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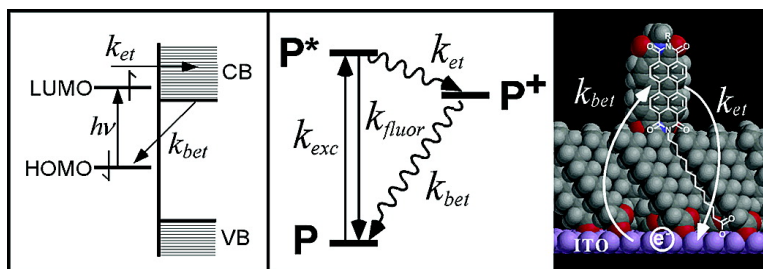# Single-Molecule Spectroscopy of Interfacial Electron Transfer

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Single-Molecule Spectroscopy of Interfacial Electron Transfer

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Abstract: It is widely appreciated that single-molecule spectroscopy (SMS) can be used to measure properties of individual molecules which would normally be obscured in an ensemble-averaged measurement. In this report we show how SMS can be used to measure photoinduced interfacial electron transfer (IET) and back electron transfer rates in a prototypical chromophore−bridge−electrode nonadiabatic electron transfer system. *N*-(1-hexylheptyl)-*N'*-(12-carboxylicdodecyl)perylene-3,4,9,10-tetracarboxylbisimide was synthesized and incorporated into mixed self-assembled monolayers (SAMs) on an ITO (tin-doped indium oxide, a *p*-type semiconductor) electrode. Single-molecule fluorescence time trajectories from this system reveals "blinks", momentary losses in fluorescence (>20 ms to seconds in duration), which are attributed to discrete electron transfer events: electron injection from the perylene chromophore into the conduction band of the ITO leads to the loss of fluorescence, and charge recombination (back electron transfer) leads to the return of fluorescence. Such blinks are not observed when an electrode is not present. The fluorescence trajectories were analyzed to obtain the forward and back electron rates; the measured rates are found to lie in the millisecond to second regime. Different rates are observed for different molecules, but the lifetime distributions for the forward or back electron transfer for any given molecule are well fit by single exponential kinetics. The methodology used is applicable to a wide variety of systems and can be used to study the effects of distance, orientation, linker, environment, etc. on electron transfer rates. The results and methodology have implications for molecular electronics, where understanding and controlling the range of possible behaviors inherent to molecular systems will likely be as important as understanding the individual behavior of any given molecule.

A crucial aspect of the understanding and realization of any future molecular electronics[1−4] will be the connections between the molecular-scale components, whatever their nature, and the meso- and macroscopic metal or semiconductor components which will transmit energy or information from these molecules or molecular assemblies to more traditional electronic components. Interfacial electron transfer (IET) between molecules and bulk electrodes has received extensive theoretical[5−8] and experimental[9−13] treatment, typically relying on ensemble-averaged optical spectroscopic and electrochemical measurements. There is a tremendous need for new methodology and experiments designed to probe the *discrete* electronic and molecular dynamic fluctuations of *single molecules* near elec-

trodes. Single-molecule spectroscopy (SMS)[14−18] has emerged as an important method for the study of the fluorescence behavior of single molecules in ambient environments and has been used to probe the discrete excited-state electronic[19−22] and molecular dynamic processes[23,24] of molecules. SMS has been used to estimate the average interfacial electron transfer excited-state quenching rates of organic chromophores at semiconductor electrodes[25] and has been shown to be particularly well suited for the study of low quantum yield excited-state deactivation processes such as the photoinduced ionization of semiconductor nanoparticles.[26−28] Our laboratory has recently used SMS to follow electron transfer processes in donor−bridge−acceptor

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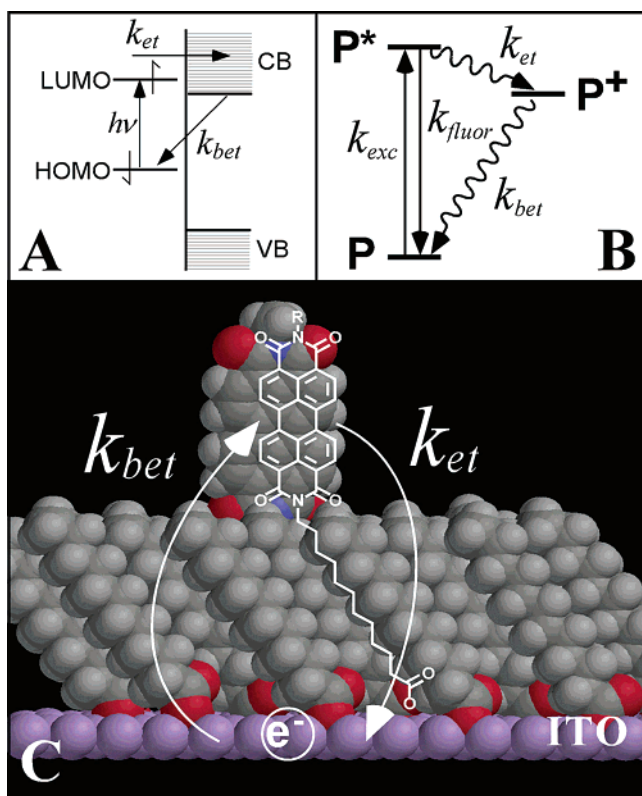
Figure 1. (A) Relative electronic energy levels and (B) kinetic scheme for (C) the interfacial electron transfer system based on **1** self-assembled in a mixed monolayer on an ITO electrode (R = 1-hexylheptyl).

and molecular sensors systems.[29,30] Yet, despite the intense interest in the molecular electronic possibilities of organic self-assembled systems at electrodes, similar studies have not been attempted to follow the *discrete* electron transfer and charge separation fluctuations in such systems at the single-molecule level. Such single-molecule studies of ordered systems have the potential to unlock information hidden in the ensemble average of bulk experiments, and to contribute greatly to the theoretical understanding of these systems.[15,17,18,21]

In this report we show how SMS can be used to measure photoinduced IET rates in a prototypical chromophore–bridge–electrode system. Our system is composed of an asymmetric perylene bisimide chromophore **1** self-assembled in a mixed monolayer on an ITO electrode (tin-doped indium oxide, a *p*-type semiconductor) via a carboxylic acid terminated aliphatic bridge (Figure 1C). Perylene bisimides show strong fluorescence ($\epsilon \approx 80000$; $\Phi_F \approx 1$) and their synthetic flexibility and accessible oxidation (1.61 eV vs SCE) and reduction (-0.59 eV) potentials[31] make them good candidates for building blocks of molecular electronic structures and studies of photoinduced charge transfer.[32–36] Optical excitation of a perylene near an

ITO electrode leads to creation of its lowest-energy singlet excited state (**P***) which can either relax radiatively to the ground state (**P**) or undergo charge injection from the perylene LUMO into the conduction band of the ITO to form the cation radical (**P⁺**).[10,25,37–38] At room temperature, the forward rate of electron transfer (k_{et}) is significantly slower than the rate of fluorescent relaxation of the exited state (k_{fluor}) due to weak electron coupling between the chromophore and the electrode, leading to slow IET through the long aliphatic bridge. While a k_{et} significantly slower than k_{fluor} results in an extremely low quantum yield of IET, such rare electron transfer events are nevertheless easily detectable at the single-molecule level as momentary losses in fluorescence. In this study, we show how the fluorescence time trajectories can be analyzed to yield the forward and back electron transfer rates for single molecules in these layers.

Experimental Procedures

N-(1-Hexylheptyl)-*N*′-(12-carboxylicdodecyl)perylene-3,4,9,-10-tetracarboxylbisimide **1** (Figure 1C), was synthesized by standard methods[39] (see Supporting Information for additional details). Briefly, perylene-3,4,9,10-tetracarboxyldianhydride (Aldrich) was reacted with 1-hexylheptylamine[40] to give the symmetric bisimide, which was then treated with KOH[41] to provide the monoimide monoanhydride. Reaction of this product with 12-aminododecanoic acid (Aldrich) gave **1** in high yield.

Absorption and emission spectra (Figure 2) of **1** were measured in CHCl₃ solution on a Perkin-Elmer Lambda 25 UV/vis and a Cary Eclipse fluorescence spectrophotometer. The excitation wavelength was 490 nm for emission spectra.

To form the monolayers, glass slides coated with ITO (Metavac, ∼2 nm RMS roughness) were cleaned by sonicating 1 h in a 25:75 ethanolamine:water mixture, rinsing thoroughly (>100 mL) with deionized water and then with methanol, and drying in a vacuum oven (60 °C) 1 h. The slides were then immersed for 3–4 h in a 5×10^{-3} M solution of undecanoic acid in hexadecane,[42] and then 24 h in an "exchange solution"[9] of 5×10^{-3} M undecanoic acid and 5×10^{-9} M **1** in hexadecane to form the self-assembled structure rendered in Figure 1C. After removal from the final self-assembly solution the slides were rinsed carefully with acetonitrile to remove excess hexadecane and undecanoic acid. The contact angle of water with the slide was found to increase from ∼20° to up to ∼100° upon monolayer formation, indicating good coverage. Using oven-dried glassware and keeping the self-assembly solution free of water was found to improve the quality of the monolayers, which were also observed to degrade in quality over the course of a few hours when left out in air. Self-assembled films prepared by this procedure show well-separated (>500 nm) isolated single

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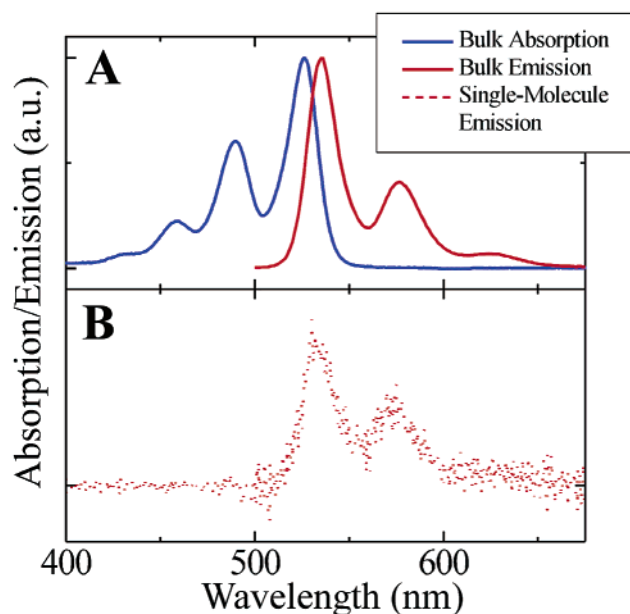
Figure 2. (A) Solution absorption (solid-line blue curve) and emission (solid-line red curve) spectra of **1** measured in CHCl3 solution and (B) typical single-molecule fluorescence spectrum (dashed-line red curve) of **1** in a mixed self-assembled monolayer on ITO.

perylene chromophores in the monolayers in fluorescence images. Similar films prepared with higher perylene concentration showed uniform fluorescence over large areas ($>100\ \mu m^2$) with little evidence of defects or multilayer formation.

Single-molecule fluorescence images, traces, and spectra were collected with a scanning confocal microscope (SCM), in which a tightly focused laser spot ($\sim$400 nm) was used to excite one molecule at a time in these dilute films. In this microscope, samples are raster scanned over the diffraction limited laser spot as fluorescence images are collected to locate single molecules. Fluorescence traces (fluorescence vs time) and fluorescence spectra were collected over single molecules. These data were collected using a Digital Instruments Aurora-3 near-field scanning optical microscope (NSOM), with a $100\times/1.25$ NA objective (Nikon), modified to function as an SCM. A dichroic mirror (Chroma 505DCXRU) was used to bring in circularly polarized 488 nm CW excitation light (Melles-Griot 543, 300 mW tunable argon-ion laser system) with an excitation intensity at the sample of $\sim$1500 W/cm^2. The collected fluorescence passes through the dichroic mirror and a 488 nm holographic notch filter (ThermoOriel SuperNotch) to remove backscattered laser light, and can be diverted onto a liquid nitrogen cooled CCD (Roper Instruments) via a diffraction grating (Acton Research Corp. SpectraPro-300i) to collect spectra, or passed through a 500$-$700 nm band-pass filter (Chroma HQ600/200m) to further remove residual laser light and other background light, and focused onto a single-photon counting avalanche photodiode (APD) (EG&G SPCM-AQR-14) to monitor fluorescence intensity for images and traces. The sample was kept under an argon atmosphere to stave off eventual photobleaching and to preserve the integrity of the monolayers.

Results and Discussion

Fluorescence spectra from single molecules in mixed monolayers on ITO were collected and compared to the solution spectra (Figure 2). The background-subtracted single-molecule

spectra closely match the solution spectra, as observed for other single-molecule systems,[43,44] and confirm that the fluorescence seen is from the first singlet excited state of an isolated perylene bisimide molecule.

Typical single-molecule traces show a single constant level of fluorescence before photobleaching occurs and the fluorescence intensity returns to background in a single step (Figure 3A). When a 1×10^{-10} M solution of **1** in CHCl$_3$ and then a 2 mg/mL solution of poly(vinylbutyral) (PVB) in THF are spin-coated onto a quartz slide at 2000 rpm, 88% of 62 single molecules studied by SCM show this typical "single-step" behavior as shown in Figure 3A. Some of these molecules show brief losses of fluorescence (down to background) before the eventual irreversible photobleaching, and these "blinks" are attributed to intersystem crossing (ISC) to a nonfluorescent triplet state,[21] or perhaps to photoinduced charge transfer to the polymer or to impurity sites in the quartz for molecules lying near the polymer$-$quartz interface,[30] as 36% show blinks that are longer than those generally associated with triplet states. When similar films are prepared on an ITO electrode and studied under identical conditions, this single-step behavior is seen for only 38% of the 71 single molecules studied; presumably these are from molecules that have been swept up into the polymer, away from the interface, whose behavior should be unaffected by the substrate. The remaining 62%, however, show very rapid fluctuations in the fluorescence intensity similar to that shown in Figure 3B. It has been shown that excited organic chromophores on an ITO surface show rapid reversible electron transfer to the ITO,[25] and we attribute the fluorescence behavior such as that in Figure 3B to molecules close to the polymer$-$ITO interface showing rapid electron transfer, at or below the time resolution (20 ms) of our experiment. In addition, among the molecules that showed single-step behavior, 59% of these displayed losses in fluorescence too long in duration to be accounted for by intersystem crossing.

In contrast, however, 85% of the 168 single molecules studied in SAMs described above show long-lived dark states, and many show well-defined blinking behavior like that in Figure 3C and 3D. Incorporating the chromophore into a SAM both separates the molecule from the ITO electrode to slow the electron transfer down into a regime where it can readily be studied by our methods and provides a well-defined geometry for understanding and modeling the system. Single-molecule traces from the SAMs often show traces like that shown in Figure 3C, having a constant level of fluorescence but periodically showing "blinks" in which the fluorescence intensity drops to background in a single step as in photobleaching but returns to the original intensity after a brief time. The blinks observed in these traces are in general too long to be accounted for by triplet states,[21,45] and translational diffusion is also not a plausible explanation for these dark states, as repeated fluorescence images over the same area over time periods from minutes to hours reveal no change in the positions of the molecules. Similarly, conformational dynamics are also an unlikely source of the dark states, given the general absence of intermediate intensity levels, except in a few cases where the blinking is not fully resolved and the

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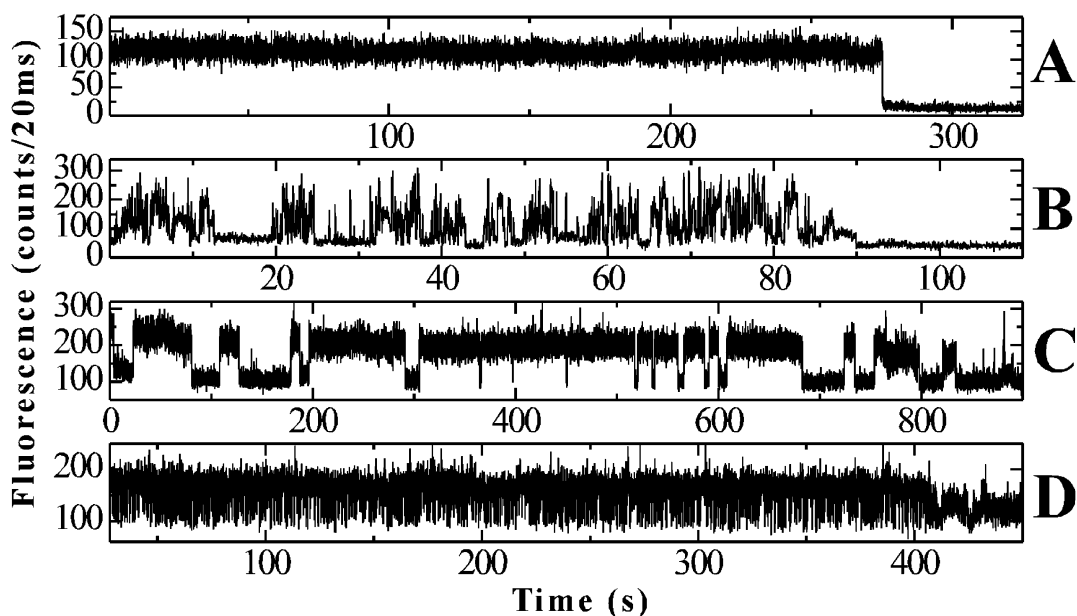
Figure 3. Fluorescence trajectories for 1 (A) on quartz, (B) on ITO, and (C,D) in a self-assembled monolayer on ITO.

molecule is frequently fluorescing for only a portion of the integration time. Since the occurrence of the longer ($\gg$20 ms) off times is clearly related to the proximity of an ITO electrode, which is expected to readily accept an electron from the photoexcited molecule,[25,37] we believe this blinking results from electron transfer to the ITO electrode as shown in Figure 1A: the molecule stops fluorescing when it loses an electron into the electrode, and remains "off" until the electron returns and the molecule comes back "on" and resumes fluorescing. Each blink off or blink on represents the observation of a single electron transfer event, and by analyzing the average duration of the on and off times the electron transfer rates can be determined.

To analyze the traces to obtain the average lifetimes of the on and off states, τ_{on} and τ_{off}, a method similar to that previously used to analyze triplet blinking[21] was used. Taking the fluorescence trace shown in Figure 3C as an example, a histogram of the fluorescence intensities (Figure 4A) shows clearly that there are two states with two different levels of fluorescence: a state with an average intensity of approximately 105 counts/ 20 ms, which is equal to the background fluorescence (the "off" state); and a state with an average intensity of roughly 170 counts/20 ms, which is equal to a typical level of fluorescence above background for a single perylene chromophore under our experimental conditions (the "on" state). Taking as a cutoff point a value of 137 counts/20 ms the trace is "rounded off": the molecule is assigned to either the on or the off state at each point in the trace (Figure 4B) as the fluorescence is greater or less than this cutoff. The duration of the on and off times are counted and histogrammed (occurrences versus duration), and the histograms are fit with single-exponential curves to determine the average lifetimes of the on and off state (Figure 4C). For this particular molecule, the average on time is $\tau_{on} = 276 \pm 11$ ms and the average off time, $\tau_{off} = 42.9 \pm 0.7$ ms. Importantly, the observed single exponential behavior for this and other molecules strongly suggests that the molecular system is fixed and well behaved and that the blinking is due to a single process, electron transfer to the electrode. Molecular reorienta-
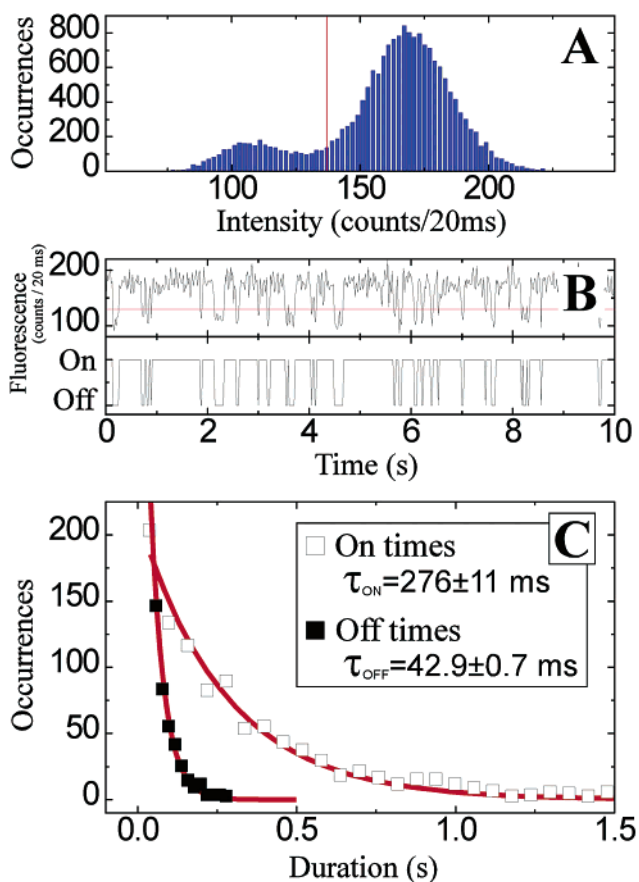

Figure 4. (A) An intensity histogram of the trace shown in Figure 3D; (B) a section of the trace and the same section rounded to on and off states; (C) histogram and single-exponential fit of the on and off time durations.

tion and/or diffusion during data collection would likely lead to dramatic changes in the electronic coupling between chromophore and electrode, resulting in multiexponential behavior in the observed kinetics.

Once τ_{on} and τ_{off} have been determined the forward and back electron transfer rates can be readily obtained. The back electron
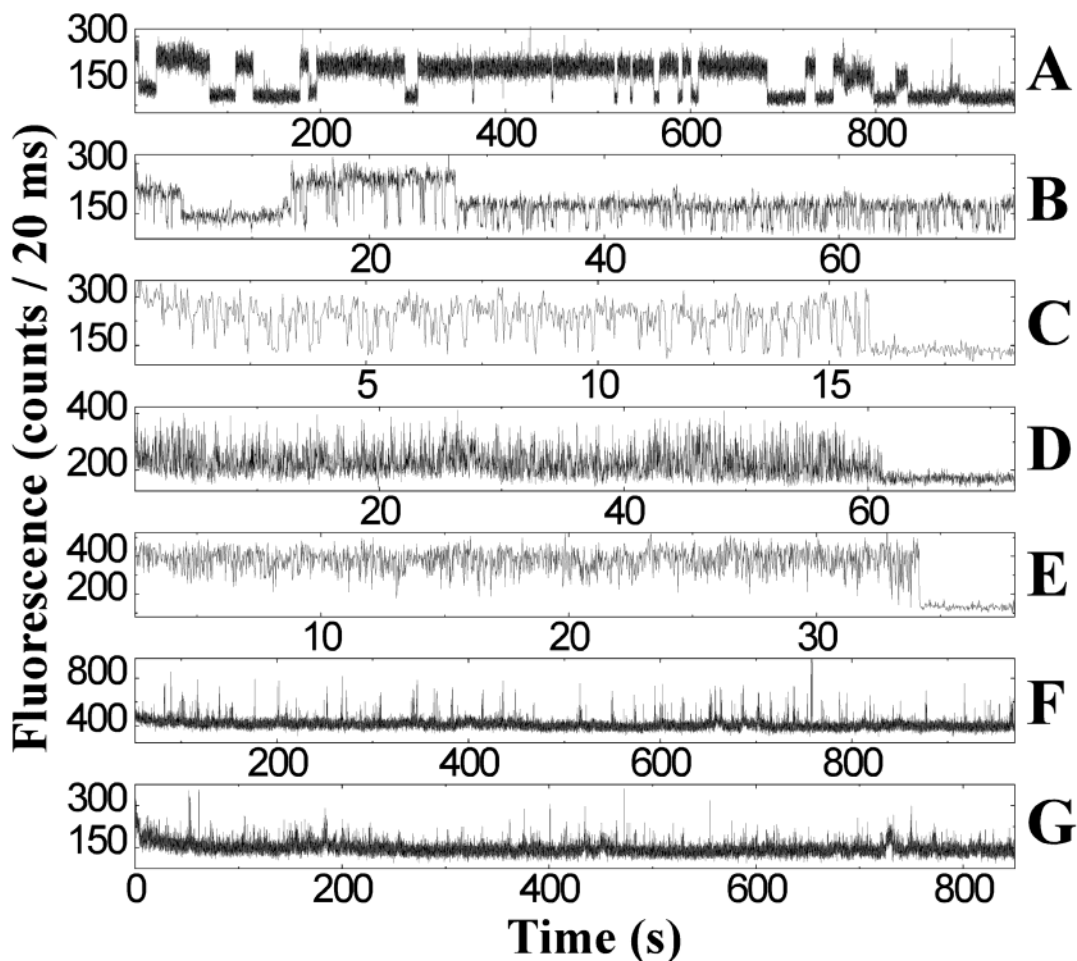
Figure 5. Representative fluorescence versus time trajectories observed for **1** in a self-assembled monolayer on ITO. Traces display the range of observed blinking behavior.

transfer rate is simply the inverse of the average off time:

$$\frac{1}{\tau_{\text{off}}} = k_{\text{bet}} \tag{1}$$

but the forward electron transfer rate also depends on the excitation rate:[21]

$$\frac{1}{\tau_{\text{on}}} = k_{\text{exc}} \frac{k_{\text{et}}}{k_{\text{et}} + k_{\text{fluor}} + k_{\text{isc}} + k_{\text{ic}}} \tag{2}$$

For this perylene chromophore $\Phi_{\text{F}} \approx 1$ so k_{isc} (rate of intersystem crossing to the triplet state) and k_{ic} (rate of other nonradiative decay) were neglected in these calculations. On the basis of laser power and detection efficiency (1500 W/cm², ~100 counts/20 ms at 5% detection efficiency), we estimate $k_{\text{exc}} \approx 10^6$ s⁻¹, and k_{fluor} is measured in solution to be 2.57×10^8 s⁻¹.

Average on and off times and the corresponding forward and back electron transfer rates for some representative single-molecule traces (Figure 5) are shown in Table 1. While not all molecules examined survived long enough before photobleaching for single-molecule electron transfer rates to be successfully calculated, for those that do, rates can be extracted from molecules showing a wide range of possible behaviors, from unusually long time-scale processes, as in Figure 5A, to cases where the blinking takes place on a time scale at or below the

Table 1. Measured ON and OFF Times and Calculated Electron Transfer Rates for the Single-Molecule Traces Shown in Figure 5

Figure 5	τ_{on} (ms)	τ_{off} (ms)	k_{et} (s⁻¹)	k_{bet} (s⁻¹)	$k_{\text{et}}/k_{\text{bet}}$
A	15800 ± 4230	6780 ± 1740	16.2 ± 4.7	0.148 ± 0.041	109
B	276 ± 11	42.9 ± 0.7	939 ± 39	23.3 ± 0.4	40.3
C	269 ± 20	37.9 ± 4.9	956 ± 71	26.4 ± 3.4	36.2
D	55.0 ± 3.3	193 ± 17	4670 ± 290	5.18 ± 0.47	902
E	41.9 ± 1.9	21.6 ± 0.5	6140 ± 280	46.3 ± 1.0	133
F	22.6 ± 1.2	77.5 ± 2.6	11400 ± 600	12.9 ± 0.4	884
G	8.51 ± 0.68	91.8 ± 3.3	30200 ± 2400	10.9 ± 0.4	2770

time-scale resolution of the experiment, as in Figure 5F or 5G. The range of behaviors observed here is presumably related to inhomogeneities in the SAMs and to variability on the surface of the ITO (RMS roughness ≈ 2 nm) affecting the degree of electronic coupling between the molecule and the electrode—a narrow or monodisperse rate distribution is not expected for single molecules in such a system. Molecules giving traces such as that shown in Figure 5A are only weakly coupled to the electrode, and are likely in well-packed regions of the monolayer and thus a maximum distance from the ITO, while those such as in Figure 5F and 5G represent molecules that are strongly coupled, presumably because disorder in the monolayer or the electrode has brought them closer to the surface of the ITO. It should be noted, however, that even in a perfect monolayer on an atomically flat surface, variability in coupling and thus in rates might be expected due to differences in the local electronic structure of the ITO related to the distribution of dopant sites

and to different orientations of the chromophores relative to the semiconductor lattice.

The forward and back electron transfer rates do not change uniformly across this range, as shown by the dispersity in the ratio k_{et}/k_{bet} (Table 1). The forward and back electron transfer processes are inherently different, and it might be expected that the forward transfer is more strongly dependent on distance and orientation. The forward electron transfer process involves charge injection from the perylene LUMO (lowest unoccupied molecular orbital) into a large energetically accessible density of states within the conduction band of the ITO while the back electron transfer involves transfer of a thermally relaxed electron from the bottom of the conduction band or from a local trap (energetically discrete states) back to the SOMO (singly occupied molecular orbital) of the perylene cation. The observed slightly larger dispersion in the forward electron transfer rates suggest differences in the structural and distance dependence to electron transfer for the two processes. The methodology employed here opens the possibility of studying this disparity in more depth, as information about the back electron transfer process is not accessible by previous methods.

Conclusions

We have shown that single-molecule fluorescence techniques can be used to measure interfacial electron transfer rates in the millisecond time regime under ambient conditions in organic optoelectronic systems. Further studies using these techniques should lead to a better understanding of the effect of the length and nature (e.g., conjugated vs nonconjugated) of the spacer and of binding functional groups on the electron transfer rates, a question of enormous interest to both molecular electricians and electron transfer experimentalists and theorists. In future experiments a metallized probe can be positioned over the sample to study the effect of an applied electric field on the electron transfer rates. These methods can be readily applied to a wide variety of systems and should provide a wealth of information on these and other problems in electron transfer and molecular electronics.

Supporting Information Available: Details of perylene synthesis and characterization (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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