Single-Molecule Interfacial Electron Transfer

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Final Report

Program Scope

Our research is focused on the use of single-molecule high spatial and temporal resolved techniques to understand molecular dynamics in condensed phase and at interfaces, especially, the complex reaction dynamics associated with electron and energy transfer rate processes. The complexity and inhomogeneity of the interfacial ET dynamics often present a major challenge for a molecular level comprehension of the intrinsically complex systems, which calls for both higher spatial and temporal resolutions at ultimate single-molecule and single-particle sensitivities. Single-molecule approaches are unique for heterogeneous and complex systems because the static and dynamic inhomogeneities can be identified, characterized, and/or removed by studying one molecule at a time. Single-molecule spectroscopy reveals statistical distributions correlated with microscopic parameters and their fluctuations, which are often hidden in ensemble-averaged measurements. Single molecules are observed in real time as they traverse a range of energy states, and the effect of this ever-changing "system configuration" on chemical reactions and other dynamical processes can be mapped. In our research, we have been integrating two complementary methodologies; single-molecule spectroscopy and near-field scanning probe microscopy (modified STM and AFM) to study interfacial electron transfer dynamics in solar energy conversion, environmental redox reactions, and photocatalysis. The goal of our project is to integrate and apply these techniques to measure the energy flow and electron flow between molecules and substrate surfaces as a function of surface site geometry and molecular structure. We have been primarily focusing on studying electron transfer under ambient condition and electrolyte solution involving both single crystal and colloidal TiO_2 and related substrates. The resulting molecular level understanding of the fundamental interfacial electron transfer processes will be important for developing efficient light harvesting systems and broadly applicable to problems in interface chemistry and physics.

In collaboration between the research groups lead by Lu and Ho, we have been integrating two complementary methodologies; single-molecule fluorescence spectroscopy, and scanning probe microscopy and spectroscopy (STM, STS, and AFM) to study interfacial electron transfer dynamics in solar energy conversion. The two teams play a complimentary role in the collaboration. Lu's lab has been primarily focusing on studying electron transfer under ambient condition and electrolyte solution involving both single crystal and colloidal TiO_2 and related substrates; whereas Ho's lab has been focused on studying electron transfer under low temperature and ultrahigh vacuum conditions involving single crystal TiO_2 and other oxides (Al_2O_3, CuO). The molecular level understanding obtained of the fundamental interfacial electron transfer processes is significant and important for developing efficient light harvesting systems for solar cells and broadly applicable to problems in interface chemistry and surface physics, including redox reaction through chemical surfaces, catalytic interfaces, and solar conversion systems.

Summary of the Accomplishments

This project is focused on the use of single-molecule high spatial and temporal resolved techniques to study molecular dynamics in condensed phase and at interfaces, especially, the complex reaction dynamics associated with electron and energy transfer rate processes. The complexity and inhomogeneity of the interfacial ET dynamics often present a major challenge for a molecular level comprehension of the intrinsically complex systems, which calls for both higher spatial and temporal resolutions at ultimate single-molecule and single-particle sensitivities. Combined single-molecule spectroscopy and electrochemical atomic force microscopy approaches are unique for heterogeneous and complex interfacial electron transfer systems because the static and dynamic inhomogeneities can be identified and characterized by studying one molecule at a specific nanoscale surface site at a time. The goal of our project is to integrate and apply these spectroscopic imaging and topographic scanning techniques to measure the energy flow and electron flow between molecules and substrate surfaces as a function of surface site geometry and molecular structure. We have been primarily focusing on studying interfacial electron transfer under ambient condition and electrolyte solution involving both single crystal and colloidal TiO2 and related substrates. The resulting molecular level understanding of the fundamental interfacial electron transfer processes will be important for developing efficient light harvesting systems and broadly applicable to problems in fundamental chemistry and physics.

We have made significant advancement on deciphering the underlying mechanism of the complex and inhomogeneous interfacial electron transfer dynamics in dyesensitized TiO2 nanoparticle systems that strongly involves with and regulated by molecule-surface interactions. We have studied interfacial electron transfer on TiO2 nanoparticle surfaces by using ultrafast single-molecule spectroscopy and electrochemical AFM metal tip scanning microscopy, focusing on understanding the interfacial electron transfer dynamics at specific nanoscale electron transfer sites with high-spatially and temporally resolved topographic-and-spectroscopic characterization at individual molecule basis, characterizing single-molecule rate processes, reaction driving force, and molecule-substrate electronic coupling. One of the most significant characteristics of our new approach is that we are able to interrogate the complex interfacial electron transfer dynamics by actively pin-point energetic manipulation of the surface interaction and electronic couplings, beyond the conventional excitation and observation.

1. Correlated topographic and spectroscopic imaging of single-molecule interfacial electron transfer at TiO_2-electrolyte interface. We have demonstrated and applied single-molecule spectroscopy combined with AFM/STM imaging at room temperature under electrolyte solution to single-molecule studies of photo-induced interfacial ET processes in porphyrin-TiO_2 nanoparticle systems, as a model (Fig. 1A and 1B). We have demonstrated STM imaging of single-molecule porphyrin derivative molecules under electrolyte solution on an Au surface, and the redox states of the molecules can be controlled by a potential applied to the substrate surface (Fig. 1C), and we have obtained both single-molecule fluorescence images and topographic images (Fig. 1C) from porphyrin derivative molecules (Fig. 1D). Fluorescence intensity trajectories of individual dye molecules adsorbed on TiO_2 NP surface showed fluorescence fluctuations and blinking, with time constants distributed from milliseconds to seconds. We have also demonstrated the single-molecule measurements of interfacial electron transfer rate processes by recording the photon stamping single-molecule fluorescence trajectories, probing single photon arrival times and the photon delay times between photon to photon.

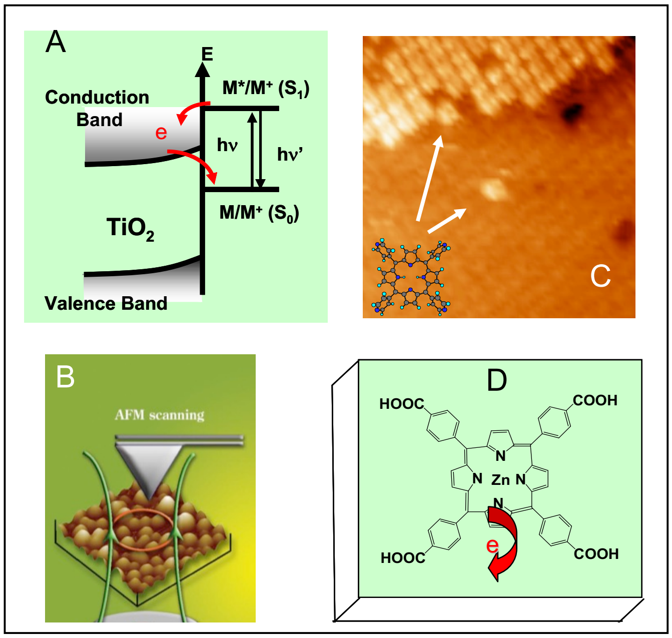

Fig. 1. Correlated single-molecule scanning probe microscopy imaging and spectroscopic imaging of porphyrin/TiO_2 interfacial electron transfer dynamics under ambient conditions. **(A)** Schematic description of the interfacial electron transfer dynamics involved with both forward and backward electron transfers: Forward electron transfer from the excited state of the porphyrin derivative molecules to the conduction band or enegetically-accesible surface states of TiO_2 single-crystals and nanoparticles; and backward electron transfer from TiO_2 to surface adsorbed porphyrin derivative molecule cations. **(B)** Correlated AFM/STM single-molecule imaging and single-molecule fluorescence imaging microscopy. The AFM/STM microscope and single-molecule fluorescence imaging microscope are coupled in an over-and-under configuration for imaging the same nanosclae local sample area with single-molecule topographic and spectroscopic sensitivity, respectively. The features on the image are TiO_2 nanoparticles (~12±4 nm). **(C)** STM imaging (150 Å X 150 Å) of single-molecule porphyrin derivative molecules on an Au surface at a potential of 0.09 V_{SCE} and under 100 mM H_2SO_4 solution. The STM imaging can also identify the redox state of the single-molecules. **(D)** Molecular structure of the porphyrin derivative molecules that involve interfacial electron transfer on TiO_2 surfaces.

2. Probing single-molecule interfacial electron transfer dynamics of porphyrin on TiO_2 nanoparticles. Single-molecule interfacial electron transfer (ET) dynamics has been studied in real time by using single-molecule fluorescence spectroscopy and microscopic imaging. In this work, real-time interfacial ET dynamics have been studied based on single-molecule zinc-tetra (4-carboxyphenyl) porphyrin (ZnTCPP)/TiO_2 nanoparticle system by using single-molecule fluorescence imaging and photon-stamping technique. For the single-molecule ZnTCPP)/TiO_2 nanoparticle system, the single-molecule fluorescence trajectories show strong fluctuation and blinking between bright and dark states. Based on a series of control experiments, we have identified that the single-molecule fluorescence intensity fluctuation is not due to triplet state or single-molecule rotational or translational motions during the measurements. The intermittency and fluctuation of the single-molecule fluorescence are attributed to the variation of the reactivity of interfacial electron transfer. We attributed the fluorescence fluctuations to the interfacial ET reaction rate fluctuations in competing with the nanosecond excited-state relaxation of the dye molecules, associating redox reactivity intermittency with the fluctuations of molecule-TiO_2 electronic and vibronic coupling. The non-exponential autocorrelation function and the power-law distribution of the probability density of dark times imply the dynamic and static inhomogeneity of the interfacial ET dynamics. On the basis of the power-law analysis, the variation of single-molecule interfacial ET reactivity is analyzed as a fluctuation according to the Lévy statistics. According this work and our previously reported work, the highly inhomogeneous ET dynamics is common for the interfacial chemical reactions that strongly regulated by the molecular interaction between adsorbed molecules and substrate surfaces. The spontaneous thermal fluctuations of the local environment and the molecular interactions occur at a wide time-scale at room temperature, resulting in the interfacial ET reaction-rate fluctuation and inhomogeneous dynamics. Our single-molecule spectroscopy analysis provides detailed information about the inhomogeneity of the interfacial electron transfer, which is novel but not obtainable from the conventional ensemble-averaged experiments.

3. Probing single-molecule interfacial electron-cation geminate recombination dynamics. Both forward electron transfer (FET) and backward electron transfer (BET) processes are involved in the photo-induced electron transfer at the dye/semiconductor interface. Previously, there has been no demonstration of measuring single-molecule BET across the molecule-TiO_2 substrate interfaces. We have probed BET dynamics for zinc-tetra (4-carboxyphenyl) porphyrin (ZnTCPP)/TiO_2 nanoparticle system at single-molecule level by precisely recording and analyzing photon-to-photon pair times. It is significant that the fluorescence trajectory from ZnTCPP/TiO_2 shows strong fluctuation with dark time at sub-seconds to seconds time scale. Demonstrating triplet blinking, cation emission and molecule rotation are not responsible for the fluctuation, we have suggested that the dark state is due to dominated ET process with high activity and bright state is due to monotonous fluorescence emission cycles from $S_0 \rightarrow S_1 \rightarrow S_0$ or low active ET process (mixed with fluorescence cycles). By deconvolution, the BET time of ZnTCPP/TiO_2 system is deduced to be inhomogeneous from molecule to molecule and span a broad range from sub-ms to ms time scale. The inhomogeneity implies the non-exponential BET dynamics in ensemble-averaged measurements and complexity of the electron-cation recombination process, which is associated with excess electron trapping, detrapping and non-Brownian diffusion motions in TiO_2.

4. Combined Single-Molecule Photon-Stamping Spectroscopy and Femtosecond Transient Absorption Spectroscopy Studies of Interfacial Electron Transfer Dynamics. Inhomogeneous interfacial electron transfer (IET) dynamics of 9-phenyl-2,3,7-trihydroxy-6-fluorone (PF) sensitized TiO_2 nanoparticles (NPs) has been probed by single-molecule photon-stamping technique and by ensemble-averaged femtosecond transient absorption spectroscopy (Fig. 2). Single-molecule photon-stamping technique and ensemble-averaged transient absorption spectroscopy provide efficient "zoom in" and "zoom out" approaches in probing the interfacial ET dynamics. The physical nature of the observed multi-exponential or stretched-exponential ET dynamics in the ensemble-averaged experiments, often associated with dynamic and static inhomogeneous ET dynamics, can be identified and analyzed by the single-molecule spectroscopy measurements.

The forward ET time shows a broad distribution at the single-molecule level, indicating the inhomogeneous interactions and ET reactivity of the PF/TiO_2 NP system. The broad distribution of the forward ET time is measured to be 0.4±0.1 ps in the transient absorption and picoseconds to nanoseconds in the photon-stamping measurements (Fig. 3). The charge recombination time, having a broad distribution at the single molecule level, clearly shows a biexponential dynamic behavior in the transient absorption: a fast component of 3.0±0.1 ps and a slow component of 11.5±0.5 ns. We suggest that both strong and weak interactions between PF and TiO_2 coexist, and we have proposed two mechanisms to interpret the observed interfacial ET dynamics. The inhomogeneous electron transfer rate due to the interaction between a dye molecule and the semiconductor surface depends on the chemical and physical nature of both dye molecule and the semiconductor.

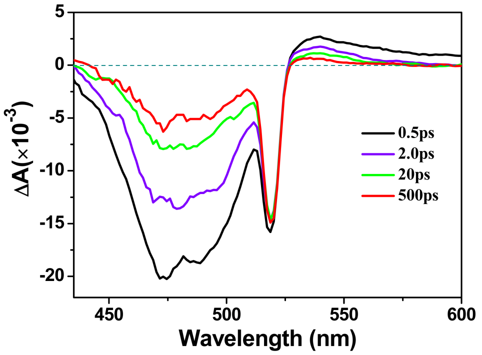

Figure 2. Transient absorption spectra of PF in TiO_2 NP aqueous solution at 0.5 ps, 2.0 ps, 20 ps and 500 ps delay times, with the pulse excitation at 518 nm. The spectrum at each time delay consists of a broad ground-state bleaching from 420 nm to 520 nm, and a positive broad charge separation band with a maximum at 540 nm. The group velocity dispersion of the probe light and spectral signal was already considered when constructing the time-resolved spectra.

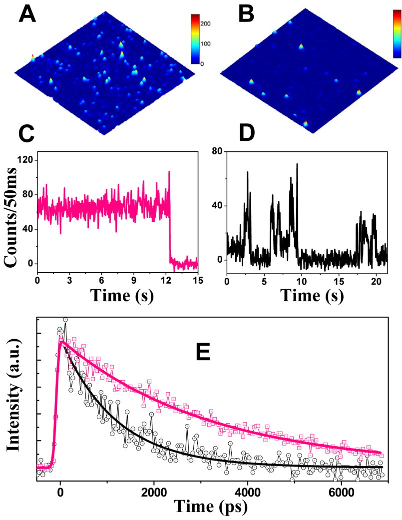

Figure 3. **(A)** and **(B).** Single molecule images of PF on a glass cover slip and on a TiO_2 NPs coated surface (size: 20×20 μm), respectively, obtained under the same experimental imaging condition. **(C)** and **(D)** are typical fluorescence trajectories of single-molecule PF on a cover slip and a TiO_2 NPs covered surface, respectively, with the binning time of 50 ms. **(E)** Typical fluorescence emission traces of single molecule PF on a cover slip (pink) and a TiO_2 NPs coated surface (black), using single photon stamping recording with the pulse laser excitation at 528 nm and 200 fs. Single exponential decay is observed with a 3.2±0.1 ns lifetime of PF on the cover slip and 1.2±0.1 ns on the TiO_2 NPs covered surface.

5. Probing Ground-State Single-Electron Self-Exchange Across a Molecule-Metal Interface. We have probed single-molecule redox reaction dynamics of Hemin (Chloride) adsorbed on Ag nanoparticle surfaces by single-molecule surface-enhanced Raman spectroscopy (SMSERS) combined with spectroelectrochemistry (Fig. 4). Redox reaction at the molecule/Ag interface is identified and probed by the prominent fluctuations of the Raman frequency of a specific vibrational mode ν_4, which is a typical marker of the redox state of the Iron center in a Hemin molecule. Based on the autocorrelation and crosscorrelation analysis of the single-molecule Raman spectral trajectories and the control measurements of single-molecule spectroelectochemistry and electrochemical STM, we suggest that single-molecule redox reaction dynamics at the Hemin/Ag interface is primarily driven by thermal fluctuations. The spontaneous fluctuation dynamics of the single-molecule redox reaction is measured under no external potential across the molecule-metal interfaces, which provides a novel and unique approach to characterize the interfacial electron transfer at the molecule-metal interfaces. Our demonstrated approaches are powerful for obtaining molecular coupling and dynamics involving in interfacial electron transfer processes. The new information obtained is critical for a further understanding, design and manipulation of the charge transfer processes at the molecule-metal interface or metal-molecule-metal junctions, which are fundamental elements in single-molecule electronics, catalysis, and solar energy conversion.

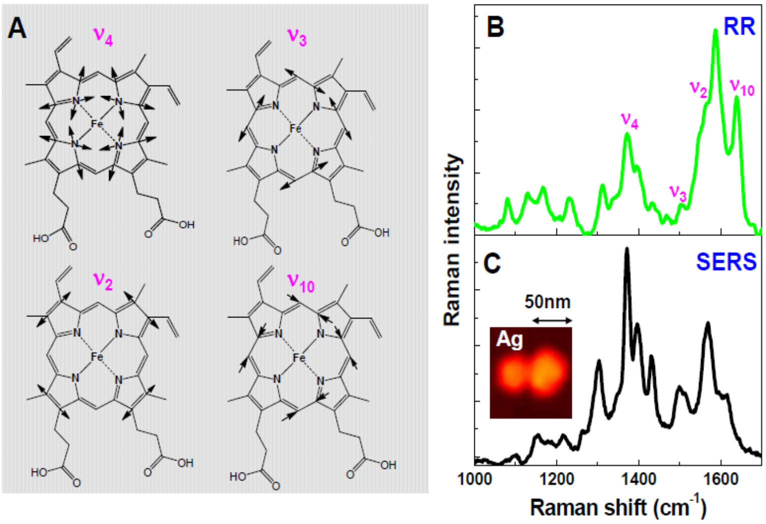

Figure 4. Typical vibrational modes and Raman spectra of Hemin. **(A)** Diagram illustrating four characteristic vibrational modes of the porphyrin skeletal structures of Hemin (or Heme). **(B)** and **(C)** show the typical Resonance Raman

spectrum and single-molecule SERS of Hemin, respectively. A SEM image of a Raman-active dimmer of Ag NPs is shown as inset in (C).

As a high-spin five-coordinate Fe(III) compound, Hemin is a model molecule to probe the redox reaction at the molecule-metal interfaces by using SERS. So far, the redox reaction at the Hemin/metal interface has been observed at both ensemble and single molecule level. However, the detailed charge-transfer dynamics as well as the inherent nature of the mechanism of the redox reaction have not been revealed yet. Several vibrational modes of Hemin such as ν_4, ν_3, ν_2 and ν_{10} are typical markers of the porphyrin core size and the Iron electronic structure. A schematic description of these four vibrational modes is shown in Fig. 4A. The ν_4 mode is the marker of Iron oxidation state and its vibrational frequency is in a range of ~1368-1377 cm^{-1} for ferric (Fe^{III}) state and ~ 1344-1364 cm^{-1} for ferrous (Fe^{II}) state. For the ν_3 mode, it is sensitive to the coordination and spin state. Fig. 4B and 3C show the resonance Raman (RR) and a typical SMSERS of Hemin. Apparently, the two spectra have similar profile, and the typical vibrational modes such as ν_4, ν_3, ν_2 and ν_{10} are all well resolved. As the Iron oxidation state marker, ν_4 peaks at 1373 and 1372 cm^{-1} in the RR and SMSERS spectra, respectively, which indicates that Hemin is in the oxidized state. In the SMSERS measurements of Hemin of 1.4×10^{-9} M or 4.8×10^{-11} M, we observed spectral fluctuations, blinking, and final quantized single-step photobleaches of the Raman spectra, the typical signatures of the measurements at the single-molecule detection limit.

To probe the single-molecule charge transfer dynamics at the Hemin/Ag interface, we have analyzed the fluctuation trajectories of vibrational mode ν_4 and ν_3 by calculating autocorrelation function (ACF) from the Raman spectral mean trajectories. We also carried out a 2D regional crosscorrelation analysis between ν_4 and ν_3, and we observed that, with ν_4 fluctuating between two redox states, ν_3 shows correlation or anticorrelation with the ν_4 fluctuations from time to time. The correlation or anticorrelation analyses reveal more detailed information such as rate of the redox reaction. The correlation or anticorrelation of two specific modes, which are the oxidation state marker and the spin state (and coordination) marker, most likely reflect the real rate of the redox reaction. From the reaction rate, we estimate that a single self-exchange charge-transfer event rate constant is about 0.01 s^{-1}. Taking the pre-exponential factor with a normal range (10^{10}-10^{13} s^{-1}), we get the activation energy in a range of 68.2-85.3 KJ/mol, i.e., 0.7 to 0.8 eV for the redox reaction at the Hemin/Ag interface. This value is close to the reported 0.3 to 0.5 eV for one electron transfer from Fermi level of Aluminum surface to the adsorbed oxygen molecule.

6. Single-Molecule Interfacial Electron Transfer Dynamics of Porphyrin on TiO_2 Nanoparticles: Dissecting the Complex Electronic Coupling Dependent Dynamics. We have studied the photosensitized interfacial electron transfer (ET) dynamics of the Zn(II)-5,10,15,20-tetra (3-carboxyphenyl) porphyrin (*m/p*-ZnTCPP)-TiO_2 nanoparticle (NP) system using single-molecule photon-stamping spectroscopy. The single-molecule fluorescence intensity trajectories of both *m*-ZnTCPP and *p*-ZnTCPP on TiO_2 NP surface show fluctuations and blinking between bright and dark states, which are attributed to the variations in the reactivity of interfacial ET, i.e., intermittent interfacial electron transfer dynamics. We also identified the effect of anchoring group binding geometry (*meta* or *para*), hence electronic coupling of sensitizer (*m*/*p*-ZnTCPP) and TiO_2 substrate, on interfacial ET dynamics. Compared to *p*-ZnTCPP on TiO_2 NP surface, with *m*-ZnTCPP, dark states are observed to dominate in single-molecule fluorescence intensity trajectories. This observation coupled with the large difference in lifetime derived from bright and dark states of *m*-ZnTCPP demonstrate higher charge injection efficiency of *m*-ZnTCPP than *p*-ZnTCPP. The nonexponential autocorrelation function decay and the power-law distribution of the dark-time probability density provide a detailed characterization of the inhomogeneous interfacial ET dynamics. The distribution of autocorrelation function decay times (τ) and power-law exponents (m_{dark}) for *m*-ZnTCPP are found to be different from those for *p*-ZnTCPP, which indicates the sensitivity of τ and m_{dark} on the molecular structure, molecular environment, and molecule-substrate electronic coupling of the interfacial electron transfer dynamics. Overall, our results strongly suggest that the fluctuation and even intermittency of excited-state chemical reactivity are intrinsic and general properties of molecular systems that involve strong molecule-substrate interactions. Furthermore, 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.

7. Probing Driving Force Dependent Single-Molecule Interfacial Electron Transfer Dynamics. There a number of key parameters that control an interfacial electron transfer dynamics in molecule/TiO_2 systems. 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. In this task, we have focused our studies on the electron transfer rate processes controlled by the electron transfer driving force (ΔG) as well as the interfacial electric field at a molecule-TiO_2 interface. Although, significant efforts made in this direction by ensemble average measurements (electrochemistry as well as spectroscopy) already indicate the importance of various factors in determining injection dynamics, further advancement of the understanding requires study at single molecule level and at specific nanoscale local environment. The complexity of the interfacial electron transfer dynamics often presents a major challenge for conventional ensemble-averaged measurements as the molecule-substrate interactions are inhomogeneous involving heterogeneous local environments. Single-molecule spectroscopy provides insightful details about interfacial ET dynamics which are beyond the realms of conventional solution-phase ensemble-averaged analyses; particularly with regard to complex mechanism and spatiotemporal heterogeneity. Combination of single-molecule fluorescence spectroscopy approach with various other techniques such as atomic force microscopy (AFM), electrochemistry, and Raman spectroscopy can further facilitate inspection of multiple-parameters with high chemical selectivity and wide temporal and spatial resolutions. Here we develop correlated single-molecule spectro-electrochemistry technique (Figure 5) to study photon-stamping measurements of individual Zn(II)-5,10,15,20-tetra (3-carboxyphenyl) porphyrin, *m*-ZnTCPP, molecule anchored to TiO_2 NP surface in aqueous solution while electrochemically controlling the energy states of TiO_2 NPs through applied electric bias. We thus concluded that the interfacial electron transfer dynamics, the excited-state lifetime of dye molecule anchored to TiO_2, and the single molecule blinking pattern can be controlled by tuning the relative energetics of the dye excited state relative to the unoccupied TiO_2 acceptor state.

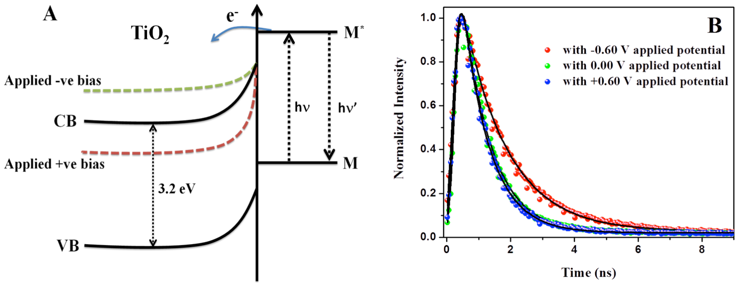

Figure 5: The fluorescence decay profiles of *m*-ZnTCPP on TiO_2 NP surface with different applied potentials. The initial study indicates that in absence of applied electric bias the single-molecule fluorescence intensity trajectories of *m*-ZnTCPP on TiO_2 NP surface show fluctuations and blinking between bright and dark states, which are attributed to the variations in the reactivity of interfacial ET, i.e., intermittent interfacial electron transfer dynamics. The blinking pattern changes significantly with –ve applied potential, whereas it remains almost same with applied +ve potential. The application of -0.6 V to the TiO_2 electrode also resulted in ~2-fold increase in excited state lifetime of *m*-ZnTCPP.

8. Single-Molecule Interfacial Electron Transfer Dynamics of Porphyrin on TiO_2 Nanoparticles: Dissecting the Complex Electronic Coupling Dependent Dynamics. The photosensitized interfacial electron transfer (ET) dynamics of the Zn(II)-5,10,15,20-tetra (3-carboxyphenyl) porphyrin (*m*-ZnTCPP)-TiO_2 nanoparticle (NP) system has been studied using single-molecule photon-stamping spectroscopy. The single-molecule fluorescence intensity trajectories of *m*-ZnTCPP on TiO_2 NP surface show fluctuations and blinking between bright and dark states, which are attributed to the variations in the reactivity of interfacial ET, i.e., intermittent interfacial electron transfer dynamics, a typical dynamically disordered chemical dynamics. We show the effect of anchoring group binding geometry (*meta* or *para*), hence electronic coupling of sensitizer (*m*/*p*-ZnTCPP) and TiO_2 substrate, on interfacial ET dynamics. The nonexponential autocorrelation function decay and the power-law distribution of the dark-time probability density provide a detailed characterization of the inhomogeneous interfacial ET dynamics sensitive to the molecular structure, molecular environment, and molecule-substrate electronic coupling. Overall, our results strongly suggest that the fluctuation and even intermittency of excited-state chemical reactivity are intrinsic and general properties of molecular systems that involve strong molecule-substrate interactions.

9. Comparative Studies of Interfacial Electron Transfer Dynamics at Different Energy Substrates: Suppressed Fluorescence Blinking of Single-Molecules on Doped Semiconductors. Photo-induced, interfacial electron transfer (ET) dynamics between *m*-ZnTCPP and Sn-doped In_2O_3 (ITO) film has been studied using single-molecule photon-stamping spectroscopy. The observed ET dynamics of single *m*-ZnTCPP adsorbed on ITO was compared with that of *m*-ZnTCPP adsorbed on TiO_2 NPs with and without applied electric potential. Compared to *m*-ZnTCPP on TiO_2 NP surface, *m*-ZnTCPP on ITO surface shows reduced lifetime as well as suppressed blinking and quasi-continuous distribution of fluorescence intensities, presumably due to higher electron density in ITO (Figure 6). The higher electron density leads to the occupancy of CB acceptor states/trap states, which supports a higher backward electron transfer (BET) rate that results in quasi-continuous distribution of fluorescence intensities. The dependence of BET rate on electron density and charge trapping is consistent with our previous observations of quasi-continuous distribution of fluorescence intensities of *m*-ZnTCPP on TiO_2 NPs with applied negative potential across the dye-TiO_2 interface. The quasi-continuous distribution of fluorescence intensities in both case of *m*-ZnTCPP on ITO surface and *m*-ZnTCPP on TiO_2 NPs with applied negative potential indicates that the electron density/occupancy in the semiconductor plays a dominant role in dictating the changes in rates of charge transfer in our system, rather than the relative energetics between electron in semiconductor and the oxidized sensitizer.

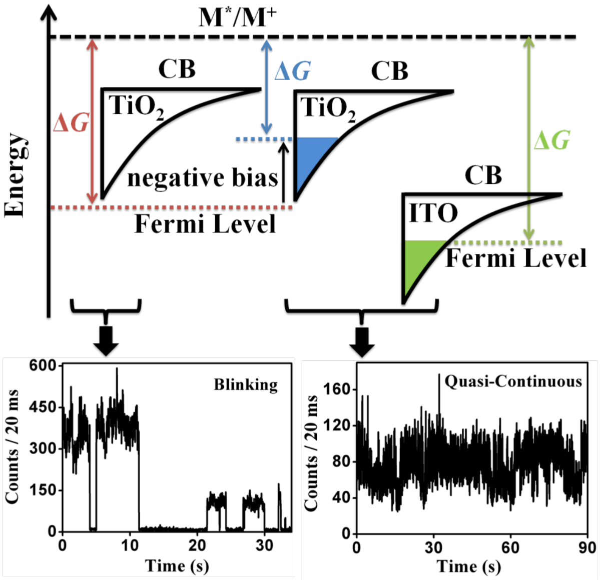

Figure 6: Schematic illustration of the sub-bandgap or trap states, Fermi level, and forward ET free energy driving force (Δ*G*) for ITO, TiO_2 NPs, and TiO_2 NPs with applied negative bias: M^*/M^+ indicate excited state energy of *m*-ZnTCPP. In TiO_2 the Fermi level lies below the trap states, application of negative potential raises the TiO_2 Fermi level, which leads to occupancy of CB electron acceptor states as well as decrease in Δ*G* value. Blue area denotes electron acceptor states unavailable for electron injection from *m*-ZnTCPP excited state. In case of ITO the Fermi level lies above the conduction band edge and the forward ET free energy driving force (Δ*G*) is also large compared to that of TiO_2. (**Lower Panel**) Typical Single-molecule fluorescence emission trajectories of *m*-ZnTCPP on ITO surface. Unlike *m*-ZnTCPP on ITO surface (**Lower right**), *m*-ZnTCPP adsorbed on TiO_2 NPs show fluorescence intensity trajectories with distinct bright and dark states (**Lower left**).

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