Modeling Dispersive Electron-Transfer Kinetics in Single Dye Molecules on TiO_2

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ABSTRACT.

The kinetics of photo-induced electron transfer in dye-sensitized TiO_2 is studied using single-molecule microscopy. The distributions of electron-transfer dynamics in rhodamine 6G (R6G), rhodamine B (RB), and 5-Carboxy-X-Rhodamine (5-ROX) sensitized TiO_2 films are probed by time-dependent emission (i.e, blinking dynamics) studies.Emissive (on) and nonemissive (off) times are compiled into cumulative distribution functions for statistical analysis. The Maximum likelihood estimation (MLE)/Kolmogorov-Smirnov (KS) method and quantitative goodness-of-fit tests are used to determine the best fit to the blinking distributions. The on-time distributions for R6G, RB, and 5-ROX on TiO_2 are fit by powerlaws, but only for ~15% of the photophysical data. The off-time distributions for dyes on TiO_2 and glass are not well represented by power-law distributions and instead demonstrate log-normal behavior. Our observations show that on-time and off-time distributions are sensitive to thedye-TiO_2 system. To understand the physical significance of the power-law and log-normal distributions, blinking dynamics are modeled using Monte Carlo(MC) simulations. MC simulations demonstrate the impact of average electron transfer kinetics and kinetic dispersionon the resulting on-time and off-time blinking distributions. Our observations support the hypothesis that the rate constants for electron transfer are log-normally distributed, with events that occur from sub millisecond to second timescales.