

# Single Molecule Electron Transfer Dynamics in Interfacial Donor-Bridge-Nanoparticle Acceptor Complexes

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Understanding interfacial electron transfer (IET) dynamics between molecular adsorbates and semiconductor nanoparticles is essential to the improvement of nanocomposite solar cells.<sup>1</sup> Ensemble averaged IET kinetics were often non-single exponential, suggesting a heterogeneous distribution of IET rates.<sup>2</sup> The heterogeneity could result from static distribution in energetics of the adsorbate and semiconductor and their electronic coupling as well as the dynamic fluctuation of these quantities. These distribution and fluctuation are masked in ensemble average kinetics but can be revealed by single molecule spectroscopy.<sup>3</sup> The IET processes to oxide (TiO<sub>2</sub> and SnO<sub>2</sub>) nanoparticles from directly attached organic chromophores are often on the picosecond or faster time scales and significantly reduce adsorbate fluorescence quantum yield.<sup>2</sup> This has hindered unbiased samplings of fast injecting molecules and/or direct observation of fast ET states by single molecule fluorescence spectroscopy.<sup>4-6</sup> In this paper, we report a study of single molecule IET in a donor-bridge-nanoparticle acceptor system, in which the bridge between the chromophore and the nanoparticle slows down the IET rate. We demonstrate that with these complexes the sum of single molecules fluorescence decay is consistent with the ensemble average result, indicating an unbiased sampling of single molecules. Fluorescence intensity and lifetime trajectories of single molecules reveal both static and dynamics heterogeneities of the IET process.

The synthesis of 3-aminopropyltrimethoxysilane (silane) conjugated Sulforhodamine B (SRhB), or SRhB-Silane, and their absorption and emission properties are described in supporting information (Figure S1). Preparation of TiO<sub>2</sub>, SnO<sub>2</sub> and ZrO<sub>2</sub> nanocrystalline thin films were based on reported methods.<sup>7</sup> To attach SRhB-Silane, its aqueous solution was dropped on the substrates and dried in the dark. The sample was then heated at 110°C for 10 minutes followed by washing with water to remove unreacted molecules. Single molecules were studied using confocal microscope coupled with time correlated single photon counting module. Excitation beam at 500 nm (~200nW) was generated by frequency doubling the output (100 fs, 80 MHz repetition rate) of a mode-locked Ti:Sapphire laser (Tsunami oscillator pumped by 10 W Millennia Pro, Spectra-Physics). Emitted photons between 540 and 625 nm were collected. Shown in Figure S2 is a raster scanned fluorescence image of single SRhB-Silane molecules attached on TiO<sub>2</sub>.

Figure 1 compares typical fluorescence intensity and lifetime trajectories of single SRhB-Silane molecules attached on ZrO<sub>2</sub>, SnO<sub>2</sub> and TiO<sub>2</sub>. The fluorescence lifetime was calculated using photons within a 2 second bin time. Single molecule trajectories on ZrO<sub>2</sub> show only small fluctuations of lifetimes, even when there is large intensity change (see Figures 1a,b). Single SRhB-Silane molecules on SnO<sub>2</sub> and TiO<sub>2</sub> show shorter lifetimes and many (35% on TiO<sub>2</sub> and 45% SnO<sub>2</sub>) exhibit large fluctuation over

the course of their trajectories. Figures 1c and 1e are examples of trajectories with small fluctuations of lifetime and intensity for single molecules on TiO<sub>2</sub> and SnO<sub>2</sub>, respectively. Examples of trajectories with large fluctuations of lifetimes are shown in Figures 1d and 1f. In these trajectories, the lifetime decrease is accompanied by a decrease in fluorescence intensity, suggesting a fluctuation in the nonradiative decay rate. Similar positively correlated fluctuations have been observed in the blinking of semiconductor quantum dots and have been attributed to the fluctuation of Auger relaxation rates.<sup>8</sup>

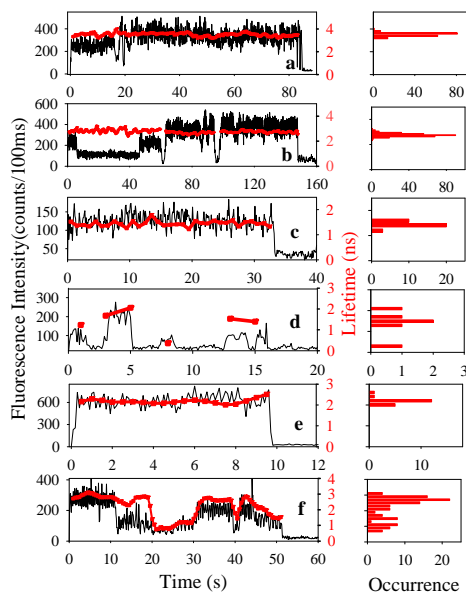


Figure 1. (Left) Typical fluorescence intensity (black) and lifetime (red) trajectories of single SRhB-silane molecules attached on ZrO<sub>2</sub> (a,b), TiO<sub>2</sub> (c,d) and SnO<sub>2</sub> (e,f). (Right) lifetime histograms of these trajectories.

To quantify the fluorescence lifetime distribution of an ensemble of single molecules, we constructed the total lifetime histograms (sums of all single molecules) of 68 single molecules on ZrO<sub>2</sub>, 103 molecules on SnO<sub>2</sub> and 67 molecules on TiO<sub>2</sub>, as shown in Figure 2a. The distributions show a clear dependence of the single molecule lifetimes on the substrate. For the molecules on ZrO<sub>2</sub>, SnO<sub>2</sub>, and TiO<sub>2</sub>, the average lifetime is 3.2, 2.5 and 1.9 ns and the standard deviation is 0.5, 0.75 and 0.90 ns, respectively, showing a trend of decreasing lifetimes and broadening distribution.

Shown in Figure 2b are ensemble averaged fluorescence decays of SRhB-Silane on ZrO<sub>2</sub>, SnO<sub>2</sub> and TiO<sub>2</sub> measured in samples with high concentration of molecules. They showed a similar dependence of lifetime on the substrates as single molecules.

Furthermore, the sums of single molecule decays agree with the corresponding ensemble averaged fluorescence decays, suggesting a complete sampling of all molecules under single molecule conditions.

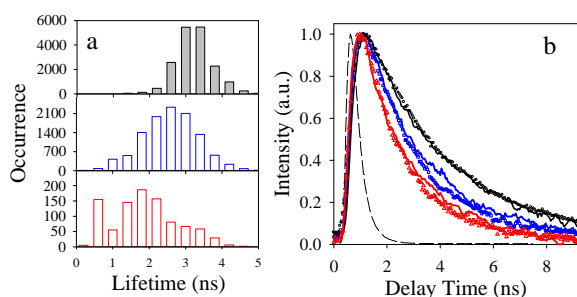


Figure 2. (a) Total lifetime histograms of single SRhB-Silane molecules on ZrO<sub>2</sub> (black), SnO<sub>2</sub> (blue) and TiO<sub>2</sub> (red). The total histograms are constructed from 68 molecules on ZrO<sub>2</sub>, 103 molecules on SnO<sub>2</sub> and 67 molecules on TiO<sub>2</sub>. (b) Ensemble averaged fluorescence decays of SRhB-Silane on ZrO<sub>2</sub> (black circles), SnO<sub>2</sub> (blue squares) and TiO<sub>2</sub> (red triangles). Average fluorescence decays constructed from the sum of single molecules on ZrO<sub>2</sub> (black lines), SnO<sub>2</sub> (blue lines) and TiO<sub>2</sub> (red lines), and instrument response function (dashed line) are also shown.

The measured total fluorescence decay rate ( $k$ ) is the sum of the rates of radiative decay ( $k_R$ ), intramolecular nonradiative decay ( $k_{INR}$ ), and IET ( $k_{IET}$ ). Ultrafast IET from Rhodamine B and related dyes to SnO<sub>2</sub> and TiO<sub>2</sub> have been observed.<sup>7,9</sup> IET from SRhB to ZrO<sub>2</sub> is not energetically allowed due to its much higher conduction band edge position.<sup>2</sup>  $k_{INR}$  of Rhodamine B is dependent on solvent environment due to the torsional motion of amino groups.<sup>10</sup> Since these oxide surfaces are likely covered with water under the experimental conditions, we assume the same  $k_{INR}$  on these substrates.  $k_R$  is dependent on the orientation of the adsorbate transition dipole relative to the interface.<sup>11</sup> However, it can only result in change of intrinsic lifetimes,  $1/(k_R+k_{INR})$ , from 3.1 and 4.1 ns for transition dipole perpendicular and parallel to the surface of SnO<sub>2</sub>, respectively (see supporting information). Therefore, in comparison to ZrO<sub>2</sub>, the observed shortened single molecule lifetimes and broadened distribution on SnO<sub>2</sub> and TiO<sub>2</sub> can be attributed to the IET processes.

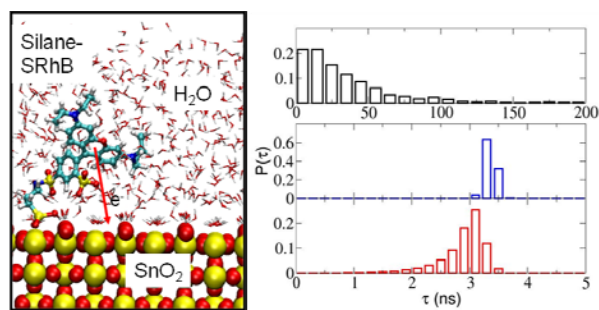


Figure 3: (Left) Snapshot of SRhB-silane on hydrated (110) surface of rutile SnO<sub>2</sub> at room-temperature. Color key: O (red), C (light blue), N (blue), H (white), S (yellow), Si (light yellow), Sn (gray yellow). (Right) Computed distributions of IET time (black), intrinsic lifetime without IET (blue), and total fluorescence lifetimes (red).

The observed distribution and fluctuation of single molecule lifetimes suggests static and dynamic heterogeneity in IET rates and/or radiative decay rates. To investigate the origin of this heterogeneity, we have performed molecular dynamics simulations of SRhB-Silane on hydrated (110) surfaces of rutile

SnO<sub>2</sub> at room temperature. The simulations revealed a distribution of adsorbate orientations and distances from the SnO<sub>2</sub> (110) surface, giving rise to a distribution of radiative decays and IET rates (see Figures S-3–S-7 for details). As shown in Figure 3, while these conformations lead to a narrow range of intrinsic lifetimes centered at 3.4 ns, their IET times show a broad distribution from ~0.1 ns to over 300 ns, broadening the distribution of total lifetimes. It is clear that the calculated fluorescence lifetimes on SnO<sub>2</sub> can account for the observed distributions (shown in Fig. 2) only when including the effects of IET. Assuming a constant intrinsic lifetime of 3.4 ns for all molecules on SnO<sub>2</sub>, the estimated ET time for the single molecule shown in Figure 1f fluctuates between 0.9 and 30 ns. The distribution of lifetimes on SnO<sub>2</sub> (Figure 2a) correspond to estimated single molecule IET times of ~ 0.2 ns to >> 10 ns, consistent with our computational results.

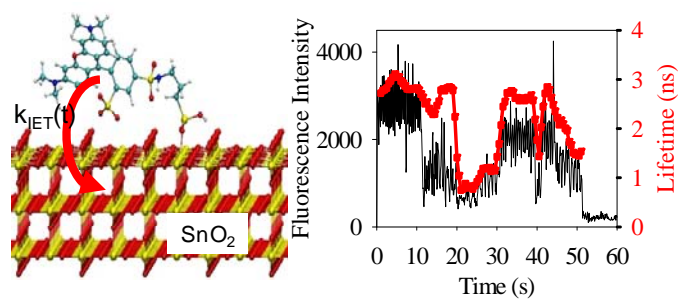
The observed positively correlated fluctuations of fluorescence intensity and lifetime have not been reported in previous single molecule ET studies. For coumarin 343 and porphyrin directly attached on TiO<sub>2</sub>, large fluctuations of single molecule fluorescence intensity with negligible change of lifetimes was observed.<sup>6</sup> It was suggested that IET active states could not be directly observed due to the subpicosecond IET time in those systems and that intermittent ET activity was responsible for the intensity fluctuation. It is shown here that the insertion of the silane bridge slows down IET process and allows a complete sampling of single molecules for direct observation of IET active states. The observed dynamical fluctuations of IET rates may be a general feature of interfacial donor-bridge acceptor systems. A detailed insight on this phenomenon requires further experimental and molecular modeling studies.

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**Supporting Information Available:** synthesis, experimental methods, and molecular modeling. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Single molecule interfacial electron transfer dynamics in a donor-bridge-nanoparticle acceptor complex was studied by time-resolved single molecule fluorescence spectroscopy and molecular modeling. It is demonstrated that the sum of the distributions of single molecule fluorescence life-times is consistent with the ensemble averaged result, suggesting an unbiased sampling of single molecules. Single molecule fluorescence intensity and lifetimes differ among molecules and fluctuate with time, revealing both the static and dynamics heterogeneities in the interfacial electron transfer processes.

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