Single-Molecule Spectroscopy of Intramolecular Electron Transfer in Donor-Bridge-Acceptor Systems

Ruchuan Liu, Michael W. Holman, Ling Zang, and David M. Adams*

Department of Chemistry, Columbia University, 3000 Broadway, New York, New York 10027

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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 article, we show how SMS can be used to investigate intramolecular electron transfer (IET) processes in model dimer systems composed of two perylene chromophores connected via an adjustable bridge. The fluorescence behaviors of a large number of molecules are cataloged and the results statistically analyzed to gauge information about the range of behaviors of the ensemble. Single-molecule fluorescence time trajectories reveal "blinks", momentary losses in fluorescence (>20 ms to seconds in duration), which are attributed to discrete IET excursions to the charge-separated (CS) state. We find that fluorescence blinking behavior is dependent on bridge length and chromophore geometry, which affect the electronic coupling and therefore the IET. The statistical trends observed in this analysis are used to corroborate the assignment of the blinking behavior to IET. These 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.

Introduction

In the emerging field of molecular electronics,[1−7] where the ambition is to make single-molecule-based devices, there is a tremendous need for new methodology and experiments designed to probe the electronic properties of *single molecules*. Many recent experimental studies have focused on conductance measurements of molecules linked to electrodes using scanning tunneling microscopy,[8−10] break junctions,[11,12] and electrostatic trapping between nanometer-sized electrodes.[5,13] Traditional electron transfer systems employing a donor-bridge-acceptor structure have been extensively studied in the context of molecular electronics to elucidate fundamental aspects of intramolecular electron transfer (IET) or to test possible structures and devices.[14−24] Typically, however, these studies have relied on ensemble-averaged optical spectroscopies. Single-molecule spectroscopy (SMS)[25−29] 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[30−33] and molecular dynamic processes[34,35] of molecules. SMS has been used to estimate the average interfacial electron-transfer excited-state quenching rates of organic chromophores at semiconductor electrodes[36] 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.[37−39] Yet, despite the intense interest in the molecular electronic possibilities of donor−acceptor molecules, similar studies have not been attempted to follow the *discrete* electron transfer and charge separation fluctuations in such systems at the single-molecule level.

In this article, we use SMS to investigate IET processes in a series of symmetric perylene-based dimer molecules, in which perylene bisimide moieties are connected via an oligo-1,4-phenylene bridge of adjustable length (Figure 1). With current single-molecule detection techniques, it is straightforward to collect fluorescence data from many molecules in a relatively short period of time, allowing us to rapidly build up a large library of data on a large number of individual molecules. We then analyze these data statistically on the basis of the detection of rare electron transfer events and a few other simple criteria and use the whole library to develop a picture of the behavior of a series of different species in a given molecular environment. In effect, instead of making a single measurement on the ensemble of molecules, we make an ensemble of measurements on individual single molecules. In addition to getting information about the ensemble that is only accessible by single-molecule techniques, this single-molecule approach is useful in that it not only provides information about the ensemble average but also about the range of possible behaviors that lead to that average. In the case of electron transfer, this level of understanding is particularly important for the field of molecular electronics: from a device-design standpoint, understanding and controlling this picture of the overall range of possible behaviors will likely prove to be as important as designing in the ideal behavior of any given molecule.

Optical excitation of a perylene dimer (**P**−**P**) leads to creation of an excited singlet state (***P**−**P**) localized on one of the chromophores, which either radiatively decays to the ground state or undergoes IET to form a charge-separated state ($\mathbf{P}^+-\mathbf{P}^-$) (Figure 1a). This photoinduced IET has been studied in related symmetric and asymmetric bichromophoric systems.[23] At room temperature in solution, the forward IET rates (k_{et}) and charge recombination (back IET) rates (k_{bet}) lie in the picosecond time regime and show a pronounced dependence on the solvent polarity, becoming faster in more polar solvents. However, in a rigid polymer matrix where steric effects become appreciable, both k_{et} and k_{bet} are expected to be significantly slower, because of the reduced stabilizing power of a rigid

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* To whom correspondence should be addressed. E-mail: dadams@chem.columbia.edu.

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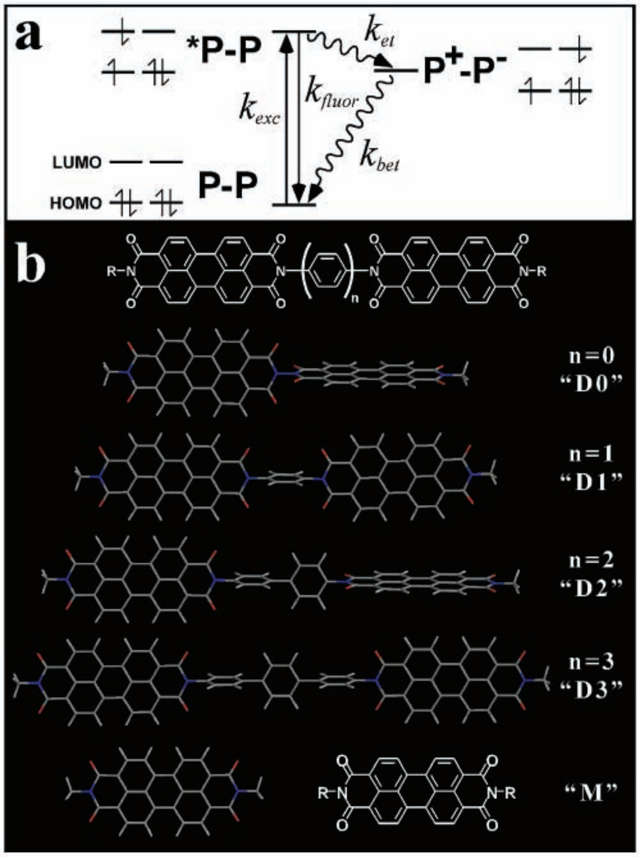

Figure 1. Energy levels and structures of molecules in this study. (a) Scheme for photoinduced intramolecular electron-transfer process in perylene dimer systems; (b) structure and names for the perylene dimers used in this study. For **D0**, R = 1-hexylheptyl; for **D1**−**D3**, R = 1-nonyldecyl; and for **M**, R = 1-hexylheptyl, 1-nonyldecyl, 2-*n*-propoxyethyl, or 12-carboxylicdodecyl.

matrix for the charge-separated state and thus a lower driving force[40,41] and because of a much larger Marcus reorganization energy[42,43] for the IET reaction. Such effects have been observed in other IET systems[44] and are expected for the symmetric perylene dimer molecules in this study, where the driving force for IET is low and the CS state may involve twisted geometries.[45] A k_{et} significantly slower than k_{fluor} results in an extremely low quantum yield for formation of the charge-separated state. While such low quantum yield processes would be nearly undetectable in most ensemble-averaged measurements, they are nevertheless easily detectible with SMS where the individual rare IET events can be discerned from momentary losses in the single-molecule fluorescence.

Experimental Section

Symmetrically substituted perylene 3,4,9,10-tetracarboxyl bisimide monomers (**M**) (see Figure 1b) and symmetric perylene dimer systems (**D0**, **D1**, **D2**, and **D3** as shown in Figure 1b) were synthesized by standard methods[46] (see Supporting Information for details). Bulky side groups R inhibit π-stacking and solubilize the perylenes to allow for facile synthesis and characterization, without affecting the spectroscopic properties of the chromophore. For **D0** R = 1-hexylheptyl, for **D1**, **D2**, and **D3**, R = 1-nonyldecyl; for **M** molecules with R = 1-hexylheptyl, 1-nonyldecyl, 2-*n*-propoxyethyl, and 12-carboxylicdodecyl were studied.

Solution absorption spectra were collected on Cary 50 and Cary 100 UV/vis spectrometers, and solution fluorescence spectra were collected on a Cary Eclipse fluorometer, using solutions with absorption intensities of 0.05−0.1 o.d. Inner filter effect corrections[47] were applied to the observed fluorescence before quantum yields were calculated. Excitation at 490 nm was used and the fluorescence quantum yields were calculated by taking the integrated fluorescence divided by the absorption at 490 nm, relative to **M** (R = 1-hexylheptyl) in the same solvent. Quantum yields of **M** (R = 1-hexylheptyl) were 0.88 in $CHCl_3$ and 0.95 in MTHF, relative to **M** (R = 1-hexylheptyl) in acetonitrile, which has $\Phi_F \sim 1$.[48]

TABLE 1: Data from the Solution Optical Spectroscopy of the Molecules Used in This Study[a]

	D0	D1	D2	D3	M
			$CHCl_3$		
Φ_F/Φ_{FM}	0.93	0.96	0.96	0.97	1.00
λ_{max}abs	534	527	530	526	527
λ_{max}fluor	540	534	536	534	534
			MTHF		
Φ_F/Φ_{FM}	0.73	0.92	0.80	0.94	1.00
λ_{max}abs	528	519	523	519	521
λ_{max}flour	534	527	530	527	528

[a] The data for **M** are for R = 1-hexylheptyl, though the effect of changing R is very slight.

For single-molecule measurements, molecules were sparsely distributed throughout a ~100-nm thin film of poly(vinylbutyral) (PVB) (Aldrich) on clean glass cover slips by spin coating a solution of 2 mg/mL PVB and 2 × 10^{-10} M perylene bisimide in THF at 1500 rpm. Single-molecule fluorescence imaging and fluorescence trajectory collection were performed using a Digital Instruments Aurora 2 near-field scanning optical microscope (NSOM) modified to function as a scanning confocal microscope (SCM), equipped with a 100 × 1.25 NA objective (Zeiss), holographic 488-nm supernotch filter (ThermoOriel) to remove the excitation light, and single-photon-counting avalanche photodiode (APD) detectors (Perkin-Elmer/EG&G SPCM-AQR-15), operated with the sample under an argon atmosphere. The typical experiment involved continuous optical excitation with circularly polarized 488-nm light from an argon-ion laser (Melles-Griot), focused to a diffraction limited spot (fwhm = 244 nm), leading to an excitation power at the sample of ~500 W/cm^2, and collection of emitted photons at the APD with a 20-ms integration time.

Results and Discussion

The solution and single-molecule fluorescence properties of perylene dimers (**D0**−**D3**) and monomers (**M**) (Figure 1b**)** were investigated. Perylene bisimides are useful molecules for single-molecule studies because of their high photochemical stability, high quantum yield of fluorescence ($\Phi_F \sim 1$), low quantum yield of intersystem crossing ($\Phi_{ISC} \sim <0.001$), and versatile reactivity.[46,48] Perylene bisimides also have accessible oxidation (1.61 V vs SCE) and reduction (−0.59 V) potentials[48] and are nonfluorescent in the oxidized and reduced states, allowing us to produce and follow photoelectrochemical processes.

The dimer systems show extremely strong fluorescence in lower dielectric solvents such as $CHCl_3$, with Φ_F similar to the perylene monomers, indicating minimal IET quenching of the excited state fluorescence, while in a higher dielectric solvent, 2-methyltetrahydrofuran (MTHF), the quantum yields can be markedly decreased relative to the monomer (Table 1, Figure 2). This reduction of Φ_F in more polar solvents is similar to what has been observed in other bichromophoric systems[23] and has been attributed to an increase in k_{et} due to stabilization of the CS state, making the (nonradiative) relaxation via the IET

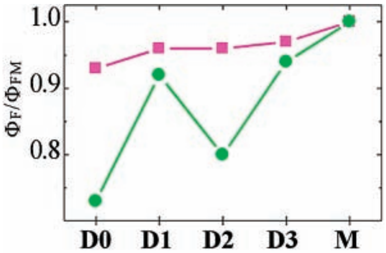

Figure 2. Trends in the fluorescence quantum yield of perylene dimers, relative to the monomers, in $CHCl_3$ (■) and MTHF (●), with the quantum yield decreased in more polar solvents because of greater IET quenching of the excited state.

pathway competitive with the radiative rate k_{fluor}. For **M**, k_{fluor} is measured at 2.6×10^8 s^{-1} and should be similar in perylene dimers, so for Φ_F ($\sim k_{fluor}/(k_{et}+k_{fluor})$) to decrease to 0.72, k_{et} should be about 10^8 s^{-1}. On the basis of other phenylene-bridged systems studied in solution,[22] the rate of IET is expected to decrease across our series and should be fastest for **D0**. However, the decrease across the series is not monotonic but follows an oscillating pattern which is repeated in single-molecule measurements and is discussed in detail below.

When dispersed in thin films of poly(vinylbutyral) and examined in a scanning confocal microscope (SCM), single molecules of **M** exhibit bright fluorescence (50−150 counts/20 ms) and dimers give approximately twice the fluorescence (100−300 counts/20 ms) indicating that fast IET is not significantly affecting Φ_F. Typical experiments involve raster scanning the sample to image an area to locate isolated molecules and then collecting fluorescence traces—fluorescence intensity versus time—by positioning one molecule at a time over the laser spot. For each molecular species studied, approximately 150 traces were acquired and categorized.

Typical single-molecule fluorescence traces of **M** show a constant level of fluorescence intensity until eventual irreversible photobleaching (because of decomposition, photooxidation, etc.) leads to sudden loss of fluorescence in a single step. Many traces also show temporary disappearance and return of fluorescence ("blinks") before final photobleaching. In some cases (Figure 3a), these blinks are very brief, at or below the time resolution of the experiment (20 ms), and can be attributed to intersystem crossing (ISC) to a nonemissive triplet state. The molecule undergoes ISC and remains in the triplet state, not fluorescing, until it relaxes back to the ground state and the normal fluorescence intensity reappears. Dimers, however, often also show blinks that are too long to be accounted for by triplet states (Figure 3c and 3d), whose average lifetimes are about milliseconds at most, even when molecules are immobilized in a polymer matrix or kept under an inert atmosphere.[32−33,49−50] These extended off times have been attributed to long-lived CS states resulting either from IET as described above or perhaps to electron transfer (ET) to or from the polymer matrix.[24,32,50−53] Though k_{et} and k_{bet} are fast in solution, they are expected to be significantly slower in a polymer matrix, as explained above. Traces showing a single constant level of fluorescence are classified as "one-step" traces and are further broken down into traces with and without long time scale blinks.

If multiple chromophores are within the excitation volume of the SCM and photobleach at different times, it is possible to observe "multistep" behavior (Figure 3b, 3e, and 3f) where fluorescence is lost in not one but two or more discrete steps. Blinking behavior can be seen in multistep traces as well, because of the same IET and ISC processes, but here it is possible to distinguish between cases when the blinking of all the chromophores occurs in concert (Figure 3e and 3f) and those in which the chromophores show no blinking or blink independently of each other. This "coupling" can arise if a dimer undergoes IET, as both P^+ and P^- species are nonfluorescent. Alternatively, creation of a triplet state on one chromophore may effectively quench the fluorescence of the other chromophore via energy transfer, since the singlet emission should overlap the triplet absorption.[48] Even allowing for possible lengthening of dark triplet state lifetimes by this energy-transfer mechanism,[49] however, lifetimes longer than hundreds of milliseconds still cannot be accounted for by triplet states,[50] and virtually all off times in the traces showing coupled blinking are longer than this limit. Traces having two or more discrete steps were classified into "multistep coupled" and "multistep uncoupled" categories. A handful of traces showing extremely erratic behavior in addition to long off times (Figure 3g), because of either rapid, unresolved electron transfer or molecular dynamics within pockets in the film or at the interfaces, were classified into a "blinky" category and grouped with the multistep coupled traces in the analysis below.

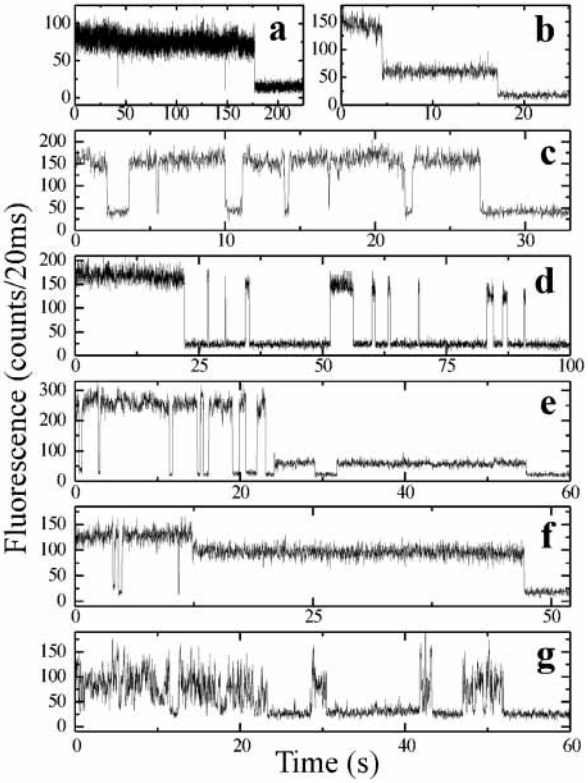

Figure 3. Characteristic single-molecule fluorescence traces. (a) Single step with triplet blinks from **M**; (b) multistep uncoupled from **M**; (c, d) single step with blinking from **D0**; **D**, from **D3**; (e) and (f) multistep coupled from **D3**; (g) rapid blinking from **D3**.

The results of this classification scheme are shown in Table 2 and plotted in Figure 4. Figure 4a shows the total percentage of all traces exhibiting evidence of long-lived CS states—long off times in single-step traces and coupled (long time scale) blinking in multistep traces—and shows that as expected these states are most common in **D0** and decreases across the series toward the baseline value of the monomers. Here again, the decrease is not uniform across the series but alternates in the same pattern that was observed in the solution measurements in MTHF (Figure 2), as discussed below.

Note (Figure 4b) that multistep traces are commonly observed both for dimers and monomers. In a monomer sample, they most likely arise when two or more molecules are within the excitation volume of the focused laser spot, too closely spaced to be resolved in the fluorescence image, perhaps loosely

TABLE 2: Statistics on Single-Molecule Traces from the Analysis of 131 Traces of D0, 100 of D1, 172 of D2, 141 of D3, 253 of M[a]

per 100 traces	D0	D1	D2	D3	M
multistep	68	58	63	55	42
coupled	56 (82%)	36 (62)	48 (76)	33 (60)	22 (53)
uncoupled	12 (18%)	22 (38)	15 (24)	22 (40)	20 (47)
single step	32	42	37	45	58
with blinking	26 (80%)	24 (57)	21 (56)	24 (53)	28 (48)
without blinking	6 (20%)	18 (43)	16 (44)	21 (47)	30 (52)
behavior indicating IET	82	60	69	57	50

[a] The subcategories with/without blinking and coupled/uncoupled show both the absolute percentage of traces that showed such behavior and the percentage within the overall category (single-step/multistep).

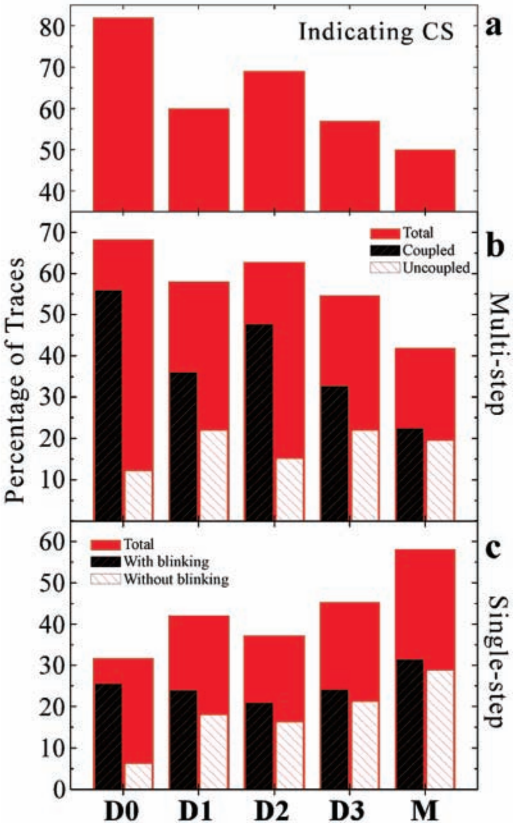

Figure 4. Histogram plot of total percentage of fluorescence traces. (a) Pecentage of traces showing behavior indicative of IET; (b) showing multistep behavior, broken down into coupled and uncoupled; (c) single-step behavior, broken down into with and without blinking.

associated by π-stacking or other van der Waals interactions. In this situation, the chromophores are not necessarily close enough or strongly coupled enough for the blinking behavior of one to influence the other, so only about half of the multistep traces show evidence of coupling for the monomers. In perylene dimers, however, there are of course always (at least) two chromophores in the excitation volume, so multistep traces are more common (Figure 4b). In addition, the chromophores are held a fixed distance apart and joined by conjugated phenylene linkers, so coupled behavior in these multistep traces is more common and increases up the series, from 60% for **D3** up to 82% of the multistep traces for **D0** (Figure 4b), once more in oscillating fashion. It is of course also possible that two dimer molecules could be found within the excitation volume of the laser spot, leading to traces with more than two discrete levels, but such traces are not common, presumably because dimers are sterically less likely to be associated in solution than are the monomers.

Monomers do show long time scale blinks in single-step (Figure 4c) and multistep traces (Figure 4b), perhaps resulting from electron-transfer processes to the polymer matrix or nearby molecules, which will no doubt be true for the dimers as well. However, the observation in the dimer series of additional evidence for CS, over and above that seen for the monomer, suggests than the appearance of additional long off times is due to IET as diagramed in Figure 1a, especially since this increase follows trends for IET rates that would be expected a priori and are observed in the bulk measurements (see below).

As expected, dimers show on average more multistep behavior than monomers, as there are always at least two chromophores in the excitation volume. However, dimers can show single-step behavior if photobleaching of one chromophore leads to efficient quenching of the fluorescence of the other, most likely by fast energy or electron transfer to a nonemissive state on the bleached chromophore, or if one chromophore has already been photobleached when the trace begins (during sample preparation or during the imaging process used to locate single molecules). The trend across the series of dimers is actually toward more single-step behavior for the dimers with larger separation (Figure 4c), but it is also found that the single-step traces tend to be of much shorter duration for the smaller dimers (single-step traces without blinking averaging, for **D0**−**D3**: 2, 8, 18, and 22 s and for **M** averaging 20 s). This shorter lifetime means that molecules of **D0** which would show single-step behavior are much more likely to be photobleached before they can be observed than are those of **D3**, and the resulting selection bias leads to the trend in the statistics toward more single-step behavior. Within those single-step traces that are observed, the percentage that show long time scale blinks attributed to CS states decreases as the length of the linker increases (Figure 4c). Adding the percentage of traces showing single step with blinking behavior to the percentage of traces showing multistep coupled behavior gives the total percentage of all single molecules observed which show evidence of the CS state, which shows the same pattern of decrease across the series (Figure 4a).

In all of these trends noted thus far, there is an oscillation superimposed on the overall trend up or down, with **D2** being an exception to the expected monotonic increase or decrease across the series. The reason for this oscillation is that, for many systems, achieving a “twisted” conformation where there is minimum overlap between the orbitals of the electron donor and acceptor is believed to be necessary for the formation of a stable CS state.[45,54] As the 3D sketches in Figure 1 show, the perylene moieties in **D0** and **D2** adopt this low-overlap conformation more naturally than in **D1** or **D3**, and so **D2** tends to show more evidence of the CS state than **D1**, bucking the trend that would otherwise be expected from considering distance effects alone. Note (Table 2) that this oscillation appears not only in the percentage of the total traces that show multistep and multistep coupled behavior but also in the percentage of the multistep traces that show coupled behavior (Figure 4b), a fundamentally independent measurement. The fact that this oscillation can be understood in terms of a well-known principle governing the formation of CS states further supports the attribution of the blinking to an IET mechanism. Significantly, the oscillation also occurs in $\Delta\Phi_F$ (Table 1, Figure 2), and since the reduction in quantum yield in more polar solvents has been shown to be related to IET rates, the observation of the same pattern here as in the blinking behavior also strongly suggests that electron transfer is the cause of the off times observed in the fluorescence traces. Theoretical studies are underway to calculate electronic coupling matrix elements for this family of dimers to corroborate this pattern of behavior and to provide greater insight into these geometrical effects on IET.

Conclusions

We have presented an approach to single-molecule spectroscopy that uses a statistical analysis of the single-molecule signals from a large number of individual molecules to follow low quantum yield processes, applied here to intramolecular electron transfer in perylene dimers. This method of cataloging and statistically analyzing traces allows us to glean a more complete picture of the behavior of the ensemble of molecules and provides insight into the interpretation of individual single-molecule traces. Though electron transfer has been studied in similar systems in solution, symmetric dimers in a polymer matrix show IET that is too slow relative to radiative decay to be followed using bulk techniques. Our methodology shows a clear dependence of IET on the separation of the chromophores and on their relative geometry; as expected, IET decreases with increased chromophore separation, but in addition we find that this decrease takes place in an oscillating pattern rather than monotonically, across the series, as it is also dependent upon the orientation of the chromophores. The same pattern of nonmonotonic decrease is seen both in multiple single-molecule measurements and in the bulk spectroscopy. Further analysis of these and similar data should allow us to calculate k_{et} and k_{bet} for individual molecules from the average on and off times in fluorescence traces. Future experiments will include application of these methods to IET in other donor-bridge-acceptor and molecular electronic systems, including asymmetric dimers and dimers with different bridges.

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Supporting Information Available: Synthesis and characterization of perylene dimers and monomers used in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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