

Electric field effect on energy transfer monitored by bimolecular annihilation

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In conjugated polymers excited singlet states are known to dissociate into polarons upon application of an electric field. We show that for excitation intensities exceeding $100 \mu\text{J cm}^{-2}$ in polyfluorene, this is not the only mechanism of field-induced decrease in the singlet population. Bimolecular annihilation is enhanced via increased overlap between singlet emission and absorption spectra due to Stark effect. We discuss the implications for Förster resonant energy transfer.

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I. INTRODUCTION

Förster resonant energy transfer (FRET) is a powerful tool to study molecular dynamics.¹ It consists in the transfer of excitation energy from a fluorescent molecule or polymer segment to an absorbing molecule/segment via dipole-dipole coupling. It is typically studied by blending a small concentration of a guest chromophore into a host matrix. In fluorescent conjugated polymers^{2,3} (CPs) energy transfer (ET) has been vastly studied, blending them with organic dyes, semiconductor quantum dots, or other CPs as guest absorbers,⁴⁻⁷ or sandwiching them with semiconductor quantum wells.⁸ However, the absorber can also be another strand of the same CP or another segment of the same strand. This way ET occurs also in pure CP samples. In the most typical case the absorber is in its electronic ground state S_0 , the emitter in its first excited state S_1 , and the excitation energy is transferred from one polymer strand/segment to another,



Yet, the absorber can also be in an excited state already. If the emission S_1-S_0 has a spectral overlap with an excited state absorption S_1-S_n , this process will bring one polymer segment to its ground state and the other to a higher excited state, from where it relaxes back to S_1 on a time scale <100 fs,⁹



This process is called bimolecular annihilation and is just another manifestation of ET, which is observed if a sizeable fraction of the chromophores are excited, i.e., at excitation intensities above $100 \mu\text{J cm}^{-2}$, as they are reached in fs pump-probe experiments or in CP lasers.

The efficiency of ET depends critically on the spectral overlap between donor emission and acceptor absorption. This overlap can be manipulated via an electric field if donor emission and acceptor absorption shift by different amounts in response to the field.⁷ Therefore, electric manipulation of ET should be observed in guest-host systems, as well as in bimolecular S_1 annihilation. Femtosecond pump-probe stud-

ies in combination with a modulated electric field generally show a rather weak signal, therefore, one has to work in a high-excitation density regime, where bimolecular S_1 annihilation naturally occurs. Hence, in a blend system one would observe an effect on both the guest-host transfer and the annihilation, which then need to be carefully untangled. For this reason we chose to work on a pure material, where we expect to see only the effect on annihilation.

We chose polyfluorene (PF), which is one of the best characterized CPs.¹⁰⁻²⁵ The photoexcitation dynamics is monitored via fs pump-probe spectroscopy in the presence of a modulated electric field. Besides S_1 dissociation into polarons,²⁶⁻²⁹ we find an increase in the S_1 bimolecular recombination rate due to Stark effect.

II. EXPERIMENT

In fs pump-probe spectroscopy the sample is excited with a pump pulse, and the relative change $\Delta T/T$ in its optical transmission is measured with a probe pulse at a defined delay t . $\Delta T/T$ is proportional to the sample thickness, the effective absorption/emission cross sections σ_i of the states i , and the pump-induced change ΔN_i in their population,³⁰

$$\frac{\Delta T(E,t)}{T} = - \sum_i \sigma_i(E) \Delta N_i(t) d. \quad (3)$$

Field-induced changes in $\Delta T/T$, defined as $\Delta^2 T/T = (\Delta T/T)_F - (\Delta T/T)_{F=0}$ are

$$\begin{aligned} \frac{\Delta^2 T}{T} &= \sum_i \Delta(\sigma_i(E) \Delta N_i(t) d) \\ &= - \sum_i \Delta\sigma_i(E) \Delta N_i(t) d - \sum_i \sigma_i(E) \Delta^2 N_i(t) d. \end{aligned} \quad (4)$$

The first term describes changes in the cross section of the involved transitions due to Stark effect. The second term regards field-induced changes in the population. The square differential accounts for the two perturbation factors acting on the sample, the pump beam and the electric field.

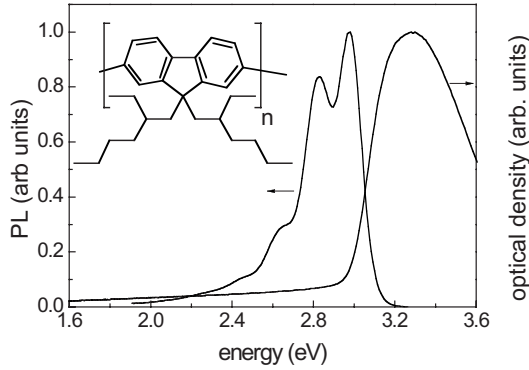


FIG. 1. Absorption and photoluminescence spectra of PF. Inset shows chemical structure.

The chemical structure of the used PF variety, together with its fluorescence and ground state absorption, is depicted in Fig. 1 (top). The well-resolved vibronic structure of the fluorescence is obscured in absorption due to the highly anharmonic potential for ring librational modes.³¹ PF films of 100 nm thickness are sandwiched between Al and a transparent indium-tin-oxide electrode coated with Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate). Details about these devices can be found in previous work.^{32,33} The details about the fs pump-probe setup and the field-modulation technique are described in Ref. 30. The devices are biased only in reverse order to avoid charge injection and degradation. The field is modulated between 0 and 1.5×10^6 V cm⁻¹ at 420 Hz, and the lock-in amplifier is referenced to this modulation.

III. RESULTS

The $\Delta T/T$ spectrum of PF is shown in Fig. 2. The shape of the spectrum changes very little with time, indicating that it is largely dominated by one electronic state. The positive signal above 2.4 eV can be attributed to a combination of photobleaching (PB) due to depletion of the S_0 absorption and to stimulated emission from S_1 .^{13,15} Hence, the negative

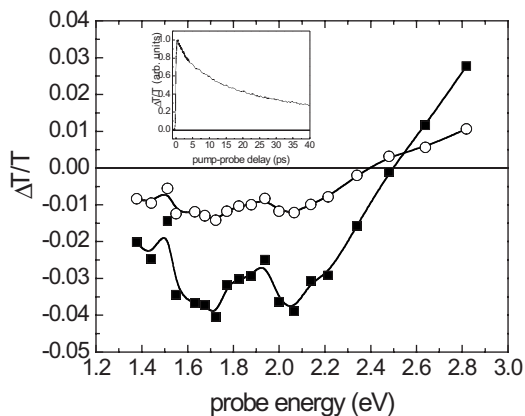


FIG. 2. Pump-probe spectra at 2 (squares) and 30 ps (open circles) pump-probe delay. Solid lines are a guide to the eye (cubic B splines interpolated by ORIGIN™ 7.5). Inset shows temporal evolution at 1.8 eV.

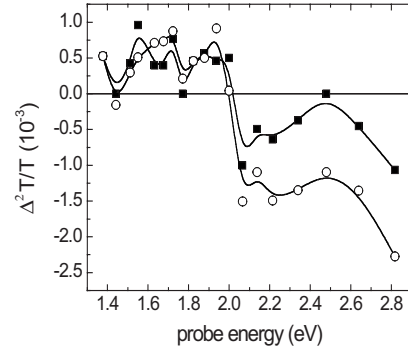


FIG. 3. Field-modulated pump-probe spectra at 2 (squares) and 30 ps (open circles) pump-probe delay. Solid lines are a guide to the eye.

signal is ascribed to absorption from S_1 to higher singlet states. The redshift of the zero-crossing point at 30 ps compared to 2 ps hints to a small contribution by polarons, which absorb in the region 1.9–2.5 eV.³⁴

The simplest model that correctly describes the temporal behavior of S_1 (indicated by the representative time trace shown as inset) assumes a combination of monomolecular S_1 (rate parameter k_1) recombination and bimolecular annihilation of two S_1 states (rate parameter γ_1),

$$\frac{dS_1}{dt} = G(t)S_0 - k_1S_1 - \gamma_1S_1^2, \quad (5)$$

where $G(t)S_0$ is the generation of S_1 via excitation of S_0 by the laser pulse $\sim G(t)$.

The field-modulated pump-probe spectrum $\Delta^2 T/T$ is depicted in Fig. 3. $\Delta^2 T/T$ and $\Delta T/T$ have opposite signs except in the region from 2.0 to 2.5 eV. This confirms that the S_1 population is reduced in the presence of an electric field, and polarons are formed.^{26–29} Equation (5) thus becomes

$$\frac{dS_{1F}}{dt} = G(t)S_{0F} - k_1S_{1F} - \gamma_1S_{1F}^2 - \gamma_2(t)S_{1F},$$

$$\frac{dP}{dt} = 2\gamma_d(t)S_{1F}, \quad (6)$$

where we assume that the polarons do not decay on the observed time scale. The time-dependent dissociation parameter $\gamma_d(t)$ describes the field-induced dissociation of S_1 into polarons; the parameter $\gamma_2(t)$ describes the field-induced reduction of S_1 , regardless of the mechanism. In previous works it has been assumed that $\gamma_2(t) = \gamma_d(t)$. Here this is not the case.

IV. DISCUSSION

In previous works $\gamma_2(t)$ has been obtained from the measured time traces via Eq. (4), which involves deriving noisy $\Delta^2 T/T$ curves and subtracting them from each other. We prefer to work with smoother curves and use populations rather than rates and directly fit the time dependence of $\gamma_2(t)$ and $\gamma_d(t)$. The total number ΔS_1 of S_1 states destroyed by the electric field after a time t is given by

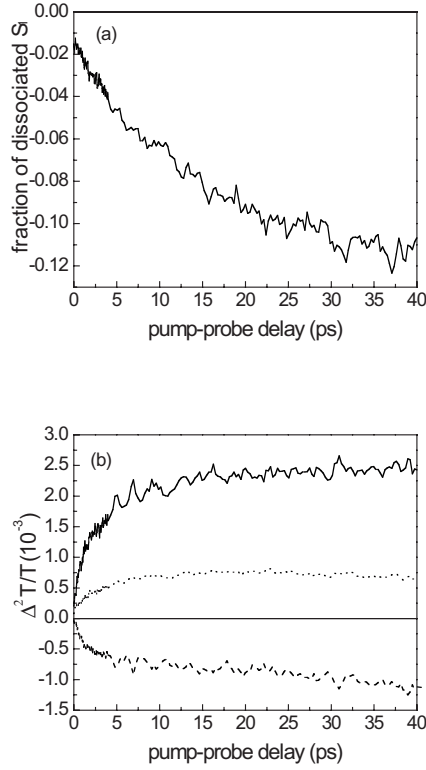


FIG. 4. (a) Ratio of field-modulated and pump-probe time traces at 1.5 eV; (b) field-modulated pump-probe traces at 1.5 eV (dot) and 2.1 eV (dash), polaron contribution to the trace at 2.1 eV (solid).

$$\begin{aligned} \Delta S_1(t) &= \int_0^t \gamma_2(t) S_{1F} d\tau \approx \left[1 - \frac{S_{1F}(t)}{S_1(t)} \right] \int_0^t G(t) S_{0F} d\tau \\ &= \frac{\Delta^2 T/T(t)}{\Delta T/T(t)} \int_0^t G(t) S_{0F} d\tau, \end{aligned} \quad (7)$$

where the $\Delta^2 T/T$ and $\Delta T/T$ signals are taken at a wavelength where one observes only S_1 . At such a wavelength ΔS_1 is therefore proportional to the ratio of $\Delta^2 T/T$ and $\Delta T/T$. The total number of polarons created is equal to the number of polarons present, since no fast decay is assumed.³⁴ Its temporal evolution can be extracted from a $\Delta^2 T/T$ trace in the region 1.9–2.5 eV by subtracting the S_1 contribution from this trace,

$$P \propto \left(\frac{\Delta^2 T}{T} \right)_2 - \frac{\sigma_2}{\sigma_1} \left(\frac{\Delta^2 T}{T} \right)_1, \quad (8)$$

where σ_i are the S_1 cross sections and the indices 2 and 1 denote wavelengths with and without polaron contributions, respectively. The ratio σ_2/σ_1 is obtained from the $\Delta T/T$ spectrum.

The absolute slope of $\Delta S_1(t)$ decreases slightly with time, but after 40 ps a strong field-induced S_1 decrease is still active [Fig. 4(a)]. The polaron time trace initially resembles the one for $\Delta S_1(t)$ [Fig. 4(b)], but after 15 ps the generation of polarons is almost over. This clearly shows that the dissociation of S_1 is not the only process that decreases their number upon electric field; hence,

$$\gamma_2(t) = \gamma_d(t) + \gamma_q(t), \quad (9)$$

with $\gamma_q(t)$ describing the additional S_1 quenching process. In order to explore the nature of this process we fitted $\gamma_d(t)$ and $\gamma_q(t)$ (see discussion below) and calculated the spectra of all involved states via Eqs. (1) and (2), as described in Ref. 35 (not shown). We initially assumed that $\gamma_q(t)$ generates a new state X and found its spectrum to be identical to that of the ground state S_0 . Hence $\gamma_q(t)$ describes a field-induced quenching of S_1 into S_0 .

From Figs. 4(a) and 4(b) it is clear that both $\gamma_d(t)$ and $\gamma_q(t)$ decrease with time. The simplest fit is an exponential decrease in $\gamma_d(t)$, which satisfactorily reproduces the data with a time constant of 3 ps. This is consistent with what has been found for the very similar material *m*-LPPP at comparable excitation densities,²⁶ while at lower excitation densities a slower decay has been observed.²⁷ The quenching parameter $\gamma_q(t)$ follows the S_1 population and can hence be written as $\gamma_q(t) = \gamma_0 S_{1F}(t)$. Thus the first Eq. (6) becomes

$$\frac{dS_{1F}}{dt} = G(t)S_{0F} - k_1 S_{1F} - \gamma_1 S_{1F}^2 - \gamma_d(t)S_{1F} - \gamma_0 S_{1F} S_{1F}. \quad (10)$$

The last term is proportional to S_{1F}^2 and can formally be united with the annihilation term

$$\gamma_{1F} = \gamma_1 + \gamma_0,$$

$$\frac{dS_{1F}}{dt} = G(t)S_{0F} - k_1 S_{1F} - \gamma_{1F} S_{1F}^2 - \gamma(t)S_{1F}. \quad (11)$$

This means that the bimolecular annihilation appears faster in the presence of an electric field either because the additional process has the same temporal behavior or because the field actually increases the efficiency of the annihilation. The second possibility finds a straightforward explanation: control of Förster transfer via Stark effect.⁷

Bimolecular annihilation of S_1 is actually a Förster transfer, where one S_1 state acts as donor and the other as acceptor [see Eq. (1)]. The efficiency of this process depends on the overlap between the donor emission and acceptor absorption spectra. The observation of S_1 annihilation confirms that such an overlap exists, i.e., that in some region of the $\Delta T/T$ spectrum, there are actually two competing contributions from S_1 , emission and absorption. The exact shape of these two contributions is not accessible. However, the emission (S_1 - S_0 transition) spectrum should reasonably resemble the fluorescence spectrum in Fig. 1. Therefore, in the range from 2.3 eV up to at least 2.5 eV, both emission and absorption from S_1 must contribute to the $\Delta T/T$ signal.

Just like energy transfer in guest-host systems,⁶ bimolecular annihilation is generally a multistep process, where excitation energy migrates within the host matrix until it comes sufficiently close to a guest molecule (in our case, another S_1 state) to transfer. The electric field can enhance either the intrahost migration or the final annihilation step, or both, depending on which spectral overlap can be increased. In the case of migration, both the emitting and the absorbing transition are between the ground state S_0 and the first excited

state S_1 . However, the absorption S_0 - S_1 involves a larger polymer segment than the emission S_1 - S_0 .³⁶ Therefore, the difference in polarizability should be larger for absorption than for emission. This means that the field-induced redshift of the emission is lower than that of the absorption, which increases their overlap. In the actual annihilation step, as discussed above, the absorbing transition is S_1 - S_n . We do not know how strong it is affected by the field as an EA signal of an excited state transition has been observed only recently in PF containing a controlled amount of fluorenone defects that harvest the excitation energy.³⁵ Therefore, both the intrahost migration, as well as the final annihilation step, can possibly be influenced by the electric field; with the present data we cannot decide in which proportions.

V. CONCLUSION

We showed that dissociation of S_1 states into polarons is not the only field-induced process in PF. While it is dominant at short pump-probe delays, its efficiency decreases fast, and the second quenching process becomes more important. We identify this process as an enhanced S_1 bimolecular annihilation due to increased overlap of S_1 absorption and emission caused by Stark effect.

The electric field gives us some control over the bimolecular S_1 annihilation. This has two types of implications. The first one is in the role it plays in emissive device applications. S_1 annihilation is a nonradiative process that activates at high excitation densities and lowers the fluorescence quantum yield. This process is somewhat enhanced by an electric field. Although this is not an issue for typical organic

light-emitting diode operation conditions, it will be at the high excitation densities, necessary for electrical injection lasing and may be a design issue there.

The other implication is in the physical nature of the annihilation process. Since it is a Förster type transfer of excitation energy, our findings imply that energy transfer can be controlled via an electric field. On the single-molecule level, it has been shown that an electric field can efficiently act as a FRET gate.⁷ This is rooted in the much narrower linewidth of single molecules, which warrants an efficient turn on and off of FRET. The ensemble linewidth is much larger, so that there are always donor-acceptor couples, which cannot be completely switched off, or which turn on as others are switched off by a change in the electric field. However, our findings show that the field still provides some control over the efficiency of the process even in the bulk, which gives the scope for a device in which the energy transfer rate can be controlled or at least fine tuned via an electric field.

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