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Probing Single-Molecule Interfacial Geminante Electron–Cation Recombination Dynamics

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Abstract: Interfacial electron–cation recombination in zinc-tetra (4-carboxyphenyl) porphyrin (ZnTCPP)/TiO2 nanoparticle system has been probed at the single-molecule level by recording and analyzing photon-to-photon pair times of the ZnTCPP fluorescence. We have developed a novel approach to reveal the hidden single-molecule interfacial electron–cation recombination dynamics by analyzing the autocorrelation function and a proposed convoluted single-molecule interfacial electron–cation recombination model. Our results suggest that the fluctuations of the interfacial electron transfer (ET) reactivity modulate the ET cycles as well as the interfacial electron–cation recombination dynamics. On the basis of this model, the single-molecule electron–cation recombination time of ZnTCPP/TiO2 system is deduced to be at time scale of 10^-8 s. The autocorrelation of photon-to-photon pair times as well as the convoluted ET model has been further demonstrated by simulation and interpreted in terms of the interfacial ET reactivity fluctuation and blinking. Our approach not only can effectively probe the single-molecule interfacial electron–cation dynamics but also can be applied to other single-molecule ground-state regeneration dynamics occurring at interfaces and within condensed phases.

Introduction

Interfacial electron transfer (ET) plays a critical role in chemical and biological systems, such as catalysis, bioremediation, and solar energy conversion. Specifically, interfacial ET in TiO2-based dye-sensitization systems is important to solar energy technology and photocatalysis.1–4 There are two major electron transfer processes involved in the photoinduced electron transfer at a dye/semiconductor interface: forward electron transfer (FET)5,6 from an excited state of a dye molecule to the conduction band or energetically accessible surface states of TiO2 semiconductor16 and backward electron transfer (BET)7,8 of the excess electron which recombines with the dye molecule’s cation. The FET is typically ultrafast in the femtosecond to several hundred picosecond range.4,7–15 Following the FET, the thermalized injected electron is localized to either the sub-band states or surface states of the TiO2 semiconductor.16–20 Typically, a BET from the semiconductor to the oxidized dye molecules will follow.7,8,18,20–26 The complex BET dynamics is often nonexponential, ranging from subnanoseconds to several milliseconds,7,8,14,18,22,24,26 probably because of the existence of trap states and non-Brownian diffusion motions of the electrons within the semiconductor. Designing an efficient solar energy harvesting system entails controlling the rate of the BET process in order to generate long-lived charge-separated states so that the excess electron can have a high probability of escaping from the BET pathway and can contribute to the buildup of photovoltaics. Characterization of the BET dynamics

is therefore important for an understanding of solar energy conversion within a solar cell and interfacial redox reactions. Conventional ensemble-averaged measurements often encounter various 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 is a powerful way of deciphering the inhomogeneous interfacial ET dynamics by studying one molecule on one TiO₂ nanoparticle involving both FET and BET of a single electron at a time. Single-molecule spectroscopy has been applied to study intramolecular and interfacial ET dynamics, and the interfacial ET dynamics were found to be intermittent because of ET reactivity fluctuations and fluctuations. Our single-molecule spectroscopy studies of single-molecule interfacial electron transfer dynamics are more focused on the fundamental understanding of the interfacial redox reactivity, which is related broadly to catalysis and surface chemistry, in addition to our interests on technically improving the solar energy conversion efficiency. In this paper, we report the single-molecule recombination dynamics of the zinc-tetra-(4-carboxyphenyl) porphyrin (ZnTCPP)/TiO₂ nanoparticle system. At the single-molecule level, the electron–cation recombination dynamics is analyzed through a convoluted interfacial electron–cation recombination process, and the recombination time of ZnTCPP/TiO₂ system is deduced to be at ~10⁻³ s time scale.

**Experimental Section**

ZnTCPP (Frontier Scientific), ethanol (Aldrich), dichloromethane (EMD chemicals), and poly(methylmethacrylate) (PMMA) (typical MW 15 000, Aldrich) were used as provided. TiO₂ nanoparticles were prepared using hydrolysis of the titanium isopropoxide as a precursor according to a typical literature method. Samples for single-molecule experiments were prepared in a similar procedure that we have reported previously. Twenty-five microliters of 0.1 nM ZnTCPP in ethanol solution was first spin-coated to a clean coverslip (Fisher, 18 mm) at 3000 rpm and was overlaid 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 and quenching. For a control experiment, 50 µL of TiO₂ NP solution was first spin-coated on a coverslip and then was overlaid by ZnTCPP and a thin PMMA film.

The detailed description of our optical measurements has been published elsewhere. Single-molecule fluorescence spectroscopy and imaging were recorded by Axiovert 135 inverted scanning confocal microscope equipped with a 100×, 1.3 NA oil immersion objective (Zeiss FLUAR) and a close-loop nanoscale-precision piezoelectric scanning stage to control the position of a sample. A continuous-wave (CW) laser (532 nm, CrystaLaser) was used to pump the sample at about 200 mW. A beam splitter, Z532rdc (Chroma), was used to reflect the excitation light into the objective. The emission light passed through the emission filter HQ545lp (Chroma) and was collected by a single-photon-counting avalanche photodiode (APD) detector (Perkin-Elmer SPCMAQR-14). Photostamping data was recorded by a time-correlated single-photon-counting (TCSPC) system (SPC-830, Becker & Hickl GmbH) in an FIFO (first-in first-out) mode.

**Results and Discussion**

ZnTCPP/TiO₂ interfacial electron transfer has been studied at the ensemble-averaged level extensively, being demonstrated as an efficient photosensitization system. Figure 1 shows the fluorescence emission trajectories and optical images for single ZnTCPP molecules on a clean cover glass (Figure 1A) and on a TiO₂ nanoparticle coated surface (Figure 1B). The fluorescence trajectory from ZnTCPP/TiO₂ (Figure 1B) shows significant fluctuations and blinkings with dark times at second to second time scales, whereas the single-molecule fluorescence of ZnTCPP on glass surface (without the possibility of interfacial ET) is essentially stable under the same experimental condition. It is an apparent paradox that single-molecule cation recombinations on the surface of a single particle, and multiple electron injection to a single particle, and multiple electron–cation recombinations on the surface of a single particle. Single-molecule spectroscopy has been applied to study intramolecular and interfacial ET dynamics, and the interfacial ET dynamics were found to be intermittent because of ET reactivity fluctuations and fluctuations. When the interfacial ET reactivity is high, the ultrafast redox reactions dictate the fate of the singlet excited state of the dye molecules, and the fluorescence quantum efficiency is low or close to zero. In contrast, when the redox reactivity is low or nonexistent, the fluorescence quantum efficiency is high and the fluorescence quantum efficiency is essentially stable under the same experimental condition. It is an apparent paradox that single-molecule fluorescence is still observable along with interfacial electron transfer processes for ZnTCPP/TiO₂ dye-sensitized interfacial system. In our previous publication about ET in this and other similar systems, we demonstrated that single dye molecules involve electron transfer activity intermittently reflected by single-molecule fluorescence blinking or fluctuations. When the interfacial ET reactivity is high, the ultrafast redox reactions dictate the fate of the singlet excited state of the dye molecules, and the fluorescence quantum efficiency is low or close to zero. In contrast, when the redox reactivity is low or nonexistent, the fluorescence quantum efficiency is high and the fluorescence quantum efficiency is essentially stable under the same experimental condition. It is an apparent paradox that single-molecule fluorescence is still observable along with interfacial electron transfer processes for ZnTCPP/TiO₂ dye-sensitized interfacial system. In our previous publication about ET in this and other similar systems, we demonstrated that single dye molecules involve electron transfer activity intermittently reflected by single-molecule fluorescence blinking or fluctuations. When the interfacial ET reactivity is high, the ultrafast redox reactions dictate the fate of the singlet excited state of the dye molecules, and the fluorescence quantum efficiency is low or close to zero. In contrast, when the redox reactivity is low or nonexistent, the fluorescence quantum efficiency is high and the fluorescence quantum efficiency is essentially stable under the same experimental condition. It is an apparent paradox that single-molecule fluorescence is still observable along with interfacial electron transfer processes for ZnTCPP/TiO₂ dye-sensitized interfacial system.
intensity is high.\textsuperscript{4,37} In our previous publications, we also reported a series of control experiments to demonstrate that the single-molecule fluorescence blinking is not due to (1) rare and slow (millisecond to subsecond) interfacial electron transfer events, (2) dye molecule triplet state blinking, or (3) molecular transition dipole rotations. We have conducted similar control experiments for the ZnTCPP/TiO\textsubscript{2} nanoparticle system and have reached the same conclusion.\textsuperscript{37} Although it is beyond the scope of this paper, we have reported Raman spectroscopy studies on the molecular dye–TiO\textsubscript{2} vibrational coupling origin of the intermittent interfacial electron transfer dynamics in a dye-sensitized TiO\textsubscript{2} nanoparticle system.\textsuperscript{49} We previously demonstrated a single-molecule photon antibunching analysis of intramolecular backward metal-to-ligand charge-transfer (MLCT) dynamics.\textsuperscript{34} Here, we focus our discussion on probing the dynamics of interfacial BET process, that is, electron–cation (ZnTCPP\textsuperscript{+}) recombination process, for ZnTCPP/TiO\textsubscript{2} nanoparticle system.

Single-molecule photostamping spectroscopy records arrival time, delay time from excitation, and time sequence of every detected emission photon from a single molecule. Therefore, the photon-to-adjacent-photon pair time can be precisely recorded (as shown in Figure 1A). In a single-molecule photostamping measurement, each photon detected is emitted from the S\textsubscript{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, S\textsubscript{0}. In the excited state, a dye molecule will not emit a photon through an S\textsubscript{1} → S\textsubscript{0} radiative transition if the molecule involves an ultrafast FET process reaching a charge-separation state of a dye cation and an excess electron in TiO\textsubscript{2}. The cation is mostly nonfluorescent, and the dye molecule can only emit another photon when a BET occurs reducing the cation back to a neutral ground state, S\textsubscript{0}. Therefore, statistical analysis of the relationship between adjacent photon-to-photon pair times can be a specific way to probe the interfacial ET dynamics. Autocorrelation function calculation is a typical approach to analyze fluctuation dynamics. Considering BET time is the main contribution to the photon-to-photon pair time since the rate of FET is typically 10\textsuperscript{10}–10\textsuperscript{13} times faster than the time of BET in an excitation event of ZnTCPP/TiO\textsubscript{2}, it is possible to probe BET dynamics by analyzing the correlation of single-molecule pair-time time trajectories. Figure 2 shows the normalized autocorrelation function of a pair-time trajectory calculated from a photon arrival time trajectory. The autocorrelation function is calculated by

$$r(m) = \left[ n \sum_{i} t_{i}t_{i+m} - \left( \sum_{i} t_{i} \right)^{2} \right] \left[ n \sum_{i} t_{i}^{2} - \left( \sum_{i} t_{i} \right)^{2} \right]$$

where \(i\) and \(m\) are the index numbers of a photon in a detected photon arrival time trajectory of total \(n\) photons; \(t_{i}\) is the pair time between a pair of photons \(i\) and \(i+1\), and \(t_{i+m}\) is the pair time between a pair of photons \(i\) and \(i+m\); \(m\) varies from \(i\) to \(n\).\textsuperscript{46} For the sample of ZnTCPP on glass, the autocorrelation result shows zero amplitude at indexes larger than zero and a spike at index zero because of measurement noise and the fast fluctuations beyond measurement time resolution (Figure 2). There is no correlation between the pair times when there is no interfacial electron transfer occurrence, which is consistent with the stochastic nature of the fluorescence cycles under CW laser excitation. Remarkably, for ZnTCPP/TiO\textsubscript{2}, the pair time of a state (color-highlighted part in the trajectory, Figure 2, inset) with relatively higher ET activity gives a well-defined correlation function. The correlation function suggests that there is a correlation in the photon-to-photon pair times and that the correlation decays exponentially with decay parameter of \(m = 110 \pm 10\). Considering the average pair time for this state to be 0.65 ms, we calculate that the correlation time is about 72 ± 7 ms. The correlation disappears when the pair times are separated by 250 index numbers or more (Figure 2).

The correlation of photon-to-photon pair times in interfacial electron–cation recombination dynamics (Figure 3) is averaged out in ensemble-averaged measurements and can only be revealed in a single-molecule measurement. Photogeneration of free carriers in low-mobility material heterojunctions has been analyzed by the geminate recombination theory of Onsager\textsuperscript{49} and Braun.\textsuperscript{50} Marsh et al.\textsuperscript{51} have demonstrated that the geminate recombination is the dominant loss mechanism for photon-excited charge separations in organic or hybrid solar cells. Photocurrent generation depends on the competition between dissociation and recombination of geminate electron–cation pairs. The electron drift mobility in nanopore TiO\textsubscript{2} (anatase, size: 15–30 nm) is about 10\textsuperscript{-4}–10\textsuperscript{-6} cm\textsuperscript{2}/(V s) and depends on the inhomogeneous interfacial transport barriers.\textsuperscript{52} For ZnTCPP/TiO\textsubscript{2} systems, after photoexcitation, ZnTCPP\textsuperscript{+} injects an electron into the conduction band or into the energetically accessible surface states of the semiconductor driven by the energy difference (\(\Delta E\)) between the lowest unoccupied molecular orbital (LUMO) of ZnTCPP (3.4 ± 0.2 eV) and the conduction band of TiO\textsubscript{2} (4.4 ± 0.2 eV).\textsuperscript{53} In our experiment as well as in other published work,\textsuperscript{7,8,54} there is no external circuit implicated in the experiment as we focus on the fundamental interfacial electron transfer dynamics and not on a specific technical development of a solar cell; therefore, the cation cannot be compensated after the BET, and the electron diffusion will be affected by the Onsager distance (\(R_c\)) because

\[(50)\text{ Braun, C. L. J. Chem. Phys. 1984, 80, 4157–4161.}\]
of the mutual Coulombic attraction force of the geminate electron–cation pair, e−/ZnTCPP+. The Onsager distance in anatase TiO2 is about 11–18 Å (according to reported dielectric constant from 31 to 50).55–57 At the Onsager distance, there is a 50% probability that a geminate pair of electron and cation escapes from a recombination. Previous Stark effect spectroscopy studies58 suggested that the FET injection distance, dFET, is averagely much shorter than 10 Å, which is therefore shorter than the Onsager distance. Driven by the Coulombic field, the excess electron comes back and recombines with the parent cation in the cycles of the single-molecule interfacial electron transfer process. For the TiO2 nanoparticles used in our experiments, the possible free-electron density is extremely low,59 and the electron–cation recombination is geminate between the excess electron and the parent cation of e−/ZnTCPP+. We have demonstrated that detected signal photons are emitted from a nanosecond transition from S1 → S0 of ZnTCPP5,57 except rare photons from background and phosphorescence; phosphorescence efficiency is lower than 10−4 at room temperature.60 Within a photon-to-photon pair time, two types of events occur: (1) fluorescence excitation and emission that are intrinsically stochastic processes giving no correlation among the pair times, as evident in Figure 2 which shows no autocorrelation for the pair times of ZnTCPP on a glass surface, and (2) interfacial electron transfer which involves both FET and BET. FET typically occurs in fs to ps time scales, whereas BET occurs in subns to ms time scales. Consequently, the photon-to-photon pair time at μs−ms time scale is dominated by BET time and the excitation-photon waiting time at the μs time scale. Furthermore, with the ET reactivity fluctuating from time to time, the ET process may continuously involve multiple FET–BET cycles before giving out a photon (as shown in Figure 3). Therefore, for the pair times involving the ET process, they include convoluted multiple Poisson events, and the convoluted multiple Poisson rate processes give rise to the correlation of the photon-to-photon pair times.

We have conducted a theoretical simulation and analysis based on the above single-molecule interfacial recombination ET model (Figure 3). The excitation-photon waiting time, τ1, is intrinsically stochastic and is defined as an exponential rate process: Pτ1 = A1 exp(−t1/τ1), where Pτ1 is the probability of the τ1, and τ1 is the mean of the distribution. From the distribution of the pair times of a bright state (Figure 2), τ1 is deduced to be ~0.32 ms for this molecule. The BET rate process, because of its complexity, has been reported to be single exponential,61,63 multiplexponential,64–66 or stretched exponential.67,68,72–77 Here, on the basis of the recombination model, the coulombic force between the electron and the cation across the interface dominates the diffusional drift of the electron typically involving trapping and detrapping in the semiconductor bulk and surface. It is reasonable to assume that the BET time will mostly be determined by the initial electron ejection depth into a TiO2 nanoparticle, however, dFET is determined by the

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stochastic fluctuation of the interfacial electronic coupling between ZnTCPP and the TiO$_2$ nanoparticle. Therefore, to simplify the fitting and simulation analysis, we take the BET time $t_2$ distribution as a single Poisson distribution, $P_{2n} = A_2 \exp(-t_2/\tau_2)$, where $P_{2n}$ is the probability of the $t_2$, and $\tau_2$ is the mean of the distribution.

Because the convolution of the excitation-photon waiting time $t_1$ and of the the BET time $t_2$ dominates the duration of an ET cycle, the probability distribution of photon-to-photon pair time $P_{Tn}$ ($Tn$ is the pair time, and $n$ is the number of ET cycles) can be described as the convolution of $P_1$ and $P_2$ as shown in Figure 3. Function $P_{Tn}$ can be directly calculated by integral calculus. For example, the probability distribution for one-cycle ET pair times is expressed as

$$P_{T1} = A_1^2 \left( k! - 1 \right) e^{-k_1} + e^{-k_1}/k^2$$

where $k_1 = 1/t_1$, $k_2 = 1/t_2$, $k = k_2 - k_1$, and $i$ is the real photon-to-photon pair time. In our data analysis, we performed programmable convolution and fitting using Matlab (R2007a). Parameters $t_2$ and $n$ can be directly obtained. According to the convoluted single-molecule ET dynamics, we analyzed the histograms of the single-molecule pair time trajectories. Figure 4 shows a fit result analyzing a portion (shown in color) of a single-molecule fluorescence trajectory (Figure 2). Our data analysis shows that the histograms of the pair times can be fitted well by assuming that there is a maximum of four ET cycles during a photon-to-photon pair time (Figure 4A). Our fitting result shows that the histograms of pair times of the zero cycles are exponential distributions whereas the histograms of pair times involved in ET cycles are nonexponential distributions. By calculating the probabilities from the histograms, we demonstrate that the excited states have a 36% probability to be involved in electron-transfer events and that the percentages of reactions involving one to four ET cycles are 20%, 8%, 4.5%, and 2.9%, respectively. In most of the ET events, the excited state performs one ET cycle ($S_0 + h\nu_{\text{excitation}} \rightarrow S_1 \rightarrow \text{ET&BET} \rightarrow S_0$) and then emits one emission photon ($S_0 + h\nu_{\text{excitation}} \rightarrow S_1 \rightarrow S_0 + h\nu_{\text{emission}}$). Moreover, an average BET time, $t_{2r}$, is fitted to be about 120 ± 10 μs by calculating the mean of the distribution of BET times (Figure 4B). Considering that not every emitted photon is detected and that a typical detection efficiency for a single-molecule imaging microscope is about 10% (i.e., only 1 out of 10 photons is detected\textsuperscript{46}), we suggest that the actual single-molecule BET rate process probes is at $10^{-5}$ s. This value is consistent with the widely reported BET times ranging from subns to several ms for dye/semiconductor systems.\textsuperscript{7,8,14.18.22.24.26}

To further analyze the single-molecule interfacial ET dynamics, we have simulated photon-to-photon pair times from zero ET cycle to four ET cycles initiated by consecutive laser photon excitation events. Because of single-molecule interfacial ET reactivity fluctuations, the experimentally detected photon-to-photon pair times in a single-molecule fluorescence trajectory are a mixture of pair times originated from radiative emission, ET events with different cycles, and background noise. To simulate the trajectory of pair times, random numbers are first generated on the basis of the fitted exponential and nonexponential curves in Figure 4. Random numbers that originated from the exponential curve are the analogue of pair times only from radiative emission (zero ET cycle). Random numbers that originated from the nonexponential curves are the analogue of pair times from ET events with different cycles (one to four). After 10% noise is randomly dispersed in the above generated pair times, a simulated trajectory of pair times is generated by programming control according to their occurring possibilities (Figure 4). Figure 5 shows the experimental and simulated autocorrelation function of pair times, where the experimental autocorrelation function is calculated from the same data shown in Figure 2 (the colored portion of the emission trajectory) and Figure 4. Although only the primary components of the experimental and simulated autocorrelation functions show the similar decay behavior, the experimental autocorrelation function contains more measurement noise, the simulated autocorrelation function essentially presents the experimental autocorrelation primary components which disappear at the index of 250 (Figure 5).

The interfacial electron transfer reactivity is highly sensitive to the molecular interactions between the adsorbed dye molecules and the TiO$_2$ substrate. There are a few parameters that contribute to the molecular interactions and in turn regulate the ET reactivity fluctuations; the parameters include (1) the driving force of free-energy gap, (2) the vibrational relaxation energy of the adsorbed molecules and the surface vibrational modes of TiO$_2$, (3) and the electronic coupling between the dye and the TiO$_2$.\textsuperscript{3,24.78–80} Among these parameters, the electronic coupling and surface bonding likely provide the most significant contributions to the interfacial electron transfer rate fluctuations. For the ZnTCPP/TiO$_2$ ET system, the correlation of the photon-to-photon pair times of an ET-active state is interpreted by the interfacial electron–cation recombination model including the interfacial ET reactivity fluctuation at an ms time scale. In previous reports by us and others, interfacial ET transfer reactivity has been demonstrated as intermittent and as fluctuat-

ing from time to time at a single-molecule level. Though the interfacial ET dynamics are complex and inhomogeneous in nature, the approach presented here is demonstrated to be effective in probing the real-time ET picture and in getting BET time.

In conclusion, we have probed and analyzed the single-molecule interfacial electron–cation recombination dynamics at a precise photon-to-photon pair time scale of subms to µs time scales by single-molecule photostamping spectroscopy. The autocorrelated photon-to-photon pair time of an ET-active state, which conceals the real-time characteristics of the interfacial electron–cation recombination dynamics, has been revealed and applied to probe the BET dynamics of ZnTCPP/TiO₂ system. On the basis of a convoluted interfacial electron–cation recombination model, the BET time is deduced to be on a 10⁻³ s time scale, which is consistent with the ensemble-averaged measurements which demonstrate the BET time ranging from subnanosecond to millisecond time scale. The autocorrelation of photon-to-photon pair times as well as the convoluted ET model has been further demonstrated by simulation and has been interpreted in terms of the interfacial ET reactivity fluctuation and blinking. Our approach not only can effectively probe the single-molecule interfacial electron–cation dynamics but also can be applied to other single-molecule ground-state regeneration dynamics at interfaces and in condensed phases.

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