Figure 2.16). Studying interfacial ET dynamics from single molecules has been an appealing and challenging effort since the first report observed single molecule ET dynamics in 1997, when Lu and Xie studied ET from single cresyl violet molecules to indium tin oxide (ITO) which demonstrated the capability to detect single molecule ET dynamics using single-molecule fluorescence spectroscopy.¹¹ A wide distribution of ET rates caused by the inhomogeneity of molecular interactions on the semiconductor surface was observed in their experiments and was used to explain the physical origin of the multiexponential kinetics of ET.³³
Figure 2.16. Schematic representation of energy levels and basic photoinduced process in dye–
TiO$_2$ system. FET, forward electron transfer; BET, back electron transfer; CB, conduction band;
VB, valence band; S, singlet state; T, triplet state; ISC, intersystem crossing.

More recently, Lu and coworkers reported studies on single molecule ET dynamics for
cresyl-violet, coumarin and porphyrin molecules on TiO$_2$ nanoparticles.$^{16,28,29,34-36}$ These
molecules on TiO$_2$ exhibited vigorous fluctuations in fluorescence intensities between higher and
lower level, and the ET times estimated by the fluorescence lifetimes were much slower than
those measured by ensemble averaged transient absorption spectroscopy.$^{37-42}$ To explain the
discrepancy between single molecule and ensemble average measurements, it has been suggested
that the ET rate on TiO$_2$ fluctuated between slow and fast kinetics. It is unlikely that interfacial
ET processes are completely turned “on” and “off” during the periods of the lower and higher
fluorescence intensity states, respectively, it rather includes occurrences of multiple FET and
BET events. In the “bright” state, molecules underwent slow (or no) ET and the fluorescence
intensities were high, and thus all detected fluorescence photons originated from the slow
injecting states. In the “dark” state, however, the molecules were undergoing ultrafast ET, but the fluorescence quantum yield of the fast injecting state was too low to be observed.\textsuperscript{43}

The molecular fluorescence intensity is typically characterized by the fluorescence quantum yield ($Q$) of the molecules. The value of $Q$ is determined by the ratio of the number of emission photons to the number of excitation photons absorbed under stable excitation photon flux. Therefore, the single-molecule fluorescence intensity fluctuation, reflected by $Q$ value fluctuation, is due to the emission photon number density fluctuation. The probability of an emission transition from the $S_1$ excited state depends on both radiative decay rate constant, $k_r$ and nonradiative decay rate constant, $k_{nr}$. The quantum yield of a dye molecule undergoing ET is:

\begin{equation}
Q = \frac{k_r}{(k_r + k_{nr})}
\end{equation}

Once an excitation photon is absorbed, a single dye molecule is excited from $S_0$ ground state to the $S_1$ excited state (Figure 2.16). If there is no nonradiative decay process ($k_{nr} = 0$) or the nonradiative decay is much slower than the radiative decay ($k_{nr} \ll k_r$), then the $Q = 1$ and the chromophore is bright. If the nonradiative decay is much faster ($k_{nr} \gg k_r$), then the $Q \to 0$ and the chromophore becomes dark. As there is always a nonradiative decay process, and the decay time can be comparable to the radiative decay time, the $Q$ has a finite value between 0 and 1. In a dye–TiO$_2$ NP system, radiative rate constant is:

\begin{equation}
k_r = \frac{1}{\tau}
\end{equation}

where $\tau$ is fluorescence lifetime, and $k_{nr}$ is dominated by FET time of femtoseconds to picoseconds as both the internal conversion from $S_1$ to $S_0$ (nanoseconds to microseconds) and the intersystem cross from $S_1$ to $T_1$ state (several nanoseconds) are much slower (Figure 2.16). The
natural fluorescence lifetime is unlikely to fluctuate at milliseconds to seconds under the single-molecule experimental condition; therefore, it is the nonradiative rate fluctuation that contributes to the Q fluctuation, which in turn contributes to the fluorescence intensity fluctuation (for example, Figure 2.17).\textsuperscript{16,31,43,44}

A prominent property of dye molecules is their fluorescence intermittence, known as blinking. This phenomenon is buried in ensemble fluorescence detection and can only be probed by using single-molecule measurements. Shown in Figure 2.17 is a typical fluorescence intensity trajectory of a single dye molecule on TiO\textsubscript{2} NP surface, presenting a strong fluorescence fluctuation between high intensity (defined as the bright state) and low intensity (defined as the dark state) levels. This blinking activity is attributed to the photoinduced transfer of an electron from molecule to the semiconductor accepting states.\textsuperscript{44}

**Figure 2.17.** A representative fluorescence intensity trajectory of a single dye molecule on TiO\textsubscript{2}. “Bright” episodes are denoted by $\tau_{\text{bright}}$ and are defined as dominant fluorescence events occurring above a predefined intensity threshold shown by the dashed line. “Dark” episodes are denoted by $\tau_{\text{dark}}$ and represent periods where background counts are seen.

One well-known source of blinking in dye-semiconductor systems is an electron transfer from an excited singlet state ($S_1$) to a semiconductor conduction band (CB), followed by back electron transfer from CB to the ground state ($S_0$). The bright-time and dark-time durations of
this process are distributed over milliseconds to several hundred seconds. Blinking can also occur by intersystem crossing (ISC) from excited singlet state \( (S_1) \) to triplet state \( (T_1) \), typically referred as “triplet blinking”. Former blinking mechanism and dynamics is particularly important as it reflects the charge transfer dynamics.

Furthermore, several alternative physical origins for blinking in condensed phase systems have been proposed. One involves physical rotation of the molecular transition dipole relative to the polarization of the incoming laser, which, in turn, causes fluctuations in the amount of absorbed and emitted light. However, polarized light measurements suggest this is not the case, as similar blinking dynamics are observed for both linear and circular polarization. Another possible explanation for blinking is spectral diffusion of the molecular absorption profile, which causes fluctuations in the emission intensity as the transition shifts into and out of resonance with the laser excitation. The influence of spectral diffusion would be greatest at low temperatures where the absorption linewidths are very narrow and, indeed, accounts for some of the intensity fluctuations observed in this regime. However, such a mechanism would be unlikely at room temperature, where the much larger linewidths require extremely large shifts ~50 nm in the absorption spectrum to account for the observed “bright”/“dark” blinking behavior.

For the dark to bright transition two different mechanisms have been proposed in the literature to explain blinking dynamics: (1) distribution of tunneling barriers for the ejected electron to return to the dye cation from a distribution of trap depths or (2) a diffusion of the ejected electron in the semiconductor to return to the dye cation. In any case more detailed information on the injection/recombination steps in the dye-sensitized semiconductor system should be obtainable from single molecular studies.\textsuperscript{45,46} The above two classes of mechanisms
have also been proposed previously as alternative interpretations of the intermittent fluorescence “blinking” of quantum dots.\(^{46-48}\)

Therefore, fluorescence blinking of molecule is not an independent activity, but is related to other photophysical and photochemical processes. Therefore, the presence of dye blinking activities triggers important fundamental questions about the interfacial ET to and from dyes. How does this blinking activity affect the interfacial ET dynamics? How does the interfacial ET influence the fluorescence properties of dyes? Are there any correlations between blinking and interfacial ET dynamics? How do the properties of semiconductor oxide substrates affect the blinking and ET processes?\(^{44}\)

In an effort to explore the answers for the above mentioned questions, the research presented in this dissertation focuses on the single molecule ET and blinking dynamics in dye–semiconductor oxide system.

### 2.5. Statistical Analyses of Single-Molecule Fluorescence Trajectories

The fascinating phenomenon known as fluorescence blinking has attracted much attention over the past 20 years for its role in single-molecule/single-particle detection.\(^{28,30,44-64}\)

Recently, there have been many single molecule studies of the fluorescence intermittency of a single photoexcited dye molecule on a semiconductor nanoparticle system or on a crystal surface.\(^{44,46,59,61,62}\) Fluorescence blinking of dye molecules is characterized by switching between the “bright” and “dark” periods over time. The blinking statistics (i.e., the bright-time and dark-time distributions) have been extensively utilized to understand the photophysics underlying the blinking behavior\(^{16,54,57,65}\) and the fluctuation dynamics of local environments encompassing single emitters. There has been a large body of work on statistical analyses of the single-molecule fluorescence trajectories. Most of the work has been in the framework of chemical
kinetics, analyzing the histograms of the bright and dark periods of the single molecules. Wang and Wolynes first discussed the role of analyses of single-molecule trajectories in understanding chemical dynamics (as opposed to chemical kinetics) on the basis of non-Poisson statistics. They pointed out that single-molecule experiment would be expected to show non-Poisson effects causing reaction events to “bunch up”, an effect called “intermittency” and the kinetics exhibiting nonexponential behavior.66,67

To analyze the single-molecule interfacial ET dynamics that is associated with the fluctuation of the single-molecule fluorescence trajectories, a histogram of emission intensity is first constructed and then a threshold is determined (dashed line in Figure 2.17). To do that, background counts in the dark region of the trajectory after photobleaching event were measured from which the average background level and its standard deviation σ were got. The threshold was defined typically at 2σ to 3σ higher than the average background level. The time durations of the dark or bright states are then obtained. Then we can go through the trace and generate the histogram of number of counts versus the duration of each “bright” and “dark” state. Wide range of the dark states duration and nonexponential dark time distributions has been observed for non-Poisson behavior of single molecules. This non-Poisson dark/bright time distribution suggests that the intrinsic physical mechanism is not originated from a single Poisson event under an exponential rate dynamics, which reflects that the interfacial ET involves complex rate process that cannot be defined by a static rate constant and the rate changes from time to time.

To analyze the ET reactivity fluctuation dynamics associated with the non-Poisson dark/bright time distributions, one can generate the dark/bright time probability densities:
Each data point of the histogram is weighted by the average time between nearest neighbor events (Figure 2.18).

\[
P(t) = \frac{\text{Occurrence}(t)}{\Delta t}
\]  

(2.3)

**Figure 2.18.** Example of generating bright/dark time probability density (lower panel) from a histogramic analysis (upper panel) of distributions. All points in \( P(t) \) are weighted by a value representing the average distance to nearest neighbor events. For example, the event occurring with a duration of 0.9 s is weighted by the algebraic mean \([(a+b)/2]\) yielding the point in the bottom panel.
In various systems, semilogarithmic plots of the single-molecule dark-time probability density distributions typically follow inverse power-law behavior:

\[ P(t) \propto t^{-m} \]  

(2.4)

where \( P(t) \) denotes the probability density function and power-law exponent \( m \) usually ranges from 1 to 3. In power-law kinetics, the time constant is not fixed, but varies with time. The power-law dark-time statistics of the charge-transfer-induced blinking have often been reported and understood well, whereas the bright-time kinetics appears to be complex and debatable.\(^{47,64,68}\)

From a histogramic analysis of the bright-time and dark-time probability densities \( P(t_{\text{bright}}), P(t_{\text{dark}}) \), one can extract meaningful values for electron injection/recombination rates from/to a single molecule. The situation becomes more complicated in dye–semiconductor systems, because a continuum manifold of states may be involved in the blinking process, potentially resulting in nonexponential behavior and an enormously large dynamic range of bright-time/dark-time probability densities.

To further understand the ET reactivity fluctuation and the dark/bright state properties, one can calculate the autocorrelation functions of the single-molecule fluorescence intensity trajectories. Most of the autocorrelation functions show nonexponential decays. The autocorrelation function (ACF) is defined as:

\[ C(t) = \frac{\langle (I(0) - \langle I \rangle)(I(t) - \langle I \rangle) \rangle}{\langle (I(0) - \langle I \rangle)^2 \rangle} \]  

(2.5)

where \( I(0) \) and \( I(t) \) represent the fluorescence intensity (photon count) of single-molecule fluorescence intensity trajectories at time zero and at time \( t \) respectively, \( \langle I \rangle \) is the mean of the intensities of single-molecule fluorescence intensity trajectories. The nonexponential
autocorrelation function indicates the dynamic disorder of the interfacial ET reactivity, that is, the reactivity fluctuation rate changes from time to time during a single-molecule measurement.

Both the autocorrelation function decay time and the power-law exponent are critical factors characterizing the interfacial ET reactivity fluctuation dynamics. These two parameters correspond to the basic properties of single-molecule fluorescence fluctuations. The autocorrelation function fluctuation time $\tau$ represents the ET reactivity fluctuation time, and the power-law exponent $m$ represents nonexponential distribution nature of the probability of the dark/bright times. The $\tau$ determines the fluctuation timescale for a single molecule to shift from a bright state to a dark state statistically. Although power-law exponent indicates the relative probability for the dark/bright state duration: a larger $m$ suggests a relatively higher distribution probability for a shorter dark/bright time states.

For a power-law distribution, the distribution is dominant by Lévy statistics at $1 < 1+\alpha < 2$:

$$P(t) \propto t^{-(1+\alpha)} \quad 0 < \alpha < 1$$

(2.6)

Lévy statistics is usually observed in complex systems with nonlinear interactions, such as in physics and biology. Its typical characteristic is the diverging variance and a broad distribution expressed by power-law rule. In single-molecule spectroscopy, Lévy statistics has been extensively investigated in the blinking dynamics of quantum dots.$^{51,53}$ In case of interfacial ET, Lévy statistics has been used to describe the complex interfacial site- and time-specific interactions between single molecules and nanoscale local environments.$^{16}$

2.6. Summary

In summary, both forward and back interfacial ET dynamics in dye-semiconductor systems have been investigated by using single-molecule photon-stamping spectroscopy. These
studies on the single molecule or single particle level are essential because they can reveal static and dynamic heterogeneities that remain hidden in ensemble measurements and provide detailed insights into the electron transfer process.

The rest of this dissertation is organized as follows: Chapter 3 introduces the electronic coupling dependent single-molecule forward interfacial ET dynamics in covalently and electrostatically attached porphyrins on TiO$_2$ NPs. Chapter 4 contains the detailed investigation of forward and back electron transfer dynamics modulated by external bias in $m$-ZnTCP–TiO$_2$ NP system. Chapter 5 focuses on studies of BET dynamics in $m$-ZnTCP–TiO$_2$ NP and $m$-ZnTCP–ITO systems. Chapter 6 describes the density function theory (DFT) Raman calculations in alizarin–TiO$_2$ system to explain the effect of electric filed on interfacial covalent bond. All works have been done and reported in various peer-reviewed scientific journals.\textsuperscript{34-36,69,70}

2.7. References


(22) Brakenhoff, G. J.; Blom, P.; Barends, P. J.; Bakker, C. *Ultramicroscopy* **1979**, *4*, 115.


CHAPTER 3. ELECTRONIC COUPLING DEPENDENT SINGLE-MOLECULE INTERFACIAL ELECTRON TRANSFER DYNAMICS

The multiexponential kinetics observed in ensemble studies indicate a broad range of ET rates in dye–semiconductor systems, which may originate from static heterogeneities in the energetics of the adsorbate and semiconductor, static heterogeneities in the electronic coupling between the adsorbate and semiconductor, and dynamic fluctuations of the energetics and electronic coupling. The inhomogeneities in the interfacial ET necessitate to investigate the role of each ET controlling parameters in single-molecule as it reveals the static and dynamic information hidden in ensemble measurement. This chapter contains the studies on effect of molecular structure, molecular environment, and molecule–substrate electronic coupling in interfacial ET dynamics. The results have been published in American Chemical Society journals.

3.1. Single-Molecule Interfacial Electron Transfer Dynamics of Porphyrin on TiO$_2$ Nanoparticles: Dissecting the Complex Electronic Coupling Dependent Dynamics

3.1.1. Introduction

Interfacial electron transfer plays a critical role in surface chemistry, catalysis, and solar energy conversion, including solar photovoltaic and solar fuel science and technology.$^{1-18}$ However, typical interfacial ET dynamics in such chemical systems often involve temporal fluctuations and nanoscale spatial heterogeneities, i.e., the dynamic disorder and static disorder,$^{7,9,19}$ presenting a high challenge for ensemble-averaged experiments for a molecular level characterization. To optimize the factors that influence interfacial electron transfer dynamics, it is essential to first experimentally measure the effects of the key physical parameters on the interfacial electron transfer dynamics. The parameters which greatly influence...
ET dynamics include electronic coupling between the molecule and semiconductor, vibrational relaxation energy of adsorbed molecule, solvent reorganization energy, driving force of the free energy gap, the surface structures, and the defect surface states. Presumably, the understanding should come from both spatially larger scales for distributions and domain as well as from molecular scales for molecular structures of both the molecules and the substrate surfaces. Dye-sensitized solar cell (DSSC) systems containing a semiconductor with wide band gap, such as TiO$_2$, SnO$_2$, ZrO$_2$, and ZnO, have wider applications in solar energy conversion systems in the development of the solar photovoltaic, solar fuel, and photocatalytic environmental sciences and technology.

In general, a typical DSSC system consists of a dye molecule anchored to the semiconductor TiO$_2$ nanoparticle surface through an anchoring group of the dye. Upon excitation, an electron populates lowest unoccupied molecular orbital (LUMO) and initiates the forward electron transfer (FET) from the molecular excited states to the conduction band or energetically accessible surface states of semiconductor nanoparticles (NPs). Following FET, the injected electrons go through different semiconductor processes such as charge trapping, detrapping, and electron Brownian and non-Brownian diffusion before (i) recombination with parent cation (back ET, BET) or (ii) diffusion away to generate photovoltaic potential energy. Unlike FET dynamics, which are predominately ultrafast in the femtosecond to several hundred picoseconds range, BET dynamics is often nonexponential or stretched exponential ranging from sub-nanoseconds to several milliseconds.

The interfacial ET dynamics were found to be inhomogeneous from molecule to molecule and at various time points, showing significant static and dynamic disorder that is
difficult to analyze by conventional ensemble-averaged measurements. Generally, ensemble-averaged measurements often encounter interferences from molecular aggregation, multiple electron injection to a single particle and multiple electron cation recombinations on the surface of a single particle. Single-molecule spectroscopy coupled with scanning confocal fluorescence microscopy and photon-stamping technique is capable of studying one molecule at a time in a specific nanoscale local environment.

The electronic coupling strength between excited states of dye molecule and the semiconductor can be modified through a number of ways including (i) the use of a bridge between the chromophore and the anchoring group of the dye molecule; (ii) the use of different anchoring groups, such as carboxylic acid, hydroxyl, sulphonic acid, phosphonic acid, salicylate, and acetylacetonate derivatives; and by (iii) the use of different numbers of anchoring groups such as bipodal, tripodal, and tetrapodal. Carboxylic acid and phosphonic acid functionalities have been shown to be the most effective anchoring groups from which, the carboxylic acid anchor has emerged as the most popular and widely used choice. The mode of attachment and the position of these anchoring groups also affect the coupling strength between the excited states of the dye molecule and the semiconductor. In this manuscript we have probed the effect of anchoring group position on interfacial ET dynamics. The interfacial ET between different derivatives of ZnTCPP on TiO$_2$ has been extensively studied at the ensemble-averaged level. For example, using different derivatives of ZnTCPP as a sensitizer an efficiency as high as 12 to 13% was reported. These studies demonstrated the ZnTCPP-TiO$_2$ system as an efficient photosensitization solar energy conversion system. It has been also shown that the position of the carboxylic acid anchoring groups on the meso-phenyl rings of the porphyrin macrocycle plays an important role on the binding mode and as a
result on the electronic coupling of dye-TiO$_2$ and other fundamental properties regulating the interfacial electron transfer dynamics.$^{40,86}$ In our previous report, the interfacial ET dynamics of Zn(II)-5,10,15,20-tetra (4-carboxyphenyl) porphyrin ($p$-ZnTCPP)-TiO$_2$ nanoparticle (NP) system was studied at the single-molecule level.$^7$ Based on our earlier reports,$^{79,80}$ we concluded that the highly inhomogeneous ET dynamics are commonly observed in interfacial chemical reactions, strongly regulated by the molecular interaction between adsorbed molecule and substrate surface. Rochford et al.$^{40}$ studied the photoelectrochemical properties of $m$-ZnTCPP and $p$-ZnTCPP on different metal oxides surfaces. Their studies suggest that the four anchoring groups (-COOH group) in the meta-position of meso-phenyl rings of the porphyrin macrocycle get directly attached to metal oxide surface and facilitate a planar binding geometry (Figure 3.1).$^{40,86}$ The computer modeling, which also study these molecules on a single molecular level predict planar vs standing conformation of the $m$-ZnTCPP vs $p$-ZnTCPP.$^{40,88}$ Carrying out different ensemble-averaged experiments, Rochford et al.$^{40}$ also demonstrated higher photocurrent conversion efficiency of $m$-ZnTCPP compared to the $p$-ZnTCPP. Although bulk properties provide useful information about the system of interest, the static disorder and dynamic disorder can be better characterized by single-molecule spectroscopy experiments as powerful and complementary approaches.$^{74-77,79,80}$ Here, we report our studies of single-molecule interfacial electron transfer dynamics and mechanism of Zn(II)-5,10,15,20-tetra (3-carboxyphenyl) porphyrin ($m$-ZnTCPP)–TiO$_2$ nanoparticle (NP) system by specifically probing the effect of anchoring group position (meta or para) hence molecular interaction between dye-TiO$_2$ nanoparticle on the inhomogeneous interfacial ET reactivity.
The different molecular binding geometry on TiO$_2$ surface contributes to different electronic coupling between the molecules and the substrate, and in turn, contributes to different interfacial electron transfer rate processes.

3.1.2. Experimental Section

The detailed description of the experimental setup and sample preparation is given in Chapter 2.

3.1.3. Results and Discussion

The interfacial ET across dye molecule–semiconductor interface represents one of the most important chemical processes in surface redox chemistry, photocatalysis, and solar energy conversion. Sufficient understanding of interfacial ET reactivity and factors influencing the ET reactivity is crucial to fundamental sciences as well as to solar cell and solar fuel technology developments. Earlier, we reported our work on systematic investigation and analysis of single-molecule interfacial electron transfer dynamics regulated by vibrational relaxation energy, vibronic coupling, and Franck-Condon factors.\textsuperscript{79,80,90-93} We have revealed the high
inhomogeneity of the vibrational relaxation energy and characterized the inhomogeneity’s impact on the measured static and dynamic disordered single-molecule interfacial electron transfer dynamics. Identifying the intermittency\textsuperscript{94-97} of the single-molecule interfacial electron transfer dynamics, we advanced a critical understanding of the complex nonexponential interfacial electron transfer dynamics reported widely over the years by time-resolved ensemble-averaged experiments from nanosecond to femtosecond time scales.\textsuperscript{79,80,91-93} Here we advance the understanding of interfacial ET reactivity by showing the effect of molecule-TiO\textsubscript{2} surface interactions on interfacial ET dynamics using single–molecule spectroscopy, aiming to shed light on the electronic coupling dependence of the interfacial electron transfer dynamics. Parts A and B of Figure 3.2 show the single-molecule fluorescence images of \textit{m}-ZnTCPP on bare cover glass and TiO\textsubscript{2} NPs-coated cover glass, respectively. Figure 3.2C displays the fluorescence emission trajectories of \textit{m}-ZnTCPP on bare cover glass, which shows a nearly constant level of fluorescence intensity before photobleaching occurs. Parts D, F, and H of Figure 3.2 show fluorescence emission trajectories of \textit{m}-ZnTCPP on TiO\textsubscript{2} NPs-coated cover glass, which show strong fluctuations and blinking between bright and dark states (histograms of the emission intensity in Figure 3.2E,G,I are shown to determine the threshold for dark and bright states) as opposed to a relatively stable emission on bare cover glass. For higher-level emission intensity we have used the term “bright” and for lower-level emission intensity we have used the term “dark”, because in all the fluorescence emission trajectories lower-level emission intensity is almost equal to the background level. Similar single-molecule fluorescence intensity fluctuation and blinking between bright and dark states were also observed in our previous works on Coumarin 343/TiO\textsubscript{2},\textsuperscript{9} \textit{p}-ZnTCPP/TiO\textsubscript{2},\textsuperscript{79} and PF/TiO\textsubscript{2}.\textsuperscript{80}
**Figure 3.2.** Confocal Fluorescence images of *m*-ZnTCPP on (A) bare cover glass and (B) TiO$_2$ NPs-coated cover glass (Image Sizes: 20 µm x 20 µm and 100 x 100 pixels). Fluorescence emission trajectories of *m*-ZnTCPP on (C) bare cover glass and (D, F, H) TiO$_2$ NPs-coated cover glass. Histograms of the emission intensity (E, G, I) are shown to determine the threshold for bright and dark states.
We recorded the fluorescence emission trajectories of more than 100 molecules of \(m\)-ZnTCPP on TiO\(_2\) NP-coated cover glass. The single-molecule fluorescence time trajectories have the essential feature of blinking between the bright states and the dark states. In our previous reports,\(^9,79,80\) we have determined that the blinking behavior is predominately a consequence of the fluctuating interfacial electron transfer rate, and for each intensity bin of a few milliseconds, multiple electron transfer events occur and interfacial ET results in dark state of the molecules. For each photoexcitation, the excited state of the single-molecule either undergoes radiative emission to yield a photon that contributes to a bright state or undergoes a non-radiative electron transfer process that contributes to the dark state (Figure 3.3). The ratio between the radiative and non-radiative rate processes, ultimately determined by the radiative rate of \(\sim\)nanoseconds vs the non-radiative rate of shorter than nanosecond down to femtoseconds that is regulated by the coupling between the molecule and the substrate.

**Figure 3.3.** Schematic diagram showing energy levels and photoinduced processes involved in ZnTCPP/TiO\(_2\) system. CB: conduction band; VB: Valence band; ISC: intersystem crossing. In ZnTCPP/TiO\(_2\) system the photoexcited single-molecule involves either radiative emission to
yield a photon that contributes to a bright state or involves a non-radiative electron transfer process that contributes to the dark state.

The trend of fluorescence emission trajectories of single molecules shows about 70% of the molecules follow the trace dominated by dark state as shown in Figure 3.2D, and 10-20% of the molecules follow the trace, where dominance of dark state is less prominence (like traces shown in Figure 3.2F,H). For majority of the molecules, the dark state is dominant in their single-molecule fluorescence trajectories, which indicates strong interaction of m-ZnTCPP with TiO₂ compared to that of p-ZnTCPP where the dark state is significantly less dominating. Evidently, m-ZnTCPP on TiO₂ has more active electron transfer such that the fluorescence process is suppressed. This difference in the behavior of m-ZnTCPP and p-ZnTCPP can be accounted for by the difference in the binding mode (Figure 3.1), hence the electronic coupling between the adsorbed molecules and TiO₂. Another possible explanation could have been attributed to the different ground state electronic nature of m-ZnTCPP and p-ZnTCPP. However, the position of the carboxyl anchoring groups has little influence in the ground-state electronic nature of the molecule, because of the orthogonal orientation of the meso-phenyl rings of the porphyrin macrocycle, evidenced by similar absorption spectra of the m-ZnTCPP and p-ZnTCPP.

Following our earlier study on interfacial electron transfer dynamics of p-ZnTCPP on TiO₂, it can be said that the fluctuation of fluorescence is not due to the rotation or translational motions of the single molecules. The covalently anchored molecules through multiple carboxylic groups do not have the flexibility of rotational or translation motions. Additionally, the long dark-time (Figure 3.2D,F,H) certainly shows that the fluctuation of fluorescence is not due to the triplet state; because the triplet state lifetime of ZnTCPP dye lies close to 1 millisecond.
Therefore, we can conclude that the dark states in fluorescence intensity trajectories of \( m \)-ZnTCPP on TiO\(_2\) originate due to the high ET reactivity, which quench the S\(_1\)-S\(_0\) radiative emission, and the bright states originate due to the low ET reactivity leaving the S\(_1\)-S\(_0\) radiative emission dominant, the same conclusion as we reported for the \( p \)-ZnTCPP on TiO\(_2\).\(^9,\)\(^{79}\)

For further understanding about the ET reactivity fluctuation and to explain the observed difference in the behavior of \( m \)-ZnTCPP and \( p \)-ZnTCPP, we measured fluorescence lifetimes of single molecules using single-molecule photon-stamping spectroscopy (Figure 3.4). Figure 3.4A shows fluorescence emission trajectory of \( m \)-ZnTCPP on TiO\(_2\) NPs-coated cover glass and Figure 3.4B shows histogram of the emission intensity to determine the threshold for dark and bright states. To determine the threshold for dark and bright states, the average background level (after photobleaching step) and its standard deviation \( \sigma \) were determined first and then the threshold was defined typically at 3\( \sigma \) higher than the average background level. The fluorescence emission trajectory of Figure 3.4A is separated to higher-level emission (marked as 1) and lower-level emission (marked as 2) based on a threshold of 77 photon-counts/50 ms. In single-molecule photon-stamping measurement, for each detected photon (each data point in Figure 3.4C,E represents a detected photon) two parameters were recorded: chronic arrival time (x-axis of Figure 3.4C,E) and delay time between the laser pulse excitation and the photon emission from the excited state (y-axis of Figure 3.4C,E). The histograms of chronic arrival times yield fluorescence intensity trajectories with a given time bin resolution and the distribution of the delay times give a typical single-molecule fluorescence decay curve.\(^9,\)\(^{79,\)\(^{80}\) The single-molecule fluorescence lifetime was analyzed for both the higher-level emission intensity and lower-level emission intensity.
**Figure 3.4.** Single-molecule fluorescence decay profile of \(m\)-ZnTCPP on TiO\(_2\) NP surface. The fluorescence emission trajectory of \(m\)-ZnTCPP on TiO\(_2\) NPs-coated cover glass and histogram of the emission intensity are displayed in (A) and (B). (C, E) and (D, F) show the photon-stamping data and corresponding histogram for a typical bright state (in “blue”, 9.0–10.0 s) and dark state (in “red”, 7.5–8.5 s). The fluorescence decay profiles of higher-level emission and lower-level emission of the whole trajectory are displayed in (G) and (H). The fit to the decay profiles (solid line) shown in (G) and (H) are biexponential fit derived by deconvolution of instrument response function (IRF).
Parts C, E, and D, F of Figure 3.4 show the photon-stamping data including chronic arrival time and delay time for each photon, and corresponding histograms respectively, for a typical bright state (in “blue”, 9.0–10.0 s) and dark state (in “red”, 7.5–8.5 s). The distributions of delay times of these two typical blinking states are different. The lifetime analysis for higher-level emission and lower-level emission of the whole trajectory is shown in Figure 3.4G,H, respectively. These single-molecule fluorescence decay curves were derived from the distribution of the delay times for higher-level emission’s and lower-level emission’s photon-stamping data of the whole trajectory. The lifetime derived from the higher-level emission intensity shows 3.48 times longer lifetime (3.90 ± 0.15 ns) than the lifetime derived from the lower-level emission intensity (1.12 ± 0.10 ns). These observations clearly indicate that the fluorescence quenching is the result of FET from excited state of the adsorbate m-ZnTCPP to the TiO$_2$ NPs. The emission intensity fluctuations further demonstrate the ET reactivity fluctuation.

For p-ZnTCPP on TiO$_2$, the lifetime derived from the higher-level emission intensity is nearly similar to the lifetime derived from the lower-level emission intensity. Contrastingly, m-ZnTCPP on TiO$_2$ shows 3.48 times shorter lifetime in case of lower-level emission intensity when the ET activity is high compared to the lifetime derived from the higher-level emission intensity when the radiative emission is dominated and ET activity is low. These observations suggest greater charge injection efficiency of m-ZnTCPP compared to the p-ZnTCPP. The difference in the ET activity of m-ZnTCPP and p-ZnTCPP can be accounted for by the difference in the binding mode (Figure 3.1): the four anchoring groups (COOH) in the meta-position of the meso-phenyl rings of the porphyrin macrocycle of m-ZnTCPP favors a planar binding mode to the TiO$_2$ surface, decreasing the distance between the molecule transition dipole and TiO$_2$ surface, which in turn favors the greater electronic coupling between the
molecule and TiO$_2$ as well as the charge injection efficiency. The greater charge injection efficiency with the decreasing distance between the sensitizer and TiO$_2$ surface is well supported by earlier reports, where it has been shown that the ET rate decays exponentially with the increasing bridge length between sensitizer and TiO$_2$ surface.$^{98-100}$ The molecular motions or the flexibility of the adsorbed molecule on semiconductor surface also influence the electronic coupling, and thus, the ET dynamics.$^{101}$ The four covalent anchor points of $m$-ZnTCPP compared to that of one or two covalent anchor points in case of $p$-ZnTCPP$^{40,86,88}$ is expected to pose greater restriction on the movement of $m$-ZnTCPP than $p$-ZnTCPP. Therefore, the higher restrictive motion of $m$-ZnTCPP on TiO$_2$ NP surface can also be considered responsible for the greater charge injection efficiency compared to that of $p$-ZnTCPP.

Although, we are not able to measure the ultrafast FET directly by single-molecule experiments in this work, the fluctuation in ET reactivity is well reflected in fluorescence emission trajectories and lifetime analysis of single molecules. Fluctuations in ET reactivity at different time points cause fluorescence blinking in individual molecules. That is why these molecules can still be observed by single-molecule imaging at single-photon counting sensitivity. The visibility of single molecules indicates that the FET time apparently fluctuates in a wide time scale from fs to ns or even slower. Had the timescale of the nonradiative decay (FET) been in fs to ps range only, the excited-state radiative emission efficiency should have been as low as $10^{-3}$ to $10^{-6}$, and the single molecules should be essentially nonfluorescent or not observable by photon detection. Here, it is also important to mention that in all our measurements we only consider those molecules which are visible. It is also interesting to note that the highly inhomogeneous interfacial electron transfer processes are widely noticeable in the ensemble-averaged time-resolved data in the literature, for example, there often are long background in the
time-resolved spectroscopic data that indicate a measurable amount of photons emitted thorough a slow radiative or non-radiative excited state process at even ns time scale. Nevertheless, the ET does not always dominate the excited state process of the \( m \)-ZnTCPP/TiO\(_2\) system. In fact, single-molecule interfacial ET processes in \( m/p \)-ZnTCPP/TiO\(_2\) systems were found to be inhomogeneous, both dynamically and statically. The static inhomogeneity is associated with the difference observed in interfacial ET reactivity fluctuation from molecule to molecule, whereas the dynamic inhomogeneity is associated with the difference observed in interfacial ET reactivity fluctuation from time to time for a same individual molecule.

To further understand the ET reactivity fluctuation, we calculated the autocorrelation functions, \( C(t) \), of the single-molecule fluorescence intensity trajectories. The autocorrelation function (ACF) is defined as:

\[
C(t) = \frac{\langle (I(0) - \langle I \rangle)(I(t) - \langle I \rangle) \rangle}{\langle (I(0) - \langle I \rangle)^2 \rangle}
\]

(3.1)

where \( I(0) \) and \( I(t) \) represent the fluorescence intensity (photon count) of single-molecule fluorescence intensity trajectories at time zero and at time \( t \) respectively, \( \langle I \rangle \) is the mean of the intensities of single-molecule fluorescence intensity trajectories.

Similar to our earlier studied Coumarin 343/TiO\(_2\)\(^9\) and \( p \)-ZnTCPP/TiO\(_2\)\(^7\) systems, the autocorrelation functions show nonexponential decays, which indicate the dynamic disorder of the interfacial ET reactivity, i.e., the fluctuation rate changes with time. The autocorrelation functions (Figure 3.5A) were fitted using biexponential functions with autocorrelation function decay time ranging from sub-seconds to seconds (Figure 3.5B). The biexponential fit to the autocorrelation function can be accounted for by the presence of two distinct states for all visible molecules: (i) the state in which the dye molecule interact strongly with TiO\(_2\) surface leading to higher interfacial ET reactivity and dark state, (ii) the state in which the dye molecule interact
weakly with TiO$_2$ surface leading to lower interfacial ET reactivity and bright state. Figure 3.5B shows the histogram of autocorrelation function decay times ($\tau$), for 23 different molecules of $m$-ZnTCPP on TiO$_2$ NP surface.

![Figure 3.5](image)

**Figure 3.5.** (A) Autocorrelation function (ACF) trace calculated from single-molecule fluorescence intensity time trajectory of $m$-ZnTCPP on TiO$_2$ NP surface. (B) Histogram of autocorrelation function decay times ($\tau$), for 23 different molecules of $m$-ZnTCPP on TiO$_2$ NP surface.

The distribution of autocorrelation function decay times for $m$-ZnTCPP molecules shows that the decay times for most molecules lie between 1-6 s, whereas in case of $p$-ZnTCPP most molecules exhibit decay times between 0.1-0.4 s (the histogram of autocorrelation function decay times ($\tau$) for $p$-ZnTCPP on TiO$_2$ NP surface is displayed in Figure 3.6.$^{79}$
Figure 3.6. Histograms of autocorrelation function decay times ($\tau$) for $m$-ZnTCPP and $p$-ZnTCPP on TiO$_2$ NP surface. The Histogram of autocorrelation function decay times ($\tau$) for $p$-ZnTCPP on TiO$_2$ NP surface is displayed for comparison only (Adapted with permission from ref. 79. Copyright 2014 American Chemical Society).

So, following the definition of autocorrelation function decay time, we can say that $m$-ZnTCPP shows lower interfacial ET fluctuation rate than $p$-ZnTCPP. This difference can be again accounted for by the fact that the four covalent anchor points of $m$-ZnTCPP compared to that of one or two covalent anchor points in case of $p$-ZnTCPP (Figure 3.1) poses greater restriction to the movement of $m$-ZnTCPP than $p$-ZnTCPP, which in turn causes lower interfacial ET fluctuation rate in case of $m$-ZnTCPP than $p$-ZnTCPP.

To quantify the emission intermittency recorded by the blinking single-molecule fluorescence trajectories, we performed statistical analysis on the stochastic durations of the dark state involving high ET reactivity compared to the bright state associated with low ET reactivity. The single-molecule fluorescence emission trajectories are used to determine the distribution of dark-time durations (vide supra). Figure 3.7A,B show the distributions of dark-time durations of $m$-ZnTCPP on TiO$_2$ NP surface for 1 molecule and 23 molecules, respectively. Broad ranges of
blinking timescales, ranging over the temporal resolution of the experiment (1 ms) to seconds. The frequency of events (occurrence) is high with \( t_{\text{dark}} \) near the minimum integration bin width, whereas the occurrences become less dense at longer times. We observed non-Poisson behavior for \( m\)-ZnTCPP as indicated by the nonexponential distribution of dark-times (Figure 3.7A,B), which suggests that the intrinsic physical mechanism is not originated from a single Poisson event under an exponential rate dynamics, rather it is the result of complex rate process where the rate of ET changes from time to time.\(^9,79,102-105\) The observed non-Poisson behavior for \( m\)-ZnTCPP is consistent with our previous findings with \( p\)-ZnTCPP.\(^79\)

To further analyze the ET reactivity fluctuation associated with non-Poisson behavior, we generated probability density distribution of the dark states (\( P(t_{\text{dark}}) = \text{Occurrence}(t)/\Delta t \)) (Figure 3.7C,D).\(^106-111\) Each data point of the histogram is weighted by the average time between the nearest neighbor events. The probability density built from different dark-times show linear dependence on \( t_{\text{dark}} \) in log-log plots (Figure 3.7C,D). This linear dependence of the single-molecule dark-time probability density distributions show typical power-law behavior, which can be mathematically described as \( P(t_{\text{dark}}) \propto t_{\text{dark}}^{-m_{\text{dark}}} \). The slope of the line in Figure 3.7C,D, gives the value of power-law exponent \( m_{\text{dark}} \) for 1 molecule and 23 molecules, respectively. The observed power-law kinetics is also consistent with our earlier results.\(^79\) Several models exist that explain the power-law blinking behavior of single molecules on semiconductor surfaces.\(^107-111\) Following our earlier studied system\(^79\) we can say that power-law blinking of organic molecule requires dynamic disorder dynamics.\(^103\) The observed power-law statistical behavior, being intrinsically derived from the interfacial ET dynamics, reflects the dynamic disorder of the ET reactivity.
Figure 3.7. Distributions of dark-time durations of $m$-ZnTCPP on TiO$_2$ NP surface for (A) 1 molecule and (B) 23 molecules. Probability densities of the dark-time durations of $m$-ZnTCPP on TiO$_2$ NP surface for (C) 1 molecule and (D) 23 molecules. In log-log scale plots (C, D) the solid lines are linear fits indicating power-law behavior. The power-law exponent, which is the slope of the linear fits, is also indicated in the figures. (E) The Histogram of power-law exponents ($m_{dark}$), for 23 different molecules of $m$-ZnTCPP on TiO$_2$ NP surface.
In Figure 3.7E, we show the distribution of the power-law exponents, $m_{\text{dark}}$, for 23 molecules. The value of $m_{\text{dark}}$ varies from 1.00 to 1.99, indicating a large spread in dark-time behavior from molecule to molecule, which in turn reflects the static inhomogeneity of the ET reactivity fluctuation. The larger spread of $m_{\text{dark}}$ in case of $p$-ZnTCPP (1.02 to 2.68) than $m$-ZnTCPP (1.00 to 1.99) again supports the higher flexibility of $p$-ZnTCPP on TiO$_2$ surface (the histogram of power-law exponents ($m_{\text{dark}}$) for $p$-ZnTCPP on TiO$_2$ NP surface is displayed in Figure 3.8. In addition to this the lower mean value of $m_{\text{dark}}$ in case of $m$-ZnTCPP (1.35) than $p$-ZnTCPP (1.79)$^{79}$ indicates a relatively higher probability for large dark-times in case of $m$-ZnTCPP than $p$-ZnTCPP. Therefore, according to our earlier discussions higher probability for large dark-times in case of $m$-ZnTCPP than $p$-ZnTCPP reflects higher ET reactivity of $m$-ZnTCPP than $p$-ZnTCPP.

**Figure 3.8.** Histograms of power-law exponents ($m_{\text{dark}}$) for $m$-ZnTCPP and $p$-ZnTCPP on TiO$_2$ NP surface. The Histogram of power-law exponents ($m_{\text{dark}}$) for $p$-ZnTCPP on TiO$_2$ NP surface is displayed for comparison only (Adapted with permission from ref. 79. Copyright 2014 American Chemical Society).

The above discussion attests to the fact that, both the autocorrelation function decay time and the power-law exponent, $m_{\text{dark}}$ are critical factors for the analysis of interfacial ET reactivity.
fluctuation dynamics. The autocorrelation function decay time, $\tau$ provides useful information about the ET reactivity fluctuation time and the specific value of $\tau$ gives statistical estimate of timescale fluctuation for a single molecule alternating between bright and dark states. The power-law exponent, $m_{\text{dark}}$, indicates the relative probability for the dark state durations: a larger $m_{\text{dark}}$ value indicates a relatively higher probability for small dark-times compared to larger dark-times. Both the autocorrelation function decay time and the power-law exponent, $m_{\text{dark}}$ are found sensitive to the molecular structure (different for $m$-ZnTCPP and $p$-ZnTCPP) and/or molecular environment. The structural change of dye molecule from $p$-ZnTCPP to $m$-ZnTCPP is always accompanied by the change in electrostatic and hydrophobic interactions between the probe molecules and their fluctuating local environment\textsuperscript{75,112,113} leading to the difference in interfacial ET reactivity. Although the conclusion derived from ensemble-averaged measurement and single-molecule measurement are consistent but the sensitivity about (i) inhomogeneous interfacial ET reactivity fluctuation, (ii) the broad range of autocorrelation function decay time, and (iii) the inherent broadness of power-law exponent may remain hidden by ensemble-averaged measurements.

Overall, the observed differences in the interfacial electron transfer reactivity of $m$-ZnTCPP and $p$-ZnTCPP can be associated with the difference in the redox reactivity intermittency with the fluctuation of molecule-TiO$_2$ electronic and Franck-Condon coupling. In fact, the difference in the inhomogeneous surface state distribution of $m$-ZnTCPP and $p$-ZnTCPP molecules plays a critical role in the electronic coupling parameter. Specifically, the formation stability and rupture of four anchoring groups of the $m$-ZnTCPP to TiO$_2$ compared to that of one or two anchoring groups of the $p$-ZnTCPP to TiO$_2$ may produce the difference in the extent of perturbed electronic coupling by local environment thermal fluctuation at room temperature.\textsuperscript{9,114-}
Understanding the role of dye molecule-semiconductor interaction on interfacial ET is central to the development of solar energy conversion science and photocatalysis. However, the quantification of electronic coupling is challenging because of the inherent heterogeneity and the involvement of different factors affecting electronic coupling. Depending on the strength of electronic coupling between the excited state of the sensitizer and the acceptor orbitals at the surface of TiO$_2$, the interfacial ET process was reported to take place on time scales ranging from less than 10 fs to several microseconds. Nevertheless, the strong electronic coupling is often the result of the anchoring of the dye molecule onto the semiconductor surface through a moiety carrying its lowest unoccupied molecular orbital (LUMO). Considering the separation distance between $m$-ZnTCPP/$p$-ZnTCPP and TiO$_2$ surface as the only factor determining the magnitude of electronic coupling for interfacial ET, we can use Gamov expression

$$|H|^2 = |H_0|^2 \exp[-\beta(r - r_0)]$$

(3.2)

where, $|H|$ and $|H_0|$ are electronic coupling between donor and acceptor at separation distance $r$ and $r_0$ respectively, $\beta$ is the damping factor (an exponential coefficient for the decay of the electronic wavefunction). The change of sensitizer from $p$-ZnTCPP to $m$-ZnTCPP is accompanied by decrease in the distance between donor (sensitizer) and acceptor, which in turn causes greater electronic coupling in case of $m$-ZnTCPP than $p$-ZnTCPP. Additionally, change of sensitizer from $p$-ZnTCPP to $m$-ZnTCPP is also accompanied by increase in the number of anchoring group from 1 or 2 in case of $p$-ZnTCPP to 4 in case of $m$-ZnTCPP, which in turn decreases the flexibility of $m$-ZnTCPP compared to $p$-ZnTCPP. The diminished flexibility of $m$-ZnTCPP can further decrease the damping factor $\beta$ leading to increase in electronic coupling between $m$-ZnTCPP and TiO$_2$. $^{100,101}$
This simplified picture is certainly not true because in a system gated with dye molecule on top of TiO$_2$ surface, the dye-TiO$_2$ electron coupling to vibrational modes of the dye molecule must be taken into consideration. Specifically, at room temperature the local thermal fluctuation is significant enough to change and perturb the molecule-TiO$_2$ electron coupling to vibrational modes of the molecule. This also accords with our earlier observations, where we showed that for alizarin/TiO$_2$ interfaces the vibrational reorganization energy barriers of interfacial ET are inhomogeneous from TiO$_2$ nanoparticle to nanoparticle and from molecular site to site. Some of the issues emerging from this finding, such as broad fluctuation subspace of the electronic coupling factor, relate specifically to the broad range of autocorrelation function decay time and the inherent broadness of power-law exponent. The conclusions derived from this study is consistent with the findings of extensive literature on ensemble-averaged measurements, which suggest that the inhomogeneous interfacial ET arises due to the surface defects, changes in electronic coupling, changes in distance between donor and acceptor, and multiple time scale of energetic relaxation and solvation dynamics. The combination of our findings reveals partially the origin of the complexity of the interfacial ET dynamics. However, more research on this topic needs to be undertaken before the quantification of the inhomogeneous interfacial ET dynamics.

3.1.4. Summary

We studied interfacial ET dynamics of $m$-ZnTCPP–TiO$_2$ nanoparticle system by applying single-molecule photon-stamping spectroscopy. Single-molecule fluorescence intensity fluctuations of $m$-ZnTCPP on TiO$_2$ NP surface are identified to have originated from the interfacial ET reactivity fluctuation. Similar to our earlier studied, $p$-ZnTCPP–TiO$_2$ nanoparticle system, the single-molecule interfacial ET processes in $m$-ZnTCPP/TiO$_2$ systems were found to
be inhomogeneous, both statically (molecule to molecule) and dynamically (time to time for the same individual molecules). The dominant dark states in single-molecule fluorescence intensity trajectories as well as large difference in lifetime derived from bright and dark states of \( m \)-ZnTCPP on TiO\(_2\) NP surface compared to that of \( p \)-ZnTCPP demonstrate higher charge injection efficiency of \( m \)-ZnTCPP than \( p \)-ZnTCPP. The change in four anchoring groups (-COOH group) position from \textit{para}\-position to \textit{meta}\-position of \textit{meso}\-phenyl rings of the porphyrin macrocycle produces changes in binding geometry, hence electronic coupling, which in turn facilitates interfacial ET reactivity. The higher charge injection efficiency of \( m \)-ZnTCPP compared to \( p \)-ZnTCPP is explained by considering the shorter distance between the sensitizer (\( m \)-ZnTCPP) and TiO\(_2\) surface as well as the higher restrictive motion of the sensitizer (\( m \)-ZnTCPP) on TiO\(_2\) surface.

The nonexponential autocorrelation function decay and a large spread in power-law exponent, \( m_{\text{dark}} \), derived from single-molecule fluorescence intensity trajectories reflect inhomogeneous interfacial ET dynamics. The analysis of autocorrelation function decay time and the power-law exponent, \( m_{\text{dark}} \) show different behavior of \( m \)-ZnTCPP and \( p \)-ZnTCPP, which indicates the sensitivity of \( \tau \) and \( m_{\text{dark}} \) on the molecular structure and molecular environment of the dye molecule.

Our single-molecule study provides detailed molecular-level understanding of the inhomogeneous interfacial ET reactivity and the factors influencing the ET reactivity. The molecular-level understanding of the interfacial ET reactivity further sheds light on the intrinsic fluctuating and inhomogeneous interfacial electron transfer dynamics, which may, for example, help the development of solar energy conversion science and photocatalysis.
3.1.5. References


3.2. Electronic Coupling-Decoupling Dependent Single-Molecule Interfacial Electron Transfer Dynamics in Electrostatically-Attached Porphyrin on TiO$_2$ Nanoparticles

3.2.1. Introduction

Interfacial electron transfer (ET) processes and the factors controlling them such as electronic coupling between the molecule and semiconductor, vibrational relaxation energy of adsorbed molecule, solvent reorganization energy, reaction driving force, the surface structures, and the defect surface states between molecular adsorbates and semiconductor nanomaterials have attracted much interest because it plays a key role in many applications such as surface chemistry, catalysis, solar energy conversion technologies, including dye-sensitized solar cells (DSSCs), dye-sensitized photoelectrosynthesis cells (DSPECs), and molecular electronics.$^{1-22}$ Typical interfacial ET process at dye–semiconductor surfaces can be divided into two parts: forward electron transfer (FET) and back electron transfer (BET). Photoexcitation of the sensitizing dye to its excited state above the conduction band or the surface states of the semiconductor initiates electron injection at the interface (FET) within femtoseconds to nanoseconds$^{13,23-28}$ following the recombination with the oxidized dye (BET) on a timescale of sub-nanoseconds to milliseconds,$^{13,26,27}$ involving possibly trapping and detrapping, non-Brownian diffusion, and scattering in the bulk of the semiconductor.$^{23,24}$

Interfacial ET dynamics between dye and wide band-gap semiconductor, such as TiO$_2$,$^{13,29-41}$ SnO$_2$,$^{42,43}$ and ZrO$_2$$^{27,28,445,46}$ have been widely studied in covalently attached dyes on the surfaces due to their greater stability in the solution phase.$^{44,47}$ Instead of covalently attached dye which is widely used in DSSCs, the sensitization of electrostatically bound dye molecules on TiO$_2$ surface would be a different strategy for optimization of solar cell efficiency-related factors.$^{48,49}$ There have been many studies of systems comprising of non-covalent (or
electrostatic) associations of porphyrins with polymers, DNA, metallic nanoparticles, and semiconductor quantum dots. ET process in systems utilizing electrostatic stabilization—for instance, coulombic binding of a cationic dye to a semiconductor of negative or positive surface charge is critical in order to fully understand the electronic coupling factor in a modest range of redox potentials and modest range of driving forces of such weakly interacting systems. Electrostatic binding of a cationic dye to a semiconductor featuring net negative surface charges also provides a different approach for surface sensitization.

It is desirable to characterize each individual parameters and their role in ET dynamics with specificity and accuracy. Specifically, a characterization of electronic coupling in strongly coupled and weakly coupled systems is critical for fundamental understanding of the complexity of interfacial ET dynamics. A suitable dye–semiconductor system is necessary to understand the contribution of electronic coupling factor on interfacial ET dynamics. Given the importance of electronic coupling in dye-sensitized systems, prior studies have focused on examining various dyes on TiO$_2$ NPs with different coupling strength, where accurate interpretation of the electronic coupling dependency was difficult since the dyes used in those studies have different molecular structure, properties and energetics. Zinc porphyrins have attracted much attention due to many advantages such as diversity of their molecular structure, high extinction coefficient, low cost and environmental friendliness. Also, high photon-to-current conversion efficiency has been reported on zinc porphyrin sensitized systems. Here, we have examined the dynamics of interfacial electron transfer under conditions where dye-attachment surface chemistry does not affect or only minimally affects the semiconductor surface states. We have used cationic zinc porphyrin Zn(II) meso-tetra (N-methyl-4-pyridyl) porphine tetrachloride (ZnTMPyP)/TiO$_2$ NP system (as shown in Figure 3.9) in order to fully understand the role of
electronic coupling factor by using single-molecule fluorescence imaging coupled with photon-stamping technique.

\[ \text{Figure 3.9. Schematic diagram of electrostatically attached ZnTMPyP on TiO}_2 \text{NP surface. The difference in net surface charge on TiO}_2 \text{results into the change in electronic coupling between positively charged molecule and substrate which alters the interfacial ET rate processes.} \]

The chosen system, ZnTMPyP–TiO\(_2\), is unique that the distance and electronic coupling between them can moderately varied by altering the surface charge on TiO\(_2\) NPs by simply changing the pH of colloidal solutions.\(^{55,64,65}\) It is noteworthy that oxide surfaces develop a surface charge depending on pH.\(^{49,66,67}\) As a result, the ZnTMPyP–TiO\(_2\) system is susceptible to electrostatic attractions and repulsions with charged species formed in the photoinduced electron transfer processes.\(^{68}\) Also, the large energy difference of the lowest unoccupied molecular orbital (LUMO) of ZnTMPyP and conduction band of TiO\(_2\) makes the electron injection favorable at the ZnTMPyP–TiO\(_2\) interface. Several studies confirmed that ZnTMPyP molecules lie flat-on geometry and very little evidence of aggregation has been observed owing to its four positive charges on periphery, causing the \(\pi\)-electron cloud of porphyrin ring systems to be more diffuse over the surface of the molecule.\(^{69–71}\)
The inhomogeneity of complex interfacial ET dynamics and perturbation by local environment are often not observed or hidden in ensemble-averaged experiments.\textsuperscript{72–78} Inhomogeneity in interfacial ET dynamics arises from the heterogeneity and fluctuations of the local driving force, the vibrational reorganization energy, the solvent reorganization energy, the electronic and Franck-Condon couplings, and the electron trapping and scattering at the interfaces and in the bulk of the semiconductor substrates.\textsuperscript{1,11,13,79} Single-molecule photon-stamping spectroscopy is capable of dissecting the static and temporal dynamics in complex system by studying one molecule at a time in specific nanoscale local environment.\textsuperscript{74,80–91} Study of mechanistic details of the ET dynamics in weakly interacting systems in single-molecule level serves as the nano-probe to measure the nano-environment dynamics based on the detection of fluorescence characteristics of single molecules. The optical signals of single molecules provide information about dynamics of their nanoscale environment, free from space and time averaging.\textsuperscript{83} More precisely, identification of spatial and temporal inhomogeneities can be carried by studying specific surface–molecule interaction and ET dynamics at a single-molecule level. In our previous reports,\textsuperscript{88,92} we have characterized the electronic coupling dependent ET dynamics in dye-sensitized system with covalently favored orientation of molecule on the substrate by its anchored group. In this work, we investigate the ET dynamics of non-covalently interacting system by single-molecule spectroscopy, involving fluorescence imaging and time correlated photon-stamping technique. Electrostatic interactions being governing force at the substrate–molecule interface, herein, we envisage the critical role of substrate surface charge controlling the electronic coupling to govern the interfacial ET rate processes. To the best of our knowledge, this is the first single-molecule study of the electronic coupling dependent interfacial ET dynamics on dye-sensitized system relying on the electrostatic interaction driven coupling
changes. The heterogeneous nature of interfacial FET dynamics at the single-molecule level indicates the fluctuation of local environment, intermittency of ET reactivity dominated by dye–semiconductor interaction regulated by various factors including electronic coupling.

3.2.2. Experimental Section

The detailed description of the experimental setup and sample preparation is given in Chapter 2.

3.2.3. Results and Discussion

Water soluble cationic porphyrins are used as the sensitizers in dye-sensitized and biological systems as they bind specifically to the substrate while the binding mechanism can be modulated by nature of central metal atom and size and location of substituent groups on the periphery of porphyrin. ZnTMPyP contains four positive charges on periphery that can bind with charged TiO$_2$ surface electrostatically. The emission of ZnTMPyP in TiO$_2$ NPs solution is significantly quenched which is consistent with the literature and can be interpreted on the basis of electron transfer mechanism due to electrostatic coupling between ZnTMPyP and TiO$_2$. The emission spectrum of aqueous ZnTMPyP shows no pH dependence as there are no sites for protonation and deprotonation. However, ZnTMPyP–TiO$_2$ emission intensity decreases with an increase in the pH value as shown in Figure 3.10.

![Emission spectra of ZnTMPyP on TiO$_2$ NP aqueous solution at pH 2 (black) and pH 9 (red).](image)

**Figure 3.10.** Emission spectra of ZnTMPyP on TiO$_2$ NP aqueous solution at pH 2 (black) and pH 9 (red).
The decrease in emission intensity can be explained on the basis of charge developed on the surface of TiO$_2$. Firstly, when we introduce TiO$_2$ NPs in alkaline environment the change of TiOH$_2^+$ into TiO$^-$ will occur. It is evident from literature that oxide surfaces develop a surface charge from proton transfer to and from hydroxyl (–OH) group in acidic and alkaline aqueous environment respectively.\(^{98}\)

\[
\begin{align*}
\text{Ti–OH}_2^+ & \xrightleftharpoons{\text{Increase of pH}} \text{Ti–OH} & \xrightleftharpoons{\text{Increase of pH}} \text{Ti–O}^- \\
\end{align*}
\]

Secondly, negative charges developed on the surface of TiO$_2$ NPs in alkaline environment interacts electrostatically with four positive charges on ZnTMPyP resulting into strong electronic coupling between them. The dominant non-radiative ET pathway in case of negatively charged TiO$_2$ NPs further quenched the emission as observed in Figure 3.10.

To further our understanding of electronic coupling changes in molecular level, we have performed single-molecule photon-stamping spectroscopy combined with confocal fluorescence imaging. Figure 3.11A, B show the single-molecule confocal fluorescence images of ZnTMPyP on bare cover glass and TiO$_2$ NPs-coated cover glass, respectively. Each bright spot represents the diffraction limited image of an individual ZnTMPyP molecule. Apparently, single molecules weakly interacting with TiO$_2$ NPs are visible and demonstrate fluorescence intensity fluctuation because the system fluctuates between higher ET-activity states and lower ET-activity states otherwise we would not see the molecule optically. Figure 3.11C, D show the single-molecule fluorescence trajectories for ZnTMPyP on glass and on TiO$_2$ NP surfaces (binning time, 20 ms), respectively. The fluorescence intensity trajectory of ZnTMPyP on TiO$_2$ (Figure 3.11D) shows a strong fluctuation with respect to a relatively continuous emission on the glass surface (Figure 3.11C).
Figure 3.11. Optical images of ZnTMPyP on (A) bare cover glass and (B) TiO$_2$ NPs-coated cover glass (image size, 30 $\mu$m $\times$ 30 $\mu$m). Fluorescence intensity trajectories of ZnTMPyP on (C) bare cover glass and (D) TiO$_2$ NPs-coated cover glass.

Figure 3.12 shows the single-molecule fluorescence lifetime distributions for single ZnTMPyP molecules on cover glass (gray) and on TiO$_2$ NPs-covered surfaces (magenta). In a control experiment, the narrow distribution in lifetime of ZnTMPyP molecules on cover glass (4.6–5.8 ns) in comparison to on TiO$_2$ NPs (3.4–5.3 ns) demonstrates the inhomogeneous FET rate which attributes the ET reactivity fluctuation dynamics. The lower lifetime (mean value $\sim$ 4.2 ns) of ZnTMPyP molecules on TiO$_2$ NPs compared to lifetime on glass (mean value $\sim$ 5.2 ns) further confirms the fluorescence quenching is due to interfacial FET from the excited states of the ZnTMPyP to TiO$_2$ NPs.
Figure 3.12. Fluorescence lifetime distribution of ZnTMPyP on bare cover glass (gray) and on TiO$_2$ NPs-coated cover glass (magenta).

Figures 3.13A,B and C,D show typical fluorescence intensity trajectories of ZnTMPyP on negatively charged TiO$_2$ NPs-coated cover glass with corresponding histogram, and Figures 3.13E,F and G,H represent fluorescence intensity trajectories of ZnTMPyP on positively charged TiO$_2$ NPs-coated cover glass with corresponding histogram. Histograms of the emission intensity are shown to determine the threshold for dark and bright states, where the “dark state” is used for the lower level (or background) emission and the “bright state” is used for the higher level (or fluorescence) emission for each trajectory. Each single-molecule fluorescence trajectory shows fluctuation and blinking between bright and dark states, which is also observed in our previous reported works.$^{13,88,92}$

We observed and analyzed more than 140 single molecules of ZnTMPyP on TiO$_2$ NP coated cover glass. Each trajectory intermittently fluctuates between dark and bright state which is well evidenced in literature for dye molecules on TiO$_2$ NP surface.$^{13,99–102}$ According to earlier reported works,$^{13,88,92,89,92–94}$ the intensity fluctuation is due to the intermittent interfacial ET reactivity fluctuations, which is also true for present system. The emission intensities of ZnTMPyP molecules are substantially decreased on TiO$_2$ relative to that on glass, consistent with
electron injection to TiO$_2$ to populate a nonemissive state probability of the molecule. In case of ZnTMPyP on negatively charged TiO$_2$ NPs, majority of molecules follow the intensity trace as shown in Figure 3.13A,C predominating in dark states. A large number of dark states or long dark state times are indicative of the active electron transfer reactivity arising from strong interaction of ZnTMPyP with TiO$_2$ consistent with our earlier report on $m$-ZnTCPP/TiO$_2$ system. Electrostatic attraction between negative charges on TiO$_2$ NPs and positively charged ZnTMPyP facilitates the strong electronic coupling and interaction. However, in case of ZnTMPyP on positively charged TiO$_2$ NPs, bright states are dominant mostly in each trajectories as shown in Figure 3.13E,G. Small population of dark states or short dark state time also refers the less active electron transfer reactivity and weak electronic coupling factor between adsorbed molecule and TiO$_2$ due to electrostatic repulsion. Presumably, the observed difference in intensity fluctuation is due to electronic coupling changes under conditions of weak interaction. Intensity fluctuation due to triplet state of ZnTMPyP is precluded as the triplet state lifetime is in sub-millisecond to microsecond time scale which is not responsible to show the fluctuation dynamics slower than 1 ms. Thus, the blinking of ZnTMPyP on TiO$_2$ surface is most likely originated from ET activity intermittency due to ET rate fluctuations in the system. Dark states are observed when excited state of ZnTMPyP actively transfers its electron to TiO$_2$ non-radiatively from its singlet excited state, quenching the fluorescence pathway of radiative relaxation, the bright states originate from less frequent ET activity, prioritizing the fluorescence as radiative relaxation to the ground state. Similar conclusion was also drawn in various reported works. To monitor the ET activity and origin associated with it, we measured fluorescence lifetimes of ZnTMPyP single molecules using time correlated photon-stamping spectroscopic technique on positively charged and negatively charged TiO$_2$ NPs.
Figure 3.13. Fluorescence intensity trajectories of ZnTMPyP on (A, C) negatively charged TiO$_2$ NPs, and (E, G) positively charged TiO$_2$ NPs coated cover glass with corresponding histograms of emission intensity to determine the threshold for bright and dark states, (B, D) and (F, H), respectively.
Figure 3.14 shows the typical fluorescence decay curves of ZnTMPyP single molecules on positively charged TiO$_2$ NPs (triangle) and negatively charged TiO$_2$ NPs (square). The solid lines are biexponential fit of each decay curve with deconvolution of instrument response function (IRF). Clearly, shorter fluorescence lifetime of ZnTMPyP molecule on negatively charged compared to on positively charged TiO$_2$ NP indicates the greater electron injection efficiency on negatively charged TiO$_2$ NP which can be accounted for by the strong electronic coupling induced by strong electrostatic interaction.

![Figure 3.14. Typical fluorescence decay profile of single ZnTMPyP molecule on positively charged (triangle) and negatively charged (square) TiO$_2$ NP. The fitted lines (solid line) shown are biexponential fits derived by deconvolution of instrument response function (IRF). However, each single-molecule behaves differently from time to time and from site to site, which gives broad distribution of excited state lifetime in typical single-molecule experiments. The inhomogeneous fluctuation of lifetime derived from nanoscale local environment change, electronic coupling, and specific molecule–substrate interaction due to molecular motion is also observed in many single-molecule experiments.](image-url)
The inhomogenously broadened lifetime distribution of individual molecules can be utilized to understand the behavior of many molecules in a specific system. Figure 3.15 shows the fluorescence lifetime distribution of typical 42 single ZnTMPyP molecules on positively charged (red) and negatively charged (blue) TiO$_2$ NPs. The distribution clearly indicates the influence of TiO$_2$ NP surface charge on lifetime of ZnTMPyP molecules.

![Figure 3.15. Lifetime distribution of 42 single ZnTMPyP molecules on positively charged (red) and negatively charged (blue) TiO$_2$ NPs.](image)

It is reported in literature that the TiO$_2$ CB edge is pH dependent (or surface charge dependent) according to Nernst-like equation:

$$E_{CB}(pH) = E_{CB}(pH = 0) - 0.06 \text{ eV } * pH$$

The Nernstian pH dependence of the conduction band edge leads to a pH-dependent interfacial electron transfer due to driving force change. Lian et al. reported the retardation of electron injection rate by a factor of $>250$ from pH 2–8 in dye–TiO$_2$ systems in solution.$^{104}$ In alkaline
condition, TiO$_2$ CB edge shifts closer to the adsorbed molecular excited state decreasing the driving force for FET whereas in acidic condition the opposite is true. The increased driving force presumably increases the FET rate and vice versa.$^{104}$ However, overall FET rate process depends on many factors including the electronic coupling between adsorbate excited state and semiconductor acceptor states, a prominent factor in many dye–semiconductor systems.$^{1,92,99–102}$ Our results indicate that the electronic coupling factor predominantly governs the electron injection for weakly interacting system. The observed ET dynamics is the result of compromise between two competing parameters: driving force and electronic coupling, of which latter predominates. Forward electron transfer driving force for ZnTMPyP molecules on positively charged TiO$_2$ NPs is high due to downward shift of CB edge, but the electronic coupling is less because of electrostatic repulsion between them responsibly showing the electronic decoupled ET dynamics. Additionally, redox potential of the electrostatically adsorbed species is likely to be unchanged,$^{55}$ unlike on covalently attached adsorbed species,$^{47}$ which further corroborates the observed ET transfer dynamics is due to or mostly regulated by the electronic coupling changes. To further confirm the strong interaction on ZnTMPyP–negatively charged TiO$_2$ NP system, we have measured single-molecule fluorescence anisotropy by single-molecule time-resolved photon-stamping experiment. Since the fluorescence anisotropy of the dye molecules is directly related to the reorientational dynamics of flexibility of excited dye molecule, it is suitable technique for the investigation of local molecular dynamics near the adsorption site. Figure 3.16A shows a typical fluorescence anisotropy trajectory for a single ZnTMPyP molecule on TiO$_2$ NP surface from parallel (black) and perpendicular (gray) channel, and the corresponding anisotropy distribution from bright states is shown in Figure 3.16B.
Figure 3.16. (A) Parallel (black) and perpendicular (gray) polarized fluorescence intensity trajectories for a single ZnTMPyP molecule on TiO$_2$ NP surface. Fluorescence anisotropy distribution from bright states of 23 single ZnTMPyP molecules on (C) negatively charged TiO$_2$ NPs and (D) positively charged TiO$_2$ NPs.

The anisotropy is calculated by using an equation:

$$ r(t) = \frac{I_{\parallel}(t) - G I_{\perp}(t)}{I_{\parallel}(t) + 2GI_{\perp}(t)} $$ \hspace{1cm} (3.4) $$

where $I_{\parallel}(t)$ and $I_{\perp}(t)$ are the fluorescence intensities of the vertically (||) and horizontally (⊥) polarized emission components under vertically polarized excitation. $G$ is the correction factor for the different instrumental detection efficiencies of the parallel and perpendicular polarized components of the emission and is estimated to be $\sim 1.9$. Error! Bookmark not defined.

We have considered the anisotropy distribution of higher level intensity (bright states) only because the fluorescence intensity level for dark states is almost equal to the background
level. Higher value of anisotropy for the ZnTMPyP–negatively charged TiO$_2$ NP (0.21 ± 0.04) (Figure 3.16C) compared to the anisotropy for the ZnTMPyP–positively charged TiO$_2$ NP (0.15 ± 0.04) (Figure 3.16D) indicates greater restriction on the flexibility of ZnTMPyP molecules on the negatively charged TiO$_2$ NP. We note that fluorescence anisotropy is indicative of molecular rotational flexibility and its immediate environment. Considering surface charge on TiO$_2$ is the only difference between the two cases, any change in the anisotropy should be originated from strong vs weak interaction with TiO$_2$. So, the greater restriction on the flexibility of ZnTMPyP molecules on negatively charged TiO$_2$ NP surface than on positively charged TiO$_2$ NP surface corroborate with the strong electrostatic interaction leading to strong electronic coupling. Nevertheless, anisotropy may also vary from molecule to molecule depending on the heterogeneity of the local environment. The broad distribution of anisotropy (Figure 3.16C,D) demonstrates the heterogeneity of TiO$_2$ NPs surface.

Surface accepting states on TiO$_2$ nanoparticles also play a critical role in ET dynamics. It has been shown that surface states govern interfacial electron transfer dynamics as well as carrier mobility.$^{105}$ Changing the surface charge not only changes the conduction band edge but also changes the surface accepting states of NPs. At negatively charged TiO$_2$ surface, the conduction band moves up toward vacuum level which results in the less density of surface accepting states. However, at positively charged surface of NPs conduction band shifts down, away from vacuum level, increasing the driving force of forward ET simultaneously increasing the density of surface accepting states.$^{104}$ Electron injection rate increases with increased density of accepting states. Had the driving force and surface state density been only deciding factor for interfacial ET dynamics, we should have observed dominant dark states in case of positively charged nanoparticles as driving force and surface accepting state density are larger in this case.
However, the observed dynamics in this report is mainly governed by electronic coupling between dye molecule and NP regardless of the role of surface accepting states and free energy driving force. Nevertheless, the small difference in the lifetime of dye molecules at two differently charged TiO$_2$ surfaces indicates overall effect of driving force and surface accepting state density vs. electronic coupling. More clearly, even though driving force for ET is high in certain case, the overall dynamics comes from the interplay between principle governing factors as shown in Figure 3.17. It is evident from our observations that the dependence of electronic coupling on pH induced surface charge on TiO$_2$ and hence on forward ET rate provides a useful way to understand and dissect the role of individual parameter on a molecular level.

**Figure 3.17.** Schematic diagram showing (A) electronic coupling change due to electrostatic force of interaction at the interface and corresponding intensity trajectories and (B) electronic coupling regulated interfacial ET processes in a ZnTMPyP–TiO$_2$ system. S and S$^*$ are the ground state and excited state of ZnTMPyP and S$^+$ is its oxidized state. VB, valence band; CB$^+$, conduction band of positively charged TiO$_2$ NP; CB$^-$, conduction band of negatively charged TiO$_2$ NP; f, fluorescence; hv, photon. The observed ET dynamics is an interplay between the driving force and electronic coupling on ZnTMPyP–TiO$_2$ interface.
The conclusion obtained from our work supports the fact that the electronic coupling plays a critical role during electron injection in dye loaded semiconductor system. According to non-adiabatic ET theory, the rate of electron transfer, $k_{ET}$, between donor (D) and acceptor (A) states is given by,

$$k_{ET} = \frac{H^2}{\sqrt{4\pi\lambda k_B T}} \exp\left(-\frac{(\Delta G^0 - \lambda)^2}{4\lambda k_B T}\right)$$

(3.5)

where $H^2$ is the electronic coupling between donor and acceptor states, $\Delta G^0$ is the reaction driving force, and $\lambda$ is the reorganization energy.$^{106,107}$ Apparently, the ET dynamics can be modulated by varying the factors depicted in eq 4. However, for the system involving dye on semiconductor with large number of acceptor states, like that found in TiO$_2$, the reorganization energy is less important to control the ET dynamics. In such cases, the rate constant of ET reaction, $k_{ET}$, is the product of a Franck–Condon weighted density of states (FCWD), which depends on the interaction between the acceptor and donor vibrational wave functions (which is same as acceptor states density in TiO$_2$) and an electronic term proportional to $|H|^2$, the electronic coupling matrix element squared:$^{1,108}$

$$k_{ET} = |H|^2 \times FCWD$$

(3.6)

If the FCWD is not dependent on the distance, the rate constant of electron transfer depends mainly on the electronic coupling element related to distance ($r$) between donor (dye) and acceptor (TiO$_2$) by,

$$|H|^2 = |H_0|^2 \exp(-\beta r)$$

(3.7)

where $|H_0|$ is electronic coupling between donor and acceptor at van der Waals separation, and $\beta$ is the damping factor, a function of the electron tunneling barrier height of the media between
It is attributed that the electron transfer is highly sensitive to the distance between donor and acceptor. Studies had indicated that $\beta$ has a greater value for through-space coupling compared to through-bond coupling. However, the quantitative estimation of $\beta$ value related to a true electron transfer distance and hence the electronic coupling between the excited state of the sensitizer and acceptor orbitals at the surface of TiO$_2$ is challenging because of the complexity, inherent heterogeneity, and the involvement of different factors affecting the electronic coupling at the interface. A small distance between ZnTMPyP and TiO$_2$ NP surface would enhance the electron injection efficiency to TiO$_2$. In porphyrin sensitized semiconductor system, electron transfer takes place from porphyrin moiety to substrate through space. Having the exponential distance dependence of electronic coupling parameter in the given system, ZnTMPyP molecule on negatively charged TiO$_2$ NP is expected to lie closer to each other resulting into a strong electronic coupling and hence a higher forward ET rate. Overall, the observed difference in the interfacial electron transfer reactivity of ZnTMPyP on positively charged and negatively charged TiO$_2$ surface is most likely originated from the fluctuation of molecule–TiO$_2$ electronic coupling. It is also worth to mention that various factors, such as driving force, the density of electron-accepting states in the semiconductor, energetically-accessible surface states, surface chemical bonding structure, and electron trapping, would simultaneously contribute to the inhomogeneous interfacial ET dynamics. The finding of this work is significant in understanding the ET dynamics in electrostatically attached vs. covalently attached dye molecules on semiconductor and raises a question whether the difference in dynamics reflects the method of attachment or rather the chemical composition of the semiconductor under various pHs. Evidently, more research is needed to address this issue and relate it to the complexity of interfacial ET dynamics in this as well as other dye-semiconductor
systems. The answer may most likely potentially shed light on characterizing and optimizing the parameters affecting the interfacial ET in DSSCs.

3.2.4. Summary

We have used single-molecule photon-stamping spectroscopy to probe the ET dynamics of ZnTMPyP on positively and negatively charged TiO$_2$ NP surface. Our results reveal that the fluorescence lifetime and blinking dynamics of single molecules of ZnTMPyP are different depending on the charge of TiO$_2$ NP surface. Negatively charged NP surface favors efficient electron injection into the TiO$_2$ whereas positively charged NP surface decouple the interaction of dye with TiO$_2$ resulting into the less efficient electron injection. The observed difference in the ET dynamics in two systems can be explained by considering the alteration of electronic coupling, surface states on TiO$_2$ and forward ET driving force. The observed difference in the fluorescence lifetime between two systems is accounted for by the interplay between the electronic coupling, the driving force, and surface accepting states for forward electron transfer. Change in surface interaction forces by changing surface charge on TiO$_2$ is further confirmed by higher anisotropy value of single ZnTMPyP molecule on negatively charged TiO$_2$ NP compared to that of ZnTMPyP on positively charged TiO$_2$ NP. Study of such electrostatically bound system highlights the contribution of electronic coupling factors in interfacial electron transfer dynamics. Kinetic control of electronic coupling for ET from electrostatically attached dye molecule to TiO$_2$ versus covalently attached dye molecule to TiO$_2$ could be significantly different depending on the surface perturbation due to the method of attachment. The experimental finding reported in this work has implications in solar energy conversion devices and the optimization of DSSC efficiency-related physical factors.
3.2.5. References


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CHAPTER 4. SINGLE-MOLECULE INTERFACIAL ELECTRON TRANSFER DYNAMICS OF PORPHYRIN ON TiO$_2$ NANOPARTICLES: DISSECTING INTERFACIAL ELECTRIC FIELD AND ELECTRON ACCEPTING STATE DENSITY DEPENDENT DYNAMICS

Single-molecule photon-stamping spectroscopy correlated with electrochemistry was used to dissect complex interfacial electron transfer (ET) dynamics by probing $m$-ZnTCPP molecule anchored to TiO$_2$ NP surface while electrochemically controlling the energetically accessible surface states of TiO$_2$ NPs. Application of negative potential raises the electron density in TiO$_2$ NPs, resulting in hindered forward ET and enhanced backward ET due to the changes of the interfacial electric field and the occupancy of acceptor states. However, density of states plays a dominant role in dictating the interfacial ET dynamics.

4.1. Introduction

Interfacial electron transfer (ET) mechanism and dynamics at the nanoscale play a critical role in surface chemistry, catalysis, and solar energy conversion, involving significant spatial and temporal complexity and inhomogeneity.\textsuperscript{1-20} Hence understanding the underlying rate processes and mechanisms that govern the interfacial ET is imperative. Structure-function studies of different dye-semiconductor systems show that the efficiency of electron injection is guided by the effective electronic and vibronic coupling between dye molecule and semiconductor as well as the free energy driving force associated with the energetic positions of both excited dye molecule and semiconductor conduction band.\textsuperscript{13,14,17-24} Therefore, tuning relative energetics of the dye excited state relative to the TiO$_2$ accepting states can provide an appropriate control over interfacial ET dynamics, revealing the mechanistic details of the interfacial charge transfer rate process.\textsuperscript{17-20,22-25} For a system consisting of dye molecules adsorbed on semiconductor
nanoparticle (NP) surface, the driving force can be altered by changing the semiconductor Fermi-level through an application of potential across semiconductor surface while keeping the energetics of the dye molecule surface binding state constant.\textsuperscript{17,20,22-24} Studying the interfacial ET dynamics of one molecule at a time in a specific nanoscale local environment, can be highly informative about the underlying processes. For such investigations, single-molecule spectroscopy is particularly powerful in resolving spatiotemporal heterogeneity.\textsuperscript{3,4,26-29} Although single-molecule spectroscopy has ushered in a new era of experimental methodology, it remains challenging to correlate the observed intermittency of interfacial ET dynamics to the fundamental physical properties, such as the driving force, surface state density, and electronic coupling, based on single-molecule fluorescence spectroscopic measurements alone.\textsuperscript{30-33}

Here we report a correlated single-molecule spectroelectrochemistry approach\textsuperscript{34-36} to study the effect of applied electric potential to the interfacial ET dynamics of Zn(II)-5,10,15,20-tetra (3-carboxyphenyl) porphyrin (\textit{m}-ZnTCPP) molecule anchored to TiO$_2$ NP surface in aqueous electrolyte solution. The choice of four carboxylic acid group containing \textit{m}-ZnTCPP as a sensitizer emerges from the fact that the four anchoring groups (-COOH group) in the \textit{meta}-position of \textit{meso}-phenyl rings of the porphyrin macrocycle provides a planar binding geometry as well as strong bonding of \textit{m}-ZnTCPP with TiO$_2$ NPs.\textsuperscript{37,38} Porphyrin dyes and its various derivatives are also widely used as sensitizer in dye sensitized NP systems.\textsuperscript{2,37-39} Recently, using different derivatives of Zn-porphyrin as a sensitizer, an efficiency as high as 13\% was reported.\textsuperscript{2} These studies demonstrated the Zn-Porphyrin–TiO$_2$ system as an efficient photosensitization solar energy conversion system.\textsuperscript{40}
4.2. Experimental Section

The detailed description of the experimental set-up and sample preparation is given in Chapter 2.

4.3. Results and Discussion

4.3.1. Surface Stability of \textit{m}-ZnTCPP Bound to TiO\textsubscript{2} in Aqueous Solution

The surface stabilization of dye molecules, catalysts, and dye-catalyst assemblies attached to metal oxide surfaces plays important role in dye sensitized solar cells, electrocatalysis, and photoelectrocatalysis. So replacing expensive solvents with water requires extensive research on long term stability of dye-catalyst assemblies in water.\textsuperscript{41,42} Considering the electrochemical window of water\textsuperscript{43} as well as the reported redox behavior of Zn-Porphyrin systems\textsuperscript{38} (due to insolubility of \textit{m}-ZnTCPP in water we are not able to do electrochemical measurements) we have chosen -0.6 to +0.6 V potential range. In this potential range the \textit{m}-ZnTCPP molecule remains stable towards any reduction or oxidation due to applied potential.

The surface stabilization of dye molecules, catalysts, and dye-catalyst assemblies attached to metal oxide surfaces plays important role in dye sensitized solar cells, electrocatalysis, and photoelectrocatalysis. Different strategies evolved over the time for the surface stabilization of dye/catalyst molecule on metal oxide surfaces.\textsuperscript{44-46} Cooperative binding of dye molecule to metal oxide surfaces through anchoring groups is one of the strategies.\textsuperscript{45} Here, we have used four carboxylic acid anchoring group containing \textit{m}-ZnTCPP as a sensitizer. To demonstrate the surface stabilization of \textit{m}-ZnTCPP surface-bound to TiO\textsubscript{2} we have used single-molecule confocal fluorescence imaging. Figures 4.1A1,A2 show the single-molecule confocal fluorescence images of \textit{m}-ZnTCPP on TiO\textsubscript{2} NPs-coated ITO surface and TiO\textsubscript{2} NPs-coated ITO surface after 30 minutes in presence of 0.1 M NaCl aqueous electrolyte, respectively.
Figures 4.1B1,B2 show the single-molecule confocal fluorescence images of $m$-ZnTCPP on TiO$_2$ NPs-coated ITO surface and TiO$_2$ NPs-coated ITO surface after 30 minutes with -0.60 V applied potential in presence of 0.1 M NaCl aqueous electrolyte, respectively. Each bright spot is attributed to a molecular fluorescence image of a single $m$-ZnTCPP molecule. A close look at the images indicates same position of the observed $m$-ZnTCPP molecule, clearly demonstrating the surface stabilization of $m$-ZnTCPP surface-bound to TiO$_2$ NPs even in presence of aqueous electrolyte and applied bias.

**Figure 4.1.** Single-molecule confocal fluorescence images of $m$-ZnTCPP on (A1) and (A2) TiO$_2$ NPs-coated ITO surface and TiO$_2$ NPs-coated ITO surface after 30 minutes (scan area is same for A1 and A2); (B1) and (B2) TiO$_2$ NPs-coated ITO surface and TiO$_2$ NPs-coated ITO surface after 30 minutes with -0.60 V applied potential (scan area is same for B1 and B2). All the images were taken in presence of 0.1 M NaCl aqueous electrolyte. Image sizes are 10 µm x 10 µm.

This observation can be accounted for by the fact that the four covalent anchor points$^{8,9}$ of $m$-ZnTCPP lead to its strong bonding with TiO$_2$ NPs, which in turn provides resistance to the desorption. The surface stabilization of $m$-ZnTCPP surface-bound to TiO$_2$ NPs further indicates that the cooperative action of the four anchoring groups has a positive effect in stabilizing the dye on the TiO$_2$ NPs surface in aqueous electrolyte solution.$^{47}$
4.3.2. Effect of Applied Electric Potential in Blinking

Figures 4.2A-C show the typical single-molecule fluorescence intensity trajectories of $m$-ZnTCPP at different applied potential across the dye-TiO$_2$ interface. At any fixed potential, the blinking behaviour of each single molecule is significantly different from others. However, for majority of the molecules the blinking pattern is dominated by dark states in case of zero and positive applied potential (Figure 4.2A,C), whereas in case of negative applied potential we observed a quasi-continuous (intensity trajectory with no distinct bright and dark states) distribution of fluorescence intensities (Figure 4.2B). The observed single-molecule fluorescence time trajectories have the characteristic blinking between bright and dark states in absence of applied potential (Figure 4.2A), which is associated with temporal fluctuation or dynamic disorder of interfacial ET dynamics.$^{3,4,27,29}$

**Figure 4.2.** Single-molecule fluorescence intensity trajectories of $m$-ZnTCPP on TiO$_2$ NPs-coated ITO surface in presence of 0.1 M NaCl aqueous electrolyte with (A) 0.00 V, (B) -0.60 V, and (C) +0.60 V applied potential. (D) Series of single-molecule fluorescence decays with different applied potentials.
To explain how the applied potential significantly alters the blinking behavior of the molecules, we need to examine the underlying processes that contribute to blinking. The uniqueness of single-molecule photon-stamping spectroscopy lies in the fact that for each photoexcitation, if the excited state of the dye molecule involves an ultrafast forward electron transfer (FET) process reaching a charge-separation state of an oxidized dye and an excess electron in TiO$_2$, then the dye molecule will not emit a photon through an $S_1$ to $S_0$ radiative transition (Figure 4.3). The oxidized dye is mostly nonfluorescent, and the dye molecule can only emit another photon when a backward electron transfer (BET) occurs reducing the oxidized dye back to a ground state, $S_0$. Therefore, a close look of single-molecule fluorescence intensity trajectories can provide information about FET and BET dynamics. For each photoexcitation, the excited state of the single-molecule either undergoes radiative emission to yield an emission photon that contributes to a bright state or undergoes a nonradiative interfacial ET process that contributes to the dark state. The occurrence of the dark and bright states is ultimately determined by the dominance of radiative or the nonradiative interfacial ET rate process, which further depends on the other ET rate regulating parameters, such as the electronic and vibrational coupling between the molecule and the substrate.$^{5,13,17,23,24,29,35,48,49}$ Following an interfacial ET to TiO$_2$, the injected electrons go through charge trapping, detrapping, and electron Brownian and non-Brownian diffusion before mostly recombining with parent oxidized dye, the BET.$^{3,4,13,17,20,23,24}$ Surface traps play an important role in dynamics of injected electrons in TiO$_2$. Therefore, a fundamental understanding of the surface states, such as their nanoscale distribution and involved charge transfer coupling, is crucial to the improvement of the photoelectrical performance of semiconductor materials.$^{13,17,20,23,24,31}$ Previously, a near-field scanning microscopic imaging analysis of surface states on a TiO$_2$ (110) surface was demonstrated and
We have shown that for a molecule adsorbed on the semiconductor surface, the surface state charge-transfer pathways are primarily affected by the density and energy distributions of the surface states.\textsuperscript{31}

The BET rate depends on the time spent by an excess electron on TiO\textsubscript{2} NPs, which further depends on the distribution of excess electron trap states within the NPs. Consequently, the BET rate typically influence the blinking behavior of the single-molecules anchored to TiO\textsubscript{2} NPs. The BET process, i.e., the excess electron and oxidized dye recombination, has been reported to occur in the range of picoseconds (ps) to several milliseconds (ms) under various cross interfacial electric bias conditions.\textsuperscript{5,17,19,20,22,50} Therefore, considering the nanosecond radiative relaxation lifetime of the excited state of $m$-ZnTCPP and the picoseconds to milliseconds timescale of BET, we attribute that fluorescence fluctuation dynamics strongly depends on BET rate. If the BET time is in the order of ms-$\mu$s, longer than ns radiative relaxation time of the excited state of a dye molecules, then the dye molecule will be expected to spend more time in a given charge state M/M$^+$ ($M = m$-ZnTCPP).

This leads to slow switching between M and M$^+$ within the bin time, resulting in distinct bright and dark states. On the other hand, if the BET time is of the order of ns-ps, faster than the ns radiative relaxation time, then the dye molecule will be expected to spend less time in a given charge state M/M$^+$ leading to fast switching between M and M$^+$ within the bin time, which results in a quasi-continuous distribution of fluorescence intensities.

The preceding discussion attests to the fact that the observed quasi-continuous distribution of fluorescence intensities at applied negative potential (Figure 4.2B) can be attributed to either (i) absence of FET at applied negative potential or (ii) fast BET rate. Literature reports suggest that the decrease in FET rate with applied negative potential is
minimal (5-25 times) compared to the enhancement in BET rate ($10^3$-$10^8$ times).\textsuperscript{17,19,20,22} For TiO\textsubscript{2} NPs the BET rate was found to be in the rage of milliseconds to microseconds at positive or zero applied potential, whereas a dramatic increase in recombination rate (in the rage of nanoseconds to picoseconds) has been reported at negative potential.\textsuperscript{17,20,22,51-53} Hence here the substantial increment in BET rate is deemed to be the determining factor for the observed change in blinking pattern. This behavior can be further explained by considering the modulation of Fermi level of TiO\textsubscript{2} NP as well as the changed electron occupancy in TiO\textsubscript{2} conduction band (CB) and energetically accessible surface traps states under the applied electric bias (Figure 4.3).

**Figure 4.3.** Schematic illustration of the effect of applied negative bias on the TiO\textsubscript{2} sub-bandgap or trap states. DOS, density of states; and VB, valence band. The applied negative potential raises the TiO\textsubscript{2} Fermi level, which leads to occupancy of CB electron acceptor states. Green areas denote electron acceptor states unavailable for ET from $m$-ZnTCPP excited state.

Several previous reports have indicated the existence of a high density of sub-bandgap or trap states lying below the CB of TiO\textsubscript{2} NPs, which results in an exponential tail to the CB density of states.\textsuperscript{3,4,19,21,22,52} With the application of negative potential, the Fermi level approaches or exceeds the potential of CB acceptor states/trap states, which results in occupancy of these states (Figure 4.3).\textsuperscript{13,19-21,23,24} Higher occupancy of CB acceptor states/trap states as well as increased
electron density supports a higher BET rate. However, applied positive bias does not affect the
density of electron accepting states of TiO$_2$ NPs and has no effect on BET rate and blinking
behavior (Figure 4.2).$^{19,20,22-24}$

Plausibly, the higher BET rate can be assigned to the observed quasi-continuous
distribution of fluorescence intensities of $m$-ZnTCPP. The dependence of BET rate upon applied
bias has already been reported and modelled as a random walk between an exponential energetic
distribution of trap sites.$^{54,55}$ This random walk model was also suggested by our earlier single-
molecule interfacial ET dynamics studies with $p$-ZnTCPP and $m$-ZnTCPP along with other
literature reports.$^{27,29,56,57}$ We have shown power-law distribution of dark times, related to
geminate recombination dynamics, dominant by Lévy statistics.$^{27,29,58,59}$ The combination of our
findings partially reveals the role of trap sites on interfacial ET dynamics. This, by far, is the first
report of an indirect evidence of BET rate at single molecule level.

### 4.3.3. Effect of Applied Electric Potential in Lifetime

Overall, the number of molecules studied in our system was more than 100 molecules. To
ensure that the observed dye molecules are representative of the ensembles, we compared our
observed results with the literature reports on ensemble level measurement. The fluorescence
lifetime of ZnTCPP in water was found to be in the range of 1.9 ns to 3.0 ns.$^{20,60}$ So, we can
epect the lifetime of $m$-ZnTCPP on TiO$_2$ NPs, in presence of water, will be less than 1.9 ns due
to interfacial electron transfer from excited state of $m$-ZnTCPP to TiO$_2$. The lifetime distribution
observed for $m$-ZnTCPP on TiO$_2$ NPs in absence of applied bias is in the range of 0.7 ns to 1.4
ns, which suggest that the observed single dye molecules are representative of the ensembles.

We note that the percentage of molecules that exhibited continual emission with applied
potential varies from sample to sample but it is certainly higher than 25%. The lower percentage
arises because the specific applied potential does not always guarantee the same potential sensed by each single molecule owing to the inhomogeneous potential distributions in the semiconductor and at the semiconductor-electrolyte interfaces. This inhomogeneity in potential distributions arises due to the inherent roughness of the TiO$_2$ NP surface, nanoscale gradient of dielectric constants and electric conductivity, and inhomogeneous surface electric work functions. Additionally, the quick photobleaching for some molecules is also responsible for lower percentage of molecules that exhibited continual emission with applied potential.

We also note that the intersystem crossing to the triplet state of $m$-ZnTCPP molecules is not likely to be the cause of fluorescence intensity fluctuation or blinking, because the triplet-state lifetime of ZnTCPP dye lies close to 1 ms or less. The long dark time (from sub seconds to seconds) for $m$-ZnTCPP on TiO$_2$ shows that the fluctuation of fluorescence is not likely due to the triplet state. In our control experiment we have observed much less or no blinking for $m$-ZnTCPP on cover glass comparing to that in the $m$-ZnTCPP on TiO$_2$ systems, which rule out a significant contribution from the dark triplet state to the blinking. Had the triplet state of $m$-ZnTCPP molecules been responsible for the blinking, we should have observed similar blinking for $m$-ZnTCPP on glass.

To further dissect the complex interfacial electron transfer dynamics, we have studied the effect of driving force on FET and hence on the lifetime of $m$-ZnTCPP. The increase in the lifetime of $m$-ZnTCPP molecule anchored to TiO$_2$ NP surface with applied negative potential (Figure 4.2D) indicates decrease in ET efficiency. Figure 4.4A shows single-molecule fluorescence lifetime distributions of $m$-ZnTCPP molecules at different applied potential. The lifetime distribution from 0.7 ns to 1.4 ns with 0.00 V applied potential clearly demonstrates the individuality of each molecule in a specific environment associated with the inhomogeneous
surface state distribution of $m$-ZnTCPP molecules on rough TiO$_2$ NP surface. The shift towards longer lifetime indicates retardation of FET rate with applied negative potential. This retardation can be assigned to (i) an increase in electron density within the TiO$_2$ CB (Figure 4.4B), which reduces the density of unoccupied states available for electron injection and (ii) decrease of the FET free energy driving force (Figure 4.3).$^{19,20,22-24}$ Nevertheless, compared to eight order of magnitude change of BET rate the FET rate changes only by one order of magnitude.$^{17,19,23,24,53}$ The Fermi level of TiO$_2$ with applied negative potential (in our working range) lies within the Schottky barrier, and only states near the band edge are filled (Figure 4.3).$^8$ So most electron accepting states of TiO$_2$ CB with applied negative potential remain unoccupied and the density of accepting states for ET from excited $m$-ZnTCPP molecule should not be significantly smaller than $m$-ZnTCPP on TiO$_2$ NPs.

**Figure 4.4.** Fluorescence lifetime distributions of $m$-ZnTCPP on TiO$_2$ NPs-coated ITO surface in presence of 0.1 M NaCl aqueous electrolyte with +0.60 V, 0.00 V and -0.60 V applied potential. (B) Schematic depiction of interfacial ET in absence and presence of applied electric bias. In absence of electric bias the efficiency of photoinduced ET is high (indicated by large arrow), whereas the application of negative potential raises the electron density in TiO$_2$ NPs, leading to decrease in the efficiency of ET (indicated by small arrow).
It should be noted that our measurements only consider those molecules which are visible in single-molecule confocal fluorescence images. The visibility of single molecules suggests that the FET time fluctuates in a wide time scale from femtoseconds to nanoseconds or even slower. The lifetime variation range with applied potential also indicates presence of a time component having nanosecond fluctuation of FET. Had the time scale of the FET been solely in the femtosecond to picosecond range, the excited state radiative emission efficiency would have been as low as $10^{-3}$ to $10^{-6}$ and the single molecules would essentially be undetectable by photon detection. This highly inhomogeneous interfacial electron transfer processes are well supported by ensemble-averaged time-resolved data in the literature.\(^6\)

The single molecule fluorescence decays were fitted by biexponential function derived by deconvolution of instrument response function (IRF). The lifetime distribution from 0.7 ns to 1.4 ns with 0.00 V applied potential clearly demonstrates the individuality of each molecule in a specific environment, which cannot be observed by ensemble average measurements. This static disorder of the single-molecule interfacial ET process is closely associated with the inhomogeneous surface state distribution of \(m\)-ZnTCPP molecules on rough TiO\(_2\) NP surface. The static disorder also leads to difference in lifetime as well as blinking pattern as we had discussed in our previous publications on the intermittent single-molecule interfacial ET dynamics.\(^2,4,7\)

We also considered the observed insensitivity of positive applied potential on blinking pattern as well as excited state lifetime of \(m\)-ZnTCPP molecule anchored to TiO\(_2\) NP surface. Following earlier report \(^24\) we can attribute the bias independence at positive applied potentials to the fact that the electron occupancy induced by the applied positive potential reduced to less than one per nanoparticle. Under such low electron occupancy conditions, the effect of applied bias becomes less prominent than that induced by the laser excitation (approximately one photoinjected electron per nanoparticle). The charge recombination will therefore be dominated by electrons injected by the laser excitation only. The laser power in our experiment is so low
that we can consider only one injected electron per nanoparticle, which in turn results in power independent recombination kinetics.

The charge screening effect and Stark effect reported by Meyer et al. \(^{25-27}\) also suggest that the increased electron density into TiO\(_2\) generate significant electric field across the interface, which in turn influence ET efficiency of the surface anchored molecules. The broader distribution of lifetime in case of -0.60 V applied potential can be accounted for by the inhomogeneous potential distributions in the semiconductor and at the semiconductor-electrolyte interfaces. This inhomogeneity in potential distributions arises due to the inherent roughness of the TiO\(_2\) NP surface, nanoscale gradient of dielectric constants and electric conductivity, and inhomogeneous surface electric work functions. Furthermore, based on our intermittent single-molecule interfacial ET dynamics observations, we note that this electron density dependent inhomogeneity is likely to be dynamic rather than static due to the excess electron diffusion in the conduction band of TiO\(_2\).\(^{28}\)

The change in electrostatic charge environment of the interface due to injected electrons into TiO\(_2\) has influence on the surface anchored molecules. But, the effect of electric field on the absorption of dye molecules from the TiO\(_2\) is thought to be diminished by the large dielectric constant of TiO\(_2\), \(\varepsilon_r = 7-50\); high permittivity of water, \(\varepsilon_r = 80.1.\)^{29} Extensive analysis of double layer effect and impact of different electrolyte composition and concentration at single-molecule level requires further investigation and is beyond the scope of this manuscript.

The photoreductant properties, weak photoreductant vs strong photoreductant can also affect (i) the interfacial ET dynamics and (ii) the extent of change in FET dynamics with applied bias. However, the consideration of photoreductant properties is advantageous if we compare two dye molecules having different photoreductant properties in similar environment at single molecule level.

Even though the change in blinking pattern as well as the lifetime distributions of single \(m\)-ZnTCPP molecules demonstrates the correlation between the applied electric potential across TiO\(_2\)/ITO electrode and the kinetics of interfacial ET dynamics, it is desirable to investigate
perticular single molecules in identical conditions. To illustrate this we monitored fluorescence intensity trajectories and fluorescence lifetime of \textit{m}-ZnTCPP molecules anchored to TiO\textsubscript{2} NPs surfaces modulated by cyclic voltammetric (CV) potential scanning (Figure 4.5). The fluorescence intensity level increases and decreases with ramping down (scanning from +0.6 V to -0.6 V) and ramping up (scanning from -0.6 V to +0.6 V) the voltage, respectively. The higher fluorescence intensity with applied -0.6 V potential than +0.6 V demonstrates less fluorescence quenching due to reduced interfacial electron transfer at -0.6 V potential. The lifetime for the two regions of Figure 4.5A, marked in red and blue were derived using photon stamping spectroscopy. The lifetime obtained for red region (1.0 ns) is higher than the blue region (0.8 ns), which again reflects decrease in ET efficiency at negative potential. However, the small change in lifetime is well supported by literatures reports showing minimal effect of applied bias on FET rate.\textsuperscript{17,19,22,23,53}

\textbf{Figure 4.5.} Single-molecule spectroelectrochemistry of \textit{m}-ZnTCPP on TiO\textsubscript{2} NPs-coated ITO surface in presence of 0.1 M NaCl aqueous electrolyte: (A) single-molecule fluorescence intensity trajectory obtained during the CV scanning. (B) Potential vs. time plot of the CV scan. (C), (D) fluorescence decays derived from different time window of the trajectory shown in (A).
4.4. Summary

In conclusion we can control the blinking behavior of single-molecule anchored to TiO$_2$ NPs with applied electric potential by effectively tuning electron density inside the TiO$_2$ NPs. The applied negative potential causes (i) decrease in charge injection efficiency resulting in higher excited state lifetime of $m$-ZnTCPP and ii) increase in BET rate following charge injection resulting in quasi-continuous intensity variation. However, the applied positive bias has essentially no effect on blinking behavior and lifetime, which indicates that density of states plays a dominant role in dictating the changes in rates of charge transfer in our system. This is further supported by the preliminary results of our ongoing study on the role of density of accepting state in semiconductors that have similar density of states but large difference in driving force. Our single molecule spectroelectrochemical study provides novel insights in determining the nature of semiconductor energy states that participate in interfacial ET.

4.5. References


CHAPTER 5. PROBING DRIVING FORCE AND ELECTRON ACCEPTING STATE
DENSITY DEPENDENT INTERFACIAL ELECTRON TRANSFER DYNAMICS:
SUPPRESSED FLUORESCENCE BLINKING OF SINGLE-MOLECULES ON INDIUM
TIN OXIDE SEMICONDUCTOR

5.1. Introduction

Interfacial electron transfer (ET) dynamics between molecules and metallic or semiconductor electrodes at nanoscale is the core of surface chemistry, catalysis, and solar energy conversion, including solar photovoltaic and solar fuel science and technology.\(^1\)-\(^{24}\) Improving our understanding of the underlying processes and mechanisms that govern interfacial ET is of foremost importance for basic energy science and technology. Comprehensive introspection of interfacial ET dynamics and associated intermittency of excited-state chemical reactivity requires molecular-level understanding of all related and regulating parameters: for example, adsorbate/semiconductor interactions, Franck-Condon factor, distribution of crystal surfaces and trap states, vibronic coupling, structures and energetics of both the adsorbate and the substrate surfaces, solvation, and local environment thermal fluctuations.\(^5\),\(^10\),\(^13\),\(^16\),\(^25\)-\(^{47}\) There are two major processes involved in the photoinduced interfacial ET at a dye/semiconductor interface: forward electron transfer (FET) from an excited state of dye molecule to the conduction band or energetically accessible surface states of semiconductor, and backward electron transfer (BET) of the excess electron which recombines with the parent oxidized dye molecule.\(^10\),\(^12\),\(^16\),\(^25\),\(^28\),\(^29\),\(^31\),\(^48\) Extensive studies on interfacial ET dynamics have shown that FET kinetics are rather insensitive to variations in experimental condition,\(^34\),\(^49\)-\(^{53}\) whereas, BET kinetics exhibit greater sensitivity to experimental condition. Designing an efficient solar energy harvesting system entails controlling the rate of BET process in order to generate long-lived
charge-separated states so that the excess electron can diffuse away to generate photovoltaic potential energy.\textsuperscript{54-57} Despite the greater significance of BET dynamics, it has not been studied in great details, while FET dynamics has been well characterized. BET dynamics have been studied on an ensemble level using transient absorption spectroscopy and fluorescence measurements, but the underlying trapping and de-trapping processes have not been directly probed.\textsuperscript{32,58-63} Ensemble-average measurements are not necessarily specific to resolve heterogeneity in local environment involving inhomogeneous substrate-dye molecule interactions. Detailed understanding of the molecular mechanics of interfacial ET dynamics requires studying the system at a single molecular level.

Typical interfacial ET dynamics in sensitizer-semiconductor nanoparticle systems often involve temporal fluctuations and nanoscale spatial heterogeneities, i.e., the dynamic disorders and static disorders, respectively\textsuperscript{12,13} presenting a significant challenge for ensemble-averaged experiments for a molecular level characterization. Ensemble-averaged measurements often encounter interferences from molecular aggregation, multiple electron injection to a single particle and multiple electron-oxidized dye recombinations on the surface of a single particle. Single-molecule spectroscopy\textsuperscript{12,13,28,31,64-75} allows studying the interfacial ET dynamics one molecule at a time in a specific nanoscale local environment, specifically powerful in resolving spatiotemporal heterogeneity. At single-molecule level, dye molecule adsorbed on metallic or semiconductor NPs shows fluorescence intensity fluctuation with time, also known as blinking. In this study we have used zinc(II)-5,10,15,20-tetra(3-carboxyphenyl) porphyrin, $m$-ZnTCPP as dye molecule. In a single-molecule photon-stamping measurement, $m$-ZnTCPP molecules are adsorbed on ITO film and on TiO$_2$ NPs; each photon detected is emitted from the S$_1$ excited state of a dye molecule and the same molecule will not be able to emit another photon until the dye
molecule returns back to the ground state, S₀ (Figure 5.1). For each photoexcitation, if the excited state of the dye molecule involves an ultrafast FET process reaching a charge-separation state of an oxidized dye and an excess electron in ITO/TiO₂, then the dye molecule will not emit a photon through an S₁ to S₀ radiative transition. The oxidized dye is mostly nonfluorescent, and the dye molecule can only emit another photon when a BET occurs reducing the oxidized dye back to a ground state, S₀. Therefore, a close look of single-molecule fluorescence intensity trajectories can provide information about FET and BET dynamics.

**Figure 5.1.** Schematic depiction of different energy levels and photoinduced processes involved in the m-ZnTCPP–ITO/TiO₂ system. CB, conduction band; VB, valence band. The m-ZnTCPP binding on ITO and TiO₂ surface as well as the Fermi-level position is demonstrated.

While the blinking behavior of single-molecule on metallic or semiconductor NPs is still not fully understood, it can be considered to be the combined effect of (i) temporal fluctuation or dynamic disorder of interfacial ET dynamics, ¹²,⁷⁶,⁷⁷ intermittency of ET, and (ii) BET rate (vide infra), which depends on the time spent by an excess electron on metallic or semiconductor NPs, which further depends on the time scales of the electron trapping and de-trapping rate
fluctuations. Detailed analysis of the fluorescence blinking behavior is therefore a direct method of probing both FET and BET dynamics. Therefore, a systematic variation of parameters controlling blinking rate as well as blinking behavior at single-molecule level can yield mechanistic information about both FET and BET dynamics. Different variables have already been reported which influence BET dynamics to a larger extent than FET, e.g. effect of applied electric potential, effect of doping, effect of oxidation and reduction of metallic or semiconductor NPs, use of different dye molecule, passivation of metallic or semiconductor NPs etc.

In this study, we have compared the interfacial electron ET dynamics between \textit{m}-ZnTCPP/Sn-doped In$_2$O$_3$, ITO film to that of \textit{m}-ZnTCPP adsorbed on TiO$_2$ NPs, with and without applied electric potential. Transparent \textit{n}-type conducting oxides like ITO are heavily doped and are of particular interest as semiconductor materials due to their relatively high electron densities ($> 10^{19}$ cm$^{-3}$). The higher electron density in ITO than TiO$_2$ is likely to affect blinking behavior due to the increased occupancy of trap states in ITO. This can provide information regarding the role of trap states on BET rate. Furthermore, the conduction band of both ITO as well as TiO$_2$ is lower than the LUMO energy of \textit{m}-ZnTCPP indicating energetically allowed photoinduced interfacial ET. The Fermi-level lies above conduction band edge of ITO, whereas the Fermi-level lies below the conduction band edge of TiO$_2$ (Figure 5.1), which causes difference in the driving force for interfacial ET in ITO vs TiO$_2$. This difference in driving force is again likely to affect the ET rate as well as fluorescence blinking behavior of \textit{m}-ZnTCPP. Nevertheless, our single-molecule studies provide novel insights in determining (i) the role of trap states on BET rate, hence on blinking behavior and (ii) the nature of semiconductor energy states that participate in interfacial ET dynamics. Figure 5.1
schematically depicts energy levels and photoinduced processes involved in the \( m \)-ZnTCPP-ITO/TiO\(_2\) systems. Here, we note that the blinking and fluctuation of the single-molecule fluorescence intensity are not due to the rotation or translational motions of the single molecules, \( m \)-ZnTCPP.\(^{12,76}\) The covalently anchored \( m \)-ZnTCPP molecules through multiple carboxylic groups do not have the flexibility for rotational or translation motions.\(^{31,76,98}\) Additionally, according to our earlier studies, the fluctuation of fluorescence intensity is not due to the triplet state of \( m \)-ZnTCPP molecules,\(^{31,76}\) because the triplet-state lifetime of ZnTCPP dye lies close to 1 ms or less.\(^{99}\) In our control experiment we have observed much less blinking for \( m \)-ZnTCPP on cover glass comparing to that in the \( m \)-ZnTCPP-ITO/TiO\(_2\) systems,\(^{31}\) which rule out a significant contribution from the dark triplet state to the blinking. Had the triplet state of \( m \)-ZnTCPP molecules been responsible for blinking, we should have observed similar blinking for \( m \)-ZnTCPP on glass. Additionally, the long dark time (from sub seconds to seconds) for \( m \)-ZnTCPP\(^{31}\) on TiO\(_2\) certainly shows that the fluctuation of fluorescence is not due to the triplet state.

In TiO\(_2\) the Fermi level lies below the trap states, which are assumed to follow an exponential distribution in energy below the conduction band.\(^{96,97}\) In ITO the Fermi level lies above the conduction band edge. The higher electron density in ITO (which is obtained by substitutional doping with Sn) compared to TiO\(_2\), supports faster BET rate,\(^{89}\) charge recombination rate.

5.2. Experimental Section

The details of the experimental setup and sample preparation is discussed in Chapter 2.
5.3. Results and Discussion

We recorded the fluorescence intensity trajectories of more than 100 molecules of \( m \)-ZnTCPP on Sn-doped In\(_2\)O\(_3\) (ITO) film. Figures 5.2A-F show three typical fluorescence intensity trajectories along with the fluorescence decays for three different single \( m \)-ZnTCPP molecules adsorbed on ITO film. The blinking behaviours of different \( m \)-ZnTCPP molecules adsorbed on ITO film are different, indicating static disorder of interfacial ET dynamics.\(^{12,31,76}\) Nevertheless, for majority of the molecules, the blinking is either dominated by bright states indicating suppressed blinking behaviour (Figure 5.2B) or show a quasi-continuous (intensity trajectory with no distinct bright and dark states) distribution of fluorescence intensities (Figure 5.2A).

**Figure 5.2.** Typical Single-molecule fluorescence emission trajectories of \( m \)-ZnTCPP on ITO surface (A, B, and C) and corresponding single-molecule fluorescence decays (D, E, and F).
Unlike \textit{m}-ZnTCPP on ITO surface (Figure 5.3A), \textit{m}-ZnTCPP adsorbed on TiO$_2$ NPs show fluorescence intensity trajectories with distinct bright and dark states (Figure 5.3B). Once again the blinking behaviours of different \textit{m}-ZnTCPP molecules adsorbed on TiO$_2$ NPs are different, indicating static disorder of interfacial ET dynamics.$^{12,31,76}$ For majority of the molecules the fluorescence intensity trajectories are dominated by dark states, which demonstrates strong bonding between \textit{m}-ZnTCPP and TiO$_2$ as described in our earlier publication.$^{31}$

\textbf{Figure 5.3.} Typical Single-molecule fluorescence emission trajectories and corresponding intensity histograms of \textit{m}-ZnTCPP on (A) ITO surface, (B) and (C) TiO$_2$ NPs without and with applied electric potential respectively.
Considering different semiconductor surfaces as the only difference between two systems, \( m \)-ZnTCPP on ITO surface vs \( m \)-ZnTCPP on TiO\(_2\) NPs, the change in the blinking behavior can be attributed to the effect of ITO surface and TiO\(_2\) NPs. The observed behavior of \( m \)-ZnTCPP on ITO surface can be associated with (i) inefficient FET leading to quasi-continuous distribution of fluorescence intensities and/or (ii) fast BET rate (vide infra). Considering larger driving force for FET in case of ITO than TiO\(_2\) NPs\(^{89,100,101}\) we posit that the FET is not inefficient in case of ITO, which is further corroborated by observed lifetime of \( m \)-ZnTCPP on ITO surface (vide infra). Therefore, to understand the observed difference in the single-molecule blinking behaviour, we focus our attention on BET dynamics, the interfacial charge recombination dynamics.

The uniqueness of single-molecule photon-stamping spectroscopy lies in the fact that it can resolve the heterogeneities in both FET and BET dynamics through careful analysis of the observed blinking behavior. In single-molecule photon-stamping spectroscopy for each detected photon, two parameters are recorded: chronic arrival time or real time and delay time between the laser pulse excitation and the photon emission from the excited state.\(^{13,95,102}\) Therefore, the photon-to-adjacent-photon pair time can be precisely recorded. Fluorescence intensity trajectories, the photon counting rate as a function of time, were constructed from photon-stamping time trajectories by binning the detected photons with few ms bin. Multiple ET events typically occur in each intensity time bin of a few milliseconds, depending on the ET efficiency during that bin. Accordingly, bright or dark states of the molecules are observed. For each photoexcitation, the excited state of the single-molecule either undergoes radiative emission to yield an emission photon that contributes to a bright state or undergoes a nonradiative ET process that contributes to the dark state. The occurrence of the dark and bright states is
ultimately determined by the dominance of radiative or the nonradiative process in terms of their rates, which further depends on the other ET rate regulating parameters, such as the electronic and vibrational coupling between the molecule and the substrate. Following an interfacial ET to ITO/TiO$_2$, the injected electrons go through charge trapping, detrapping, and electron Brownian and non-Brownian diffusion before mostly recombining with parent oxidized dye, the geminate charge recombination.$^{10,12,30,49,53,83}$ Surface traps play an important role in dynamics of injected electron in ITO/TiO$_2$. A fundamental understanding of the surface states, such as their nanoscale distribution and electronic coupling, is crucial to the interfacial ET dynamics and the mechanisms involving of the photoelectrical semiconductor materials.$^{10,30,49,53,84,103-106}$

Previously, a near-field scanning microscopic imaging analysis of surface states on a TiO$_2$ (110) surface was demonstrated and reported.$^{103}$ We have shown that for a molecule adsorbed on the semiconductor surface, the surface state charge-transfer pathways are primarily affected by the density and energy distributions of the surface states.$^{103}$

The BET rate depends on the time spent by an electron on ITO/TiO$_2$ NPs, which further depends on the distribution of trap states within the NPs as well as the electron density in the ITO/TiO$_2$ NPs. Consequently, the BET rate should greatly influence the blinking behavior of single-molecules anchored to ITO/TiO$_2$ NPs. The BET process, i.e., the electron and oxidized dye recombination, has been reported to occur in the range of picoseconds (ps) to several milliseconds (ms) under various conditions.$^{40,48,49,52,53,59,82,89,107-110}$ Therefore, considering the nanosecond lifetime of the excited state of $m$-$Zn$TCP and picoseconds to milliseconds timescale of BET, we suggest that fluorescence intensity fluctuation dynamics significantly depends on the BET rate. If the BET timescale is in the order of ms-μs, the dye molecule will be expected to spend more time in a given charge state M/M$^+$ (M = $m$-$Zn$TCP), leading to slow switching
between M and M within the bin time, resulting in distinct bright and dark states. On the other hand, if the BET is of the order of ns-ps then the dye molecule will be expected to spend less time in a given charge state M/M+ leading to fast switching between M and M+ within the bin time, resulting in a quasi-continuous distribution of fluorescence intensities. Therefore, the observed suppressed blinking (Figure 5.2B) as well as quasi-continuous distribution of single-molecule fluorescence intensity (Figure 5.2A is likely the result of faster BET in of m-ZnTCPP on ITO surface than in m-ZnTCPP on TiO\textsubscript{2} NPs. The higher BET rate in ITO is well supported by earlier reports. For example, Meyer et al. have shown significant difference in the time scale for BET which ranges from nanoseconds on ITO to microseconds and milliseconds on TiO\textsubscript{2}, SnO\textsubscript{2} and ZnO. Additionally on the basis of a convoluted interfacial electron-oxidized dye recombination model, we showed that the time scale of BET for p-ZnTCPP on TiO\textsubscript{2} NPs lies in the range of microseconds to milliseconds.

The electron density difference between ITO and TiO\textsubscript{2} presumably play a major role in the BET kinetics. The electron density for a 10\% Sn-doped In\textsubscript{2}O\textsubscript{3} (ITO) has been estimated to be \( \sim 2.2 \times 10^{21} \text{ cm}^{-3} \). The increased electron density leads to shift of Fermi level to more negative potential and filled trap states. For 10\% Sn-doped In\textsubscript{2}O\textsubscript{3} the Fermi level of ITO is estimated to be \( \sim 100 \text{ meV} \) higher than its conduction band edge. Due to the filled trap states as well as increase in number of electrons per nanoparticle, the photoinduced electrons spend less time within the semiconductor resulting in faster charge recombination. The effect of increased electron density on BET dynamics is well supported by our experimental results of applied negative bias across dye-TiO\textsubscript{2} interface. Figure 5.3C shows a quasi-continuous distribution of fluorescence intensities observed with applied potential of -0.60 V across dye-TiO\textsubscript{2} interface. It has been reported that applied electric
potential across dye-TiO$_2$ interface modulate the Fermi level of TiO$_2$ NP as well as the electron occupancy in TiO$_2$ conduction band and energetically accessible surface traps states. The applied negative bias across dye-TiO$_2$ interface also increases the electron density inside the TiO$_2$ NPs which supports faster BET rate. Evidently, the similar BET dynamics at ITO and TiO$_2$ surfaces with applied potential, at single molecule level, highlights the role of electron density and surface states density in governing charge transfer dynamics. The dependence of BET kinetics on electron density and surface states density has been revealed by observed effect of applied bias and doping using transient absorption spectroscopy. BET rate was found to vary over nine orders of magnitude, from milliseconds to picoseconds with changes in applied bias. For TiO$_2$ NPs, the BET rate was found to be in the rage of milliseconds to microseconds at positive or zero applied potential, whereas a dramatic increase in BET rate has been reported at negative potential. For TiO$_2$ NPs, the BET rate was found to be in the rage of nanoseconds to picoseconds at an applied bias of -0.6 V versus Ag/AgCl. Similarly, the BET rate increases depending on increases of the dopant and doping concentration. In the simplest consideration, with increase in doping concentration, the electron density in the materials increase and raises the Fermi level to a more negative potential, which results in increase in BET rate. In fact, the reduced blinking as well as quasi-continuous distribution of fluorescence intensity of (i) m-ZnTCPP on ITO surface (Figure 5.2) and (ii) m-ZnTCPP on TiO$_2$ NPs with applied negative potential are well in agreement with the observed fluorescence intensity trajectories of QDs in affect to different doping level and applied bias. To explain the huge variation of BET rate, Haque et al. proposed a mechanism, which supports electron transport being controlled by the energetically distributed trap sites within the TiO$_2$ NPs. According to Haque et al., BET kinetics exhibits a nonlinear
dependence on the TiO$_2$ electron occupancy, with dramatic increase of BET rate with increasing occupancy. Interestingly, the quasi-continuous distribution of fluorescence intensities in both cases of $m$-ZnTCPP on ITO surface (Figure 5.2) and $m$-ZnTCPP on TiO$_2$ NPs with applied negative potential, indicates similar range of BET rate in spite of difference in the relative energetics between excited state of $m$-ZnTCPP and ITO/TiO$_2$ (Figure 5.4). The insensitivity of BET kinetics on the relative energetics between electron in TiO$_2$ and the oxidized sensitizer corroborate with the mechanism of Haque et al., which suggests the electron occupancy, rather than the relative energetics between electron in TiO$_2$ and the oxidized sensitizer, is the most important factor in determining the BET rate.$^{49,82}$ Our findings, particularly the blinking behavior corroborate earlier reports of suppressed blinking on ITO,$^{95,101}$ dopant concentration dependent blinking,$^{50,57,81}$ and applied bias dependent blinking$^{26,113}$ all of which posit the considerable contribution of the electron occupancy and density of states.

**Figure 5.4.** Schematic illustration of the sub-bandgap or trap states, Fermi level, and forward ET free energy driving force ($\Delta G$) for ITO, TiO$_2$ NPs, and TiO$_2$ NPs with applied negative bias: $M^+/M^+$ indicate excited state energy of $m$-ZnTCPP. In TiO$_2$ the Fermi level lies below the trap
states, application of negative potential raises the TiO₂ Fermi level, which leads to occupancy of CB electron acceptor states as well as decrease in ΔG value. In case of ITO, the Fermi level lies above the conduction band edge and the forward ET free energy driving force (ΔG) is also large compared to that of TiO₂. Blue and green areas denote electron acceptor states unavailable for electron injection from m-ZnTCPP excited state.

To further analyze the complex interfacial ET dynamics and energetics involving in both FET and BET, we have studied the effect of free energy driving force on FET from the excited states of dye molecules to the conduction band and energetically accessible surface states of ITO and TiO₂ NPs, and hence on the lifetime of m-ZnTCPP. Figure 5.5 shows single-molecule fluorescence lifetime distributions of m-ZnTCPP on ITO surface and m-ZnTCPP on TiO₂ NPs. The lifetime distribution of m-ZnTCPP on ITO surface, from 0.7 ns to 2.6 ns demonstrates the individuality of each molecule in a specific environment associated with the inhomogeneous surface state distribution of m-ZnTCPP on rough ITO surface. Similarly, the lifetime distribution of m-ZnTCPP on TiO₂ NPs, from 1.4 ns to 4.8 ns indicates the individuality of each molecule in a specific environment associated with the inhomogeneous surface state distribution of m-ZnTCPP molecules on TiO₂ NPs.
Figure 5.5. Fluorescence lifetime distributions of \textit{m}-ZnTCPP on ITO surface and on TiO$_2$ NPs-coated cover glass.

The shift towards longer lifetime indicates lower efficiency of FET for \textit{m}-ZnTCPP on TiO$_2$ NPs than \textit{m}-ZnTCPP on ITO surface, which can be assigned to smaller FET free energy driving force in case of \textit{m}-ZnTCPP on TiO$_2$ NPs than \textit{m}-ZnTCPP on ITO surface (Figure 5.3). We note that the difference in refractive index of the two semiconductor materials ITO (~2.05) and TiO$_2$ (~2.30) should also affect radiative rates of \textit{m}-ZnTCPP molecule. Following Strickler-Berg equation\textsuperscript{116} higher index of refraction of the TiO$_2$ surface than that of ITO should result in a higher radiative rate and shorter lifetime for \textit{m}-ZnTCPP on a TiO$_2$ surface. On the contrary we observed longer lifetime for \textit{m}-ZnTCPP on TiO$_2$ surface than that of \textit{m}-ZnTCPP on ITO surface. Therefore, the lifetime difference between the \textit{m}-ZnTCPP on ITO vs \textit{m}-ZnTCPP on TiO$_2$ is not dominated by the refractive index difference of the two semiconductor materials, and we attribute the changes in lifetime to nonradiative FET processes. Unlike charge recombination, where the BET rate is significantly influenced by the density of surface states and electron
occupancy, the FET rate difference is mainly contributed by FET free energy driving force differences; although, assuming the other critical factors of electronic coupling, vibrational reorganization energy changes, and surface dye-substrate chemical interactions remain essentially constant. The insensitivity of FET rate on density of electron accepting states is reflected by higher efficiency of FET for *m*-ZnTCPP on ITO resulting in shorter lifetime. Had the density of electron accepting states been a deciding factor, the higher electron density within the ITO, which reduces the density of unoccupied states available for photoinduced electron injection (Figure 5.4) should have lower efficiency of FET. The insensitivity of FET rate on density of electron accepting states corroborate the observed insensitivity of FET rate to the applied electric potential effect and doping effect. Because the Fermi level in ITO at 10 % doping level is just 100 meV higher than its conduction band edge, only states near the band edge are filled. Therefore, most electron accepting states of ITO conduction band remain unoccupied and the density of accepting states in ITO for FET from excited *m*-ZnTCPP molecule should not be significantly smaller than that of *m*-ZnTCPP on TiO$_2$ NPs.

We have also analyzed the correlations in temporal variations of fluorescence intensity and fluorescence decay time calculated for a 10-ms bin size. Figure 5.6A,B show fluorescence lifetime-intensity distribution (FLID) of *m*-ZnTCPP on ITO and *m*-ZnTCPP on TiO$_2$ NPs, respectively. In Figure 5.6, the distribution of intensity and lifetime are shown along the horizontal and vertical lines for both *m*-ZnTCPP on ITO and on TiO$_2$ NPs, respectively. Figure 5.6A,B show fluorescence lifetime-intensity distributions of *m*-ZnTCPP on ITO and on TiO$_2$ NPs deduced from the single-molecule fluorescence intensity trajectories shown in Figure 5.2B and 4B, respectively. The single-molecule FLID of *m*-ZnTCPP on ITO and on TiO$_2$ NPs show wide distribution of intensity as well as lifetime. The broadness of intensity and lifetime distribution
for a single-molecule indicates the fluctuations in the reactivity of interfacial ET dynamics, i.e., intermittent interfacial ET dynamics,\textsuperscript{12,76,117-119} and variation in BET rate or trapping and detrapping dynamics.\textsuperscript{30} The \textit{m-}ZnTCPP adsorbed on TiO\textsubscript{2} NPs shows a broad fluorescence intensity distribution as well as a broad lifetime distribution. However, unlike \textit{m-}ZnTCPP adsorbed on TiO\textsubscript{2} NPs, \textit{m-}ZnTCPP on ITO surface shows a narrower fluorescence intensity distribution as well as a narrower lifetime distribution (Figure 5.6). Furthermore, Figure 5.6 shows that there are two different regions with distinct intensity for \textit{m-}ZnTCPP adsorbed on TiO\textsubscript{2} NPs, and only one region of intensity for \textit{m-}ZnTCPP on ITO surface. This observation again suggests suppressed blinking activity of \textit{m-}ZnTCPP on ITO surface.
Figure 5.6. Correlated variations of fluorescence intensity and fluorescence decay time (calculated for 10 ms bin size): (A) fluorescence lifetime-intensity distribution (FLID) of $m$-ZnTCPP on ITO for single-molecule fluorescence intensity trajectory shown in Figure 5.2B. (B) Fluorescence lifetime-intensity distribution (FLID) of $m$-ZnTCPP on TiO$_2$ NPs for single-molecule fluorescence intensity trajectory shown in Figure 5.3B. In both the FLID images the dark states of single-molecule fluorescence intensity trajectories (shown in Figure 5.2B and 5.3B) were not included because the fluorescence intensity level for dark states is almost equal to the background level.
To compare the intermittency or blinking dynamics of m-ZnTCPP on ITO and on TiO$_2$ NPs, we have performed statistical analysis on the stochastic durations of the dark state involving high ET reactivity compared to the bright state associated with low ET reactivity. Specifically, we have applied threshold method for the analysis of dark states to provide information of BET dynamics involving charge trapping and detrapping processes. The following steps are used to determine the distribution of dark-time durations and probability density distribution of the dark states for single-molecule fluorescence emission trajectories: (1) The threshold fluorescence intensity (photon count), $I_{th}$, separating the on and off states is determined using equation 5.1:

$$I_{th} = I_{av} + 3 \sigma$$

(5.1)

where $I_{av}$ is the average fluorescence intensity of the background and $\sigma$ is its standard deviation. (2) The distribution of dark-time durations, including occurrence of different dark times are determined using the threshold value. (3) Finally the probability density distribution of the dark states $P(t_{dark})$ are generated by using equation 5.2:

$$P(t_{dark}) = \frac{\text{Occurrence} (t)}{\Delta t}$$

(5.2)

where Occurrence (t) is the occurrence of dark event having duration time of t, and $\Delta t$ is the average of the dark time intervals to the preceding and following events.

Figure 5.7 shows the normalized probability densities of the dark-time durations of m-ZnTCPP on ITO and m-ZnTCPP on TiO$_2$ NPs. The probability density built from different dark time events show linear dependence on $t_{dark}$ in log-log plots for majority of events, particularly at short dark time. This linear dependence of the single-molecule dark time probability density
distributions shows typical power-law behavior, which can be mathematically described by equation 5.3:

\[ P(t_{\text{dark}}) \propto t_{\text{dark}}^{-m_{\text{dark}}} \]  

(5.3)

The observed power-law kinetics is consistent with our earlier results.\textsuperscript{31,76} We have shown that the probability density distributions of the dark times for \( p \)-ZnTCPP on TiO\textsubscript{2} NPs also follow power-law behaviour.\textsuperscript{76} However, the structural change of the dye molecule from \( p \)-ZnTCPP to \( m \)-ZnTCPP is always accompanied by the change in interfacial molecular interactions between the probe molecules and their fluctuating local environment leading to the difference in interfacial ET reactivity. Several existing models explain the power-law blinking behavior of single molecules on semiconductor surfaces.\textsuperscript{68,78,121-127} Following our earlier studied system and based on the data shown in Figure 5.7,\textsuperscript{76} we attribute that the observed power-law blinking and fluctuations of the fluorescence from \( m \)-ZnTCPP on ITO and on TiO\textsubscript{2} NPs, are due to temporal fluctuations in the reactivity of interfacial ET dynamics i.e., the dynamic disorder,\textsuperscript{119} and variation in BET rate or trapping and detrapping dynamics. The power law exponent \( m_{\text{dark}} \) is found to be 1.36 and 2.06 for \( m \)-ZnTCPP on TiO\textsubscript{2} NPs and \( m \)-ZnTCPP on ITO, respectively. The lower \( m_{\text{dark}} \) value of \( m \)-ZnTCPP on TiO\textsubscript{2} NPs than that of \( m \)-ZnTCPP on ITO indicates a relatively higher probability for longer dark times in the case of \( m \)-ZnTCPP on TiO\textsubscript{2} NPs. For \( m \)-ZnTCPP on ITO, no dark events with durations of longer than 2 seconds were observed, whereas dark events with durations up to 8 seconds were observed for \( m \)-ZnTCPP on TiO\textsubscript{2} NPs.
Figure 5.7. Normalized probability densities, \( P(t_{\text{dark}}) \) of the dark-time durations of \( m \)-ZnTCPP on ITO and \( m \)-ZnTCPP on TiO\(_2\) NPs. In log-log scale plots the solid lines are linear fits indicating power-law behavior. The power-law exponent, \( m_{\text{dark}} \), which is the slope of the linear fit, is also indicated in the figure.

To explain the long dark-events observed for \( m \)-ZnTCPP on TiO\(_2\) NPs compared to that of \( m \)-ZnTCPP on ITO, we proposed two possibilities (i) long dark events may occur due to high FET activity for a long time\(^{55} \) in \( m \)-ZnTCPP on TiO\(_2\) NPs and (ii) lower BET rate, owing to the presence of a large number of trap states in \( m \)-ZnTCPP on TiO\(_2\) NPs, resulting from longer trapping and slower detrapping processes. From our earlier discussion, it is evident that FET efficiency is lower in case of \( m \)-ZnTCPP on TiO\(_2\) NPs than to \( m \)-ZnTCPP on ITO. Nevertheless, FET activity does not describe the higher probability of longer dark time of \( m \)-ZnTCPP on TiO\(_2\) NPs than that of \( m \)-ZnTCPP on ITO surface. Therefore, the BET rate or electron trapping and detrapping dynamics plays an important role in the observed intermittency or blinking dynamics.

Overall the systematic variation of driving force and electron accepting state density (Figure 5.4) for interfacial ET in ITO vs TiO\(_2\) NPs with and without applied potential and
corresponding effect on blinking rate as well as blinking behavior at single-molecule level yield mechanistic information about both FET and BET dynamics. In our working range, the Fermi levels of both the TiO$_2$ NPs with applied negative potential$^{91}$ as well as ITO at 10% doping level reside close to their respective conduction band edge.$^{60,89,91,95,128}$ This implies that only states near the band edge are filled. We believe the results reported here, combined with our previous studies,$^{91,103}$ particularly the single-molecule spectroelectrochemistry study,$^{91}$ advance our understanding of the nature of interfacial charge transfer dynamics and energetics. Although our observations corroborate the findings of extensive literature on ensemble-averaged measurements, this study provides unique and fundamental understanding of the complex BET rate processes at single-molecule level. For example, our single-molecule results overcome interferences from molecular aggregation, multiple electron injection to a single particle, energy transfer, hopping, and multiple electron-oxidized dye recombinations on the surface of a single particle. Additionally, the observed nanoseconds lifetimes of $m$-ZnTCPP on ITO and TiO$_2$ NPs as well as the nanoseconds lifetime variation range with applied potential indicates the presence of a time component with nanosecond FET rates. Had the time scale of the FET rate been solely in the femtosecond to picosecond range, the excited state radiative emission efficiency would have been as low as $10^{-3}$ to $10^{-6}$, and the single molecules would essentially be undetectable in a typical single-molecule imaging measurement. We also note that most of the molecules, visible in single-molecule imaging, show nanoseconds lifetime components, and the fluctuations of FET rates at nanosecond time scale are significant. The highly inhomogeneous interfacial ET rate processes are typically reported in literature as non-exponential dynamics with ultrafast decay components and nanosecond decay components that present as a constant level off at ultrafast time scales. Although, the level-off amplitude is typically only a low percentage of the overall
time decay amplitudes, the integrated photon counts can be more than 70% or even 90%, which cannot be ignored. There are two significantly different dynamics and mechanisms: (1) Statically-disordered inhomogeneous dynamics: Majority of molecules is involved in ultrafast interfacial ET dynamics and only a small portion of molecules which does not engage in ultrafast ET participates only in radiative decays of nanosecond time scale; and (2) Dynamically-disordered inhomogeneous dynamics, the intermittent rate fluctuation dynamics: Majority of the molecules exhibit broad rate fluctuations, from ultrafast ET rate processes to nanosecond radiative rate processes. Seemingly identical individual molecules have significant different interfacial electron transfer rates reflects static disorder; whereas, for each individual molecule, the interfacial electron transfer rate also fluctuates significantly from time to time, which constitutes the dynamic disorder of the reaction dynamics. Should the interfacial ET be controlled by a statically-disordered inhomogeneous dynamics, the ET dynamics would be dominated by the ultrafast dynamics, and the molecules with slower ET rate and small amplitude will not be in the majority. However, should the interfacial ET be controlled by intermittent rate fluctuation dynamics, most molecules will show broad ET rate fluctuations and the molecules with slower ET rate and small amplitude will be in the majority. Since the ensemble-averaged time resolved non-exponential decay dynamics are widely reported in the literature, it is highly significant to identify if the controlling mechanism is only the static disorder or both the static and dynamic disordered rate processes, i.e., the intermittent interfacial ET dynamics. Nevertheless, our single-molecule spectroscopic analysis suggests that the systems we have studied are mostly controlled by the intermittent dynamics. Certainly, the quantification of the inhomogeneous interfacial ET dynamics, namely, the BET rate process, and FET rate process at single-molecule level, requires more research on this topic. We are currently working on
developing single-molecule ultrafast spectroscopy to resolve the interfacial ET at picoseconds to sub-picoseconds time scale. In the future, single-molecule spectroelectrochemical studies as well as the correlated single-molecule fluorescence spectroscopy approach with various other techniques such as atomic force microscopy (AFM), scanning tunneling microscopy (STM), electrochemistry, and Raman spectroscopy will continue to reveal and specify underlying processes and factors governing interfacial ET dynamics.

5.4. Summary

We have examined the role of driving force and density of accepting state on interfacial ET dynamics by comparative single-molecule photon-stamping studies of $m$-ZnTCPP adsorbed on ITO and $m$-ZnTCPP adsorbed on TiO$_2$ NPs. The two different semiconductors (ITO and TiO$_2$) present disparate adsorbing surfaces, characterized by large difference in electron densities and distinct driving forces. Without applied bias, we observed a blinking pattern associated with slower rate of BET for TiO$_2$ and a quasi-continuous distribution of fluorescence intensities and reduced lifetime for ITO. With applied negative potential, $m$-ZnTCPP adsorbed on TiO$_2$ NPs has an even larger difference in driving force compared to $m$-ZnTCPP adsorbed on ITO but similar electron densities. In both cases, a quasi-continuous fluorescence trajectory is observed. Our results suggest that the electron density in the semiconductor plays a significant role in dictating the changes in rates of charge transfer in the system of $m$-ZnTCPP adsorbed on ITO, rather than the relative energetics between electron in semiconductor and the oxidized sensitizer.

5.5. References


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CHAPTER 6. PROBING ELECTRIC FIELD EFFECT ON COVALENT INTERACTIONS AT A MOLECULE-SEMICONDUCTOR INTERFACE

Fundamental understanding of the energetic coupling properties of a molecule–semiconductor interface is of great importance. The changes in molecular conformations and vibrational modes can have significant impact on the interfacial charge transfer reactions. In this study, we probed the change in the interface properties of alizarin-TiO$_2$ system as a result of the externally applied electric field using single-hot spot microscopic surface-enhanced Raman spectroscopy (SMSERS) and provided a theoretical understanding of our experimental results by density functional theory (DFT) calculations. The perturbation, caused by the external potential, observed as a shift and splitting of the 648 cm$^{-1}$ peak, typical indicator of the strong coupling between alizarin and TiO$_2$. This chapter focuses only on the DFT calculations of Raman vibrations for the alizarin–TiO$_2$ system.

6.1. Introduction

Interfacial electron transfer (ET) at the molecule–semiconductor interface has been intensively investigated due to its crucial role in fundamental chemistry and physics, as well as in extensive applications like solar energy conversion, molecular devices, and photocatalysis.$^{1-3}$ In those systems, titanium dioxide (TiO$_2$) has been the most widely used and investigated semiconductor material due to its molecule–surface chemical interactions, large band gap, photostability, non-toxicity, and low cost. It has been reported that the dynamics of interfacial ET is directly related to the properties of the molecule–TiO$_2$ interface such as the electronic coupling, the vibrational relaxation energy of the adsorbed molecules and the local solvent, surface vibrational modes of the semiconductor.$^{1-4}$ Furthermore, electrical potential difference created either by the system or applied externally to drive the system is known to perturb the
vibrational energy levels of the adsorbed molecules on the TiO$_2$ surface, which typically is reflected in the vibrational spectra as a linear frequency shift. However, even though it is known that electrostatic fields can extensively affect the physical properties of molecules and as a result the interface properties, as well as the ET dynamics, the consequences of the electric potential applied to the system and/or created by the system to the molecule–semiconductor interface still requires a fundamental understanding.

Electric field effect (EFE) has been analyzed theoretically and reported extensively over the last 40 years; although, quantitative experimental results have only been introduced in the last two decades. Early studies of the EFE have focused only on changes in molecular geometry, considering that for a static geometry, within the harmonic approximation, there will be no dipole moment dependence of the vibrational levels. Later, it has been recognized that anharmonicity constitutes the origin of EFE. Anharmonic contributions have been separated into two parts: (i) mechanical anharmonicity, in which the interaction with the electric field causes the dipole moment to change due to the anharmonicity of the potential energy surface; and (ii) electrical anharmonicity, which causes perturbation of the harmonic bond force constant resulting in change in the transition energy between the vibrational levels.

Furthermore, the relationship between the bond length and the force constant is described by Badger’s rule which suggests that the changes in molecular geometry would result in vibrational frequency shifts. The amount of the shift observed is directly related with the strength of the electric field and its interaction with the molecule, according to the detailed theoretical studies in the literature.
In this study, we have chosen alizarin–TiO\textsubscript{2} system (Figure 6.1) due to the strong electronic coupling at the interface which has been demonstrated by the previous infrared data and structure analysis calculations.\textsuperscript{61,69-72}

![Figure 6.1. Bidentate configuration of alizarin binding to TiO\textsubscript{2}. Red, oxygen; light gray, titanium; black, carbon; and gray, hydrogen.](image)

The alizarin–TiO\textsubscript{2} system is particularly interesting because interfacial ET is essentially ultrafast in femtosecond range, whereas alizarin excited state is at the edge of the conduction band (CB) of TiO\textsubscript{2}, where the TiO\textsubscript{2} density of state (DOS) is lowest.\textsuperscript{3} Interfacial ET is sensitive to the energetics of both the dye molecules and the semiconductors, the DOS, the magnitude and energy dependence of the dye–semiconductor electronic and vibrational coupling, and the vibrational relaxation dynamics. Earlier studies suggest that when the DOS and the dye–semiconductor coupling change slowly over the relevant energy range, the interfacial ET is well described by the pure electronic limit without vibrational contributions. However, when the DOS and the dye–semiconductor coupling vary significantly over the relevant energy range, the
interfacial ET depends substantially on the vibrational Frank-Condon factors. For alizarin–TiO$_2$ system, the electronic coupling between alizarin and the semiconductor vary significantly even within a small energy range, which makes the alizarin–TiO$_2$ system highly susceptible towards an applied electric field.$^3$

Previously, it has been established that interfacial ET dynamics is directly related with the electronic coupling as well as the vibrational relaxation energy of the adsorbed molecules and surface vibrational modes of the semiconductor.$^{69,73}$ According to non-adiabatic ET theory, the rate of electron transfer, $k_{ET}$ can be expressed as the sum of ET rates to all possible accepting states in the semiconductor.$^1$

$$k_{ET} = \frac{2\pi}{\hbar} \int_{-\infty}^{\infty} dE \rho(E)(1 - f(E, E_F)) |H(E)|^2 \times \frac{1}{\sqrt{4\pi \lambda k_B T}} \exp \left[ -\frac{(\lambda + \Delta G_0 + E)^2}{4\lambda k_B T} \right]$$

(6.1)

where $\Delta G_0$ is driving force for electron injection; $\rho(E)$ is the density of states (DOS) at energy $E$ relative to the conduction band edge, which can include both bulk states and surface states; $H(E)$ is the average electronic coupling between the adsorbate excited state and all states in the semiconductor at the same energy $E$; $f(E, E_F)$ is the Fermi occupancy factor; and $\lambda$ is the total reorganization energy. A particular vibrational mode change can effectively change ET rate by changing $\Delta G_0$, DOS, electronic coupling and most importantly by changing $\lambda$ value. The total reorganization energy, $\lambda$ is contribution of both vibrational reorganization energy, $\lambda_V$ and solvent reorganization on energy, $\lambda_S$. Under consideration of harmonic vibrations $\lambda_V$ can be represented as$^{69,74}$

$$\lambda_V = 0.5 \sum \Delta_k^2 \nu_k$$

(6.2)

where $\nu$ is vibrational frequency for a particular mode, and $\Delta$ is displacement in dimensionless normal coordinates between ground- and excited-state equilibrium geometries along each normal coordinate.
Our result as well as the literature suggest that the covalent bonding of the alizarin molecule to Ti atoms through hydroxyl groups gives rise to an additional peak at 648 cm\(^{-1}\) in the Raman spectra.\(^{69,73}\) This strong electronic coupling makes this molecule–semiconductor system valuable to study the effects of applied electric field at the interface by using Raman analysis. Fundamental understanding of this phenomenon is critically related to the manipulation and design of many applications like photovoltaic devices and molecular electronics.

### 6.2. Density Functional Theory Calculations

To analyze the origin of the 648 cm\(^{-1}\) peak splitting in the presence of electric field, we performed density functional theory (DFT) calculations.\(^{75}\) The model considers that the attachment of alizarin to TiO\(_2\) occurs through two hydroxyl oxygen bonded with single or two separate Ti atoms. Alizarin is attached to Ti (IV) centers of (TiO\(_2\))\(_{15}\) bulk, which is frozen in the configuration, in bidentate mode and optimized by using B3PW91 functional, with the LANL2DZ basis set on Ti atoms, and a 6-31G(d) basis set on all other atoms. It should be noted that this simplified model of alizarin–TiO\(_2\) complex does not intend to simulate the actual surface of TiO\(_2\), but only to provide a basis for the discussion of the experimental evidence obtained in the Raman spectrum of the proposed interfacial Ti–O binding modes. Raman spectra of the complex are calculated by applying the multipole electric field in the direction normal to the TiO\(_2\) surface with no symmetry.

#### 6.2.1. Geometry Optimization

For the density functional theory (DFT) calculations, all molecular structures (dye-TiO\(_2\)) were built and preoptimized using universal force field (UFF) as implemented in Avogadro software.\(^{76}\) As the first step, the geometry was optimized by using Beche three-parameter exchange-Perdew and Wang gradient-corrected correlation functional (B3PW91) and 6-31G(d)
basis set coupled with Los Alamos National Laboratory Double Zeta (LANL2DZ) basis set for Ti atoms via Gaussian 09 software Ohio Supercomputer Center. Geometry optimization is carried out by fully relaxing all atomic positions in alizarin molecule except the atoms in TiO$_2$ cluster, which were kept fixed. The model system was optimized without symmetry constraints and presence of energy minimum was confirmed by the absence of imaginary frequencies. The optimized geometry configuration is depicted in Figures 6.2. In order to calculate the vibrational frequencies, the software uses the second derivative of the energy with respect to the nuclear coordinates and then converts it to the mass-weighted coordinates.

![Figure 6.2. Optimized structure of alizarin-TiO$_2$ cluster model in absence of electric field.](image)

6.2.2. Vibrational Frequency Calculation in Presence of Electric Field

The dye molecules were then aligned by suitable coordinate transformations using Avogadro such that the anchor oxygen atoms lie on the $z$-axis and also oriented to the electric field. The electric field was applied as multipoles and the optimization was performed with no symmetry. Calculations were carried out at B3PW91/LANL2DZ level with and without electric field applied provided in the Gaussian 09 package. The optimized structure (Figure 6.3),
calculated vibrational frequencies and Raman activities were visualized and processed by GaussView 5 software without using any scaling factors.

Figure 6.3. Optimized structure of alizarin–TiO$_2$ cluster model in presence of electric field.

The substantial change of the charge distribution especially in the close proximity of the Ti–O–C bonding suggests the sensitivity of the interface bonding to electric field. The calculations exhibited slight bond length change for both interface bonds: elongation of the interface bond in close proximity to carbonyl group ~0.09 Å and the shortening of the second interface bond ~ 0.04 Å (Figure 6.3), and the corresponding calculated Raman spectra displays two peaks with ~32 cm$^{-1}$ peak-to-peak distance (Figure 6.4).
Figure 6.4. Raman spectra obtained from corresponding optimized structure of alizarin-TiO$_2$ cluster model shown in Figures 6.2 and 6.3. Electric field applied was $\sim 5 \times 10^5$ V m$^{-1}$.

6.2.3. Electric Field Strengths and Directions

Electric field strength is defined in terms of atomic unit (a.u.), the field strength at the first Bohr orbit in the hydrogen atom, $e/4\pi\varepsilon_0a_0^2 \approx 5.14 \times 10^{11}$ V m$^{-1}$. In this work, electric fields from $5.14 \times 10^5$ to $5.14 \times 10^7$ V m$^{-1}$ (= $1 \times 10^{-6}$ to $1 \times 10^{-4}$ a.u.) were applied along the xyz-axes of the coordinate system (Figure 6.3). Electric field was aligned with the bridging Ti–O bonds to affect the vibrational frequencies maximally.

In our DFT calculation, both positive and negative fields show the splitting of interfacial Ti–O bond and the magnitude of splitting do not depend on the direction of field as shown in Figure 6.5. This observation also supports the similar shifting/or splitting of peak in experimental observation.$^{75}$
Figure 6.5. Calculated Raman spectrum of alizarin–TiO$_2$ at (A) negative and (B) positive electric field of $5.0 \times 10^6$ V m$^{-1}$. The peak-to-peak distance of Ti–O mode is $\sim 48$ cm$^{-1}$.

It has been reported that the attachment of alizarin molecule with two hydroxyl oxygens linked to a surface Ti atom makes the configuration slightly tilted$^{72}$ to the nanoparticle surface leading to the two Ti–O bond unsymmetrical. Two Ti–O surface bonds resonate at different vibrational frequency under an applied electric field due to redistribution of charge density across the alizarin–TiO$_2$ interface as shown in Figure 6.6. The distribution of the local interfacial electric field coupled with bonding electrons creates stabilized and destabilized interactions to the surface Ti–O bonds, slightly changing the bond force constants asymmetrically. As Raman spectroscopy is sensitive to the bond orientation and strength, local electric field created at the interface can be considered as the major source of the asymmetric interfacial covalent bonds vibration. Even though, the DFT calculations show correlation with the experimental data and suggests that there occurs a field-induced electronic coupling change, more investigation is necessary to fully understand all the contributing factors.
Figure 6.6. Schematic illustration of (A) alizarin adsorbed on TiO$_2$ surface and interfacial electric field and (B) energy states and electronic delocalization at the alizarin–TiO$_2$ interface. Applied negative potential shifts the TiO$_2$ Fermi level up (red) and positive potential down (pink). $F_e$ : electric field; $V_{\text{ext}}$ : applied potential; VB : valence band; CB : conduction band.

Nevertheless, electronic delocalization and redistribution at the perturbed alizarin–TiO$_2$ interface under the electric field (Figure 6.6B) have significant impact on the interfacial covalent bonds. Therefore, the field-induced shift or splitting are expected to have a prominent influence on the interfacial ET rates due to the driving force as well as electronic coupling changes. The dynamics of ET from alizarin to TiO$_2$ are modulated by the fluctuations of interfacial bond vibrational energy induced by the static electric field developed at the interface which in turn changes the electronic coupling leading to ET intermittency. Generally, the interfacial electric potential can be applied externally, as this work shows, or generated intrinsically due to the excess charge accumulation at the molecule–TiO$_2$ interfaces, as shown in many dye-sensitized TiO$_2$ solar energy conversion systems. The excess charge accumulation, diffusion, and
dissipation are stochastic, and in turn, the interfacial electric potential originated from the excess charges presumably involves significant fluctuations at spatially inhomogeneous interacting sites of nanoparticle, which likely impact the interfacial electron transfer rate processes. Therefore, the coupling energy changes may serve as a prominent and intrinsic origin of the complex interfacial electron transfer dynamics, such as the intermittent interfacial electron transfer dynamics observed by single-molecule photon-stamping spectroscopy measurements.\textsuperscript{75}

6.3. Summary

The electric field effect on the interface properties has been probed by using single-hot spot microscopic surface-enhanced Raman spectroscopy and supported by density functional theory calculations in alizarin–TiO$_2$ system. The perturbation, created by the external potential, has been observed to cause a shift and/or splitting of the 648 cm$^{-1}$ peak, typical indicator of the coupling energy changes between alizarin and TiO$_2$. This phenomenon evidences the field-dependent electronic coupling changes that definitely have a significant impact on the interfacial electron transfer dynamics, especially on the temporal and spatial inhomogeneity and fluctuation of the interfacial electron transfer rate processes. The fact that the electric field effect, due to the external electric field application or the static charge accumulation at the interface of dye–TiO$_2$ nanoparticles is inhomogeneous, suggests that the interfacial electron transfer dynamics is intrinsically inhomogeneous with static and dynamic disorders, showing the reactivity intermittency at the individual molecule level. A detailed understanding of the related interface properties and the factors affecting the molecule–semiconductor interactions is crucial for fundamental interfacial and surface chemistry and physics, as well as for further development and commercialization of the applications such as photovoltaic devices and molecular devices.
6.4. References


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