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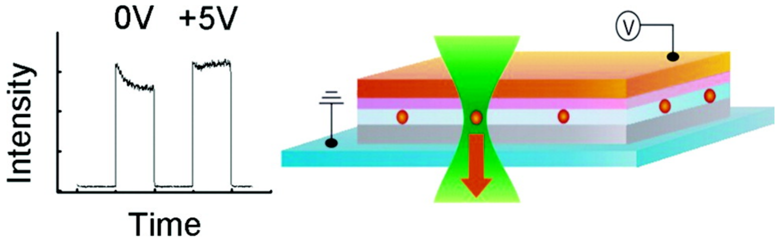

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Hole-Induced Quenching of Triplet and Singlet Excitons in Conjugated Polymers

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Abstract: Quantitative information on the mechanisms and rates of hole (radical cation)-induced quenching of triplet and singlet excitons in the conjugated polymer poly[2-methoxy-5-(2′-ethylhexyloxy)-*p*-phenylene vinylene] has been acquired by a new technique, fluorescence-voltage time-resolved single molecule spectroscopy (FV-TR-SMS). FV-TR-SMS measures the fluorescence intensity of a single conjugated polymer molecule that is embedded in a capacitor-like device while simultaneously modulating the bias on the device *and* the irradiation intensity. The results demonstrate that *triplet excitons* are efficiently quenched by holes in conjugated polymers for hole densities $>10^{16}$ charges/cm^3, while *singlet excitons* are quenched with a much lower efficiency. Detailed kinetic analysis shows that the greater efficiency for quenching of triplets by holes (compared to that for singlets) is due to a $>10^6$ times longer exciton lifetime for triplets. In fact, the results suggest that while singlet quenching is less efficient due to a much shorter singlet lifetime, the rate constant for the quenching of singlets by holes actually exceeds that for triplets by several orders of magnitude.

I. Introduction

There is a growing appreciation that dynamical processes involving the interaction of electronic excitations (excitons) with polarons (holes and electrons) can play an important role in the performance of polymer organic light-emitting diode (OLED) and related organic electronic devices. It has been shown, for example, that *singlet excitons can be quenched by holes*, leading to a reduction of the electroluminescence efficiency of a device.[1−3] An analogous process, *the quenching of triplet excitons* by holes, has received very little attention. Nevertheless, triplet excitons can be critical in optimal OLED device operation. In particular, it has recently been shown that triplet excitons can be "harvested" in OLEDs using triplet emitters (phosphors) to generate significantly higher electroluminescence efficiencies.[4−6] Triplets can also have a negative impact on device performance, since triplets can quench singlet excitons, reducing the luminescence yields, and triplets cause device degradation by sensitizing singlet oxygen formation from oxygen impurities that are present in the device.[7−10]

Measurements on the interaction of excitons and polarons in a conjugated polymer device environment are challenging due to the enormous morphological heterogeneity of conjugated polymer materials and the presence of a large number of different species in an operating OLED.[5,11−14] We have, however, recently shown that these complexities can be largely avoided by investigating the single molecule spectroscopy (SMS) of individual conjugated polymer chains as a function of device bias.[15,16] This approach, which is designated by the term fluorescence-voltage single molecule spectroscopy ($F-V$/SMS), is based on the quenching of the fluorescence intensity (singlet emission) of a conjugated polymer nanoparticle due to holes in the device.[17−19] In $F-V$/SMS the modulation of the fluorescence intensity $F(t)$ of isolated single molecules and nanoparticles is synchronously recorded while the device is subjected to a repetitive electrical bias, $V(t)$. The technique primarily probes singlet exciton−hole interactions. This is achieved by recording the single molecule fluorescence intensity

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as a function of device bias, which controls the population of holes. It is analogous in several ways to current vs voltage ($I-V$) measurements for devices and electrochemical cells. $F-V$/SMS data can be analyzed for different sweep rates to obtain information on both energetics and kinetics of charge-transfer (oxidation/reduction) processes of the isolated single molecules and nanoparticles. The $F-V$/SMS technique also offers a unique means for characterizing the chemical nature of poorly understood photochemically induced intermediate states of single molecules that are responsible for fluorescence "blinking". By studying the bias dependence of the SMS during the lifetime of the fluorescence "flickering" intermediate, information on the *oxidation/reduction properties* (e.g., HOMO energies) of the intermediate can be determined.

Herein we extend the $F-V$/SMS technique to allow for the investigation of triplet excitons by combining *electrical bias modulation* $V(t)$ with simultaneous optical *excitation intensity modulation* $I_E(t)$ on the microsecond time scale, where $I_E(t)$ signifies the time-dependent excitation intensity. Optical excitation modulation SMS has been shown to induce *triplet exciton population dynamics*, which in turn can be monitored indirectly by recording the fluorescence intensity dynamics.[20] The sensitivity of the fluorescence intensity on the triplet population in the polymer chain results from the quenching of singlet excitons by triplet excitons, which is surprisingly efficient.[20,21] Excitation intensity modulation SMS has been used to study triplet−triplet annihilation, reverse intersystem crossing, and other aspects of triplet excitons in conjugated polymer single chains with extraordinarily high signal-to-noise ratio and fast time resolution.

II. Experimental Section

A. Device Fabrication. The hole-only capacitor-like device is fabricated on top of an indium tin oxide (ITO)-coated cover glass by consecutive steps of electron beam evaporation of SiO_2, spin coating of poly(methyl methacrylate) (PMMA) and PMMA/MEH−PPV (poly-[2-methoxy-5-(2′-ethylhexyloxy)-*p*-phenylene vinylene]) layers, and thermal deposition of a TPD (*N*,*N*-bis(3-methylphenyl)-*N*,*N*-diphenylbenzidene)) hole-transporting layer and Au electrode. Further details have been described in ref 15.

B. Single Molecule Spectroscopy. The experimental apparatus is a home-built sample scanning confocal microscope. Emission was detected by an avalanche photodiode (APD) (Perkin-Elmer Optoelectronics SPCM-AQR-15). The transient signal $F(t)$ from the detector was recorded with a multichannel scalar (MCS) (FAST ComTec Gmbh, model MCA-3) that was synchronized to the sequence of excitation pulses. The sequence of excitation pulses $I_E(t)$ was derived from the output of an argon ion laser (514.5 nm) that was intensity modulated by an acoustic optical modulator (IntraAction Corp., model AOM-40). The input electronic waveform to the modulator was produced by a programmable function generator (Wavetek, model 29) that was synchronized to both the MCS and a second programmable function generator that provided the bias applied to the device.

III. Results and Discussion

Figure 1 shows FV-TR-SMS data obtained for a single MEH−PPV nanoparticle in contact with the hole-transporting layer (TPD) of a hole-injection, capacitor-like device structure.[15,16] The SMS data (Figure 1D) were recorded while *simultaneously* modulating the excitation intensity *and* stepping the applied bias (Figure 1B and C, respectively). The process was repeated for many cycles of the bias and excitation intensity pulse sequences, and the time-dependent fluorescence intensity $F(t)$ was synchronously time-averaged, to yield a higher signal-to-noise steady-state response of the nanoparticle, i.e., $F(t')$. The observed FV-TR-SMS data varied for different MEH−PPV molecules, as shown in Figure 2 for representative examples, but was constant over time for any individual molecule except after rare photo-oxidation events, which dramatically altered the FV-TR-SMS response (see below).

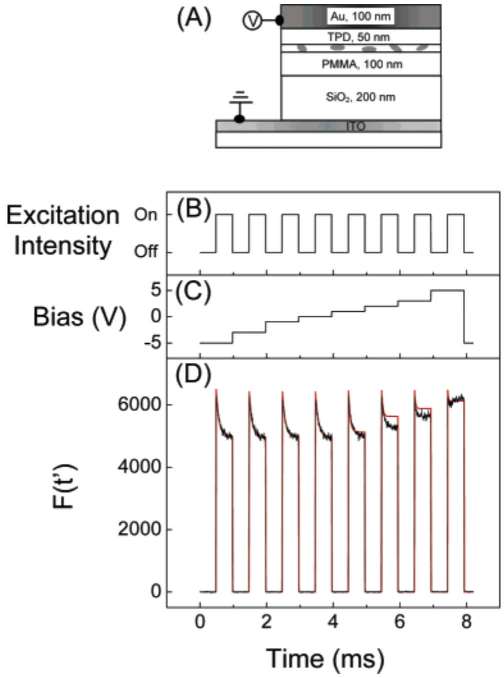

Figure 1. (A) Schematic representation of the hole injection capacitor-like device. (B) In each cycle the excitation intensity is modulated in eight steps of equal intensity (4.3 kW/cm^2). (C) For each of these excitation windows a *different* bias voltage is applied. This process is repeated over many of these cycles while the data are synchronously time-averaged. The resulting $F(t')$ is shown in panel D. The FV-TR-SMS data at positive bias show a shorter decay time and higher fluorescence "plateau" intensity compared to the data at negative bias. The red lines are fits to the kinetic model (see text).

The new results allow for an unprecedented unraveling of the complex interaction among singlet excitons, triplet excitons, and holes in conjugated polymers. At negative bias the observed $F(t')$ data for all molecules are *closely analogous* to those previously observed for MEH−PPV in an inert polymer host (polaron-free environment).[20] In particular, for each excitation pulse $F(t')$ exhibits an exponential decay to a "plateau" intensity resulting from a build-up of a steady-sate concentration of triplet excitons during the excitation pulse. The similarity of the results obtained with the negative-bias device environment to the previous inert polymer host measurements is consistent with the expectation that at negative bias the capacitor device is depleted of holes, and furthermore strongly suggests that MEH−PPV singlet and triplet excitons are not significantly perturbed by the device environment, in which MEH−PPV is in contact with the TPD hole-transport layer.

A very different situation exists for biases above 0 V, for which the FV-TR-SMS data show evidence of exciton−hole interactions. For example, above the threshold for hole injection (∼1 V) the FV-TR-SMS data reveal evidence of *triplet*

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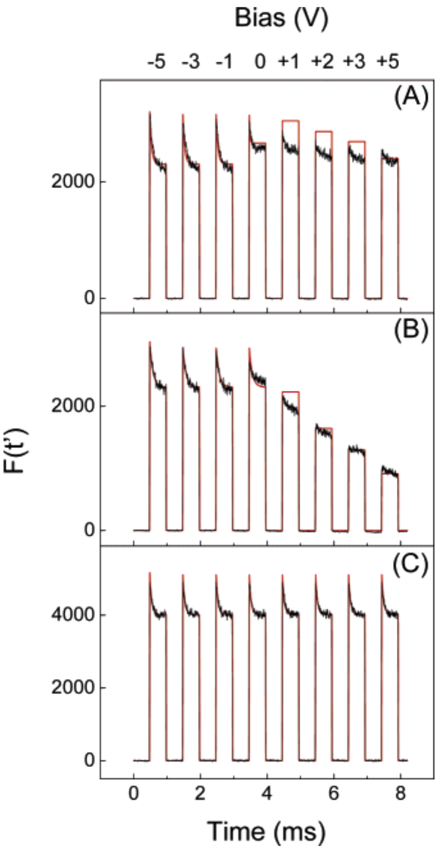

Figure 2. FV-TR-SMS data for the typical behaviors of MEH−PPV single molecules found in the hole injection capacitor-like devices. MEH−PPV molecules in oxygen-depleted (A,C) and oxygen-rich (B) devices are shown. These behaviors have been described in detail in refs 15 and 16. The red lines are fits to the kinetic model (see text). The data in panel A represent a molecule in an oxygen-depleted device, however, now with *both* triplet and singlet state quenching by holes. Excitation intensity, 2.9 kW/cm^2. (B) FV-TR-SMS data for a photo-oxidized molecule in an oxygen-rich device. At zero and positive bias a hole is effectively injected in the MEH−PPV molecule, and rapid triplet and singlet quenching occurs. Excitation intensity, 2.9 kW/cm^2. (C) This molecule is electrically disconnected from the TPD hole transporting layer. No triplet or singlet quenching by holes is observed. Excitation intensity, 4.3 kW/cm^2.

quenching by TPD holes, p^+,

$$p^+ + T_1 \xrightarrow{k_{QT}} p^+ + S_0 \tag{1}$$

which presumably occurs by a charge-transfer mechanism, perhaps also involving the intermediacy of a MEH−PPV hole. Associated with the hole-induced quenching of triplets, two effects are observed: (i) a more rapid decay of $F(t')$ is observed in each pulse time period due to a decrease in the triplet lifetime, and (ii) an increase in the fluorescence “plateau” intensity is observed due to a diminution of the steady-state triplet population due to triplet quenching. Both effects are in fact predicted by kinetics simulation (see below).

In addition to triplet quenching by holes (eq 1), evidence for singlet exciton quenching by TPD holes is also observed (eq 2).

$$p^+ + S_1 \xrightarrow{k_{QS}} p^+ + S_0 \tag{2}$$

Here the mechanism may involve spin-allowed energy transfer or charge transfer. For example, the molecules represented in Figure 2A and even more so in Figure 2B exhibit a large decrease in the fluorescence intensity (yield) with increasing bias, which we assign to singlet quenching by holes. For MEH−PPV the HOMO energy is lower than TPD, making hole injection from TPD to MEH−PPV unfavorable. The quenching process therefore involves MEH−PPV excitons but TPD holes.

While in principle it should be possible at sufficiently high positive bias ($V \gg 10$ V) to completely fill the TPD layer with holes and thereby completely quench singlets and triplets, in practice for biases above 10 V the device fails due to electrical breakdown.

An exception to this behavior occurs for photo-oxidized molecules, as shown in Figure 2B (discussed below). Photo-oxidation involves a charge-transfer process which “dopes” the nearby vicinity of a photo-oxidized MEH−PPV molecule with a negative ion. The negative ion raises the HOMO energy of the MEH−PPV molecule, allowing it to be directly oxidized by TPD holes. It should also be noted that a significant fraction (∼50%) of molecules show no effect of bias (Figure 2C). These molecules apparently have poor electrical contact with the hole-transport layer, which is a typical complication with devices fabricated by the procedure employed in these studies.

IV. Multichromophoric Photodynamic Model and Comparison to Experiment

It is informative to compare the observed FV-TR-SMS data to simulations using a recently described “population state” kinetic model for the photophysics of multichromophoric single molecules, which we modify herein to include hole−exciton interactions.[20,21] In this model the instantaneous state of a multichromophoric molecule is described by a “population state” (N_S,N_T), where N_S and N_T are the number of singlet and triplet excitons. It has been shown that conjugated polymer single molecules cycle between the (0,0) or (0,1) state at most times with short “visits” to short-lived states, such as (1,0) and (0,2). Correspondingly, the population kinetic scheme reduces to an approximate two-state model,

$$(0,0) \underset{k_B}{\overset{k_F}{\rightleftharpoons}} (0,1) \tag{3}$$

where

$$k_F = k_{exc}k_{isc}\tau_{fl} \tag{4}$$

$$k_B = k'_{isc} + k_{exc}k_{isc}\tau'_{fl} \tag{5}$$

$$k_{exc} = \sigma I_E(t')/h\nu \tag{6}$$

$$F(t') \approx k_{exc}P_{0,0}\tau_{fl} + k_{exc}P_{0,1}\tau'_{fl} \tag{7}$$

Here k_{exc} is the excitation rate, σ is the absorption cross section, $h\nu$ is the photon energy, k'_{isc} is the reverse intersystem crossing (ISC) rate, k_{isc} is the ISC rate, τ_{fl} is the fluorescence lifetime of the (1,0) state, and τ'_{fl} is the fluorescence lifetime of the (1,1) state. The lifetime of (1,1), i.e., τ'_{fl}, can be significantly shorter than τ_{fl} due to an additional relaxation process for (1,1), namely singlet quenching induced by a triplet exciton. $P_{0,0}$ and $P_{0,1}$ are the populations of the (0,0) and (0,1) states, respectively, which can be calculated from eqs 4−7 with the appropriate boundary conditions and $I_E(t')$.

Table 1. Best-Fit Kinetic Parameters for the MEH−PPV Molecules Shown in Figures 1 and 2[a]

Figure	σ (cm^2)	k'_{isc} (s^{-1})	k_{QST} (s^{-1})	k_{QT} (M^{-1} s^{-1})	k_{QS} (M^{-1} s^{-1})	E_{QT} (%)[d]	E_{QS} (%)[e]
1	1.7×10^{-17}	6.0×10^{3}	7.0×10^{9}	1.1×10^{7}	$[3.0 \times 10^{6}]^{c}$	100	0
2A	3.8×10^{-17}	6.0×10^{3}	5.3×10^{9}	1.1×10^{9}	1.6×10^{11}	100	24
2B	1.9×10^{-17}	4.0×10^{3}	4.3×10^{9}	1.1×10^{9}	1.1×10^{12}	100	70
2C	3.3×10^{-17}	6.0×10^{3}	3.8×10^{9}	*b*	*b*	0	0

[a] In the fitting procedures a quantum yield of intersystem crossing of 1.25% was used for MEH−PPV.[22] [b] No holes are interacting with the molecule, so no rate constant is reported. [c] This value is an upper limit for k_{QS}. [d] Defined as $(F(\text{plateau})_{V=5\text{V}} - F(\text{plateau})_{V<V_0})/(F(\text{initial}) - F(\text{plateau}))_{V<V_0}$ in the case of triplet quenching only (Figure 1). When singlet quenching is observed, the triplet quenching efficiency is 100%. [e] Defined as $(F(\text{initial})_{V<V_0} - F(\text{initial})_{V=5\text{V}})/F(\text{initial})_{V<V_0}$.

In this model, the effect of singlet quenching by triplets is quantified by the rate constant for singlet quenching by a triplet in a single molecule (k_{QST}):

$$k_{QST} = \frac{1}{\tau'_{fl}} - \frac{1}{\tau_{fl}} \tag{8}$$

The two-state model can be modified to include hole-induced quenching of triplet excitons by adding a third term on the right-hand side of eq 5,

$$k_B = k'_{isc} + k_{exc}k_{isc}\tau'_{fl} + k_{QT}[p^+] \tag{9}$$

where k_{QT} is the second-order rate constant for hole-induced quenching of triplet excitons and $[p^+]$ is the concentration of holes in the TPD hole transport layer. We have recently shown that in a hole-only capacitor device, the hole density should be approximately given by the relationship[15]

$$[p^+] \cong s(V - V_0) \tag{10}$$

where V is the applied bias, V_0 is the threshold bias, and s is a constant that depends on the dimensions of the various layers of the device.

Quenching of singlet excitons by holes is also accounted for, as follows,

$$1/\tau_{fl,QS} = 1/\tau_{fl} + k_{QS}[p^+] \tag{11}$$

$$1/\tau'_{fl,QS} = 1/\tau'_{fl} + k_{QS}[p^+] \tag{12}$$

where $\tau'_{fl,QS}$ and $\tau'_{fl,QS}$ are the lifetimes of the singlet exciton states (1,0) and (1,1), in the presence of TPD holes and in the presence of both triplet excitons and TPD holes, respectively.

Figures 1 and 2 show a comparison between best-fit simulations (red lines) of the experimental FV-TR-SMS data (black lines) and the data itself. The parameters for the fitting process are summarized in Table 1, with error estimates indicated by the significant numbers of the reported values. The data are well-fit by the kinetic model with the exception of the slowly varying intensity changes during each pulse region at positive bias ($V > V_0$). We assign the slowly varying intensity changes to a non-instantaneous response of the local quasi-Fermi potential in the device due to the filling of deep hole traps in the hole transporting layer of the device.[23,24] The non-hole-related photophysical parameters were determined by fitting the model to the negative bias FV-TR-SMS results using a previously determined mean value for k'_{isc}.[20] The parameters for hole-induced quenching were determined by fixing the non-hole-related parameters and adjusting V_0, k_{QS}, and k_{QT} in order to best-fit the simulated data to experiment. Obviously, the hole-related parameters vary significantly from molecule to molecule in the device as shown in Table 1. The value in brackets represents the upper limit, which applies to situations where no detectable quenching effect was observed. For the molecule in Figure 1D, the hole quenching effect can be well accounted for by the quenching of triplet excitons exclusively. In contrast, for the molecules portrayed in Figure 2A,B, both singlet quenching and triplet quenching play an important role. For the molecule in Figure 2C, no hole-induced quenching process is required to account for the experimental results.

Molecules in the device of the type shown in Figure 2B show extremely efficient hole-induced quenching and correspondingly much greater quenching rate constants. It has previously been shown that MEH−PPV molecules that are highly susceptible to quenching by holes should be assigned to an MEH−PPV/anion complex, which is formed via photoinduced electron transfer (i.e., photo-oxidation) from MEH−PPV to trace oxygen impurities. This photo-oxidation process shifts the HOMO energy of MEH−PPV toward the vacuum level, making hole injection from the TPD layer into the MEH−PPV nanoparticle energetically favorable and allowing for hole exchange between the nanoparticle/anion complex and TPD. This should increase the rates of singlet and triplet quenching by holes.[15,16] Molecules of this type are more plentiful in older devices which have been stored in ambient conditions, allowing oxygen to penetrate the device.

It should be noted that the described effects vary greatly in magnitude from molecule to molecule (charge/energy transfer rate constants, hole densities), revealing the high degree of heterogeneity and complexity at the nanoparticle/hole transport layer interface.

Perhaps the most significant result from this study is the observation that triplet excitons are much more efficiently quenched than singlet excitons. This is summarized in Table 1, where the efficiency of triplet and singlet quenching by holes, E_{QT} and E_{QS}, is shown for $V(t) = 5$ V for the various molecules. The more efficient quenching of triplets is due to a factor of 10^6 greater lifetime for the triplet exciton compared to that of the singlet exciton. The more efficient quenching of triplets occurs despite the fact that the triplet quenching rate constant k_{QT} is in fact several orders of magnitude slower than that for singlets (k_{QS}). This result suggests that singlet and triplet quenching by holes may occur by different mechanisms. The singlet quenching process can in principle occur by a spin-

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allowed energy-transfer process, analogous to that reported for the quenching of singlet excitons by triplet excitons, which has a rate constant k_{ST} of $\sim 10^{10}$ s^{-1}.[21] This process is spin-forbidden for triplet excitons, and instead a much slower charge-transfer mechanism may be operating for triplets. The proposed charge-transfer processes involves two steps. In the first step, the excited triplet state is quenched by single electron transfer to a hole in the TPD layer, neutralizing the hole site and positively charging the MEH−PPV single molecule. In the second step, the MEH−PPV hole is transferred from MEH−PPV to the TPD layer.

V. Conclusions and Summary

The presented data show that FV-TR-SMS can measure charge/energy transfer rates for both triplet and singlet excitons on a particle-by-particle basis in a functioning device. Due to the nanoscale complexity of the layers and interfaces in the device, these charge/energy transfer rates can vary by several orders of magnitude, emphasizing the need for single molecule methods in device study and optimization. A key result in this paper is the finding of highly efficient quenching of triplets excitons by holes compared to hole-induced quenching of singlet excitons, despite the fact that the triplet quenching rate constant k_{QT} is in fact several orders of magnitude slower than k_{QS} for singlets. This result suggests that singlet and triplet quenching by holes may occur by different mechanisms, i.e., energy transfer vs charge transfer, respectively.

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