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Electric-field-induced singlet and triplet exciton quenching in films of the conjugated polymer polyspirobifluorene

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An experimental investigation into the low-temperature electric-field-induced quenching of the transient triplet absorption and the prompt and delayed fluorescence of the conjugated polymer polyspirobifluorene is presented. A maximal instantaneous triplet exciton quenching of about 25% is observed for an electric field of 2.5×10^6 V/cm. The fluorescence intensity under such conditions is quenched by 97%, which, to our knowledge, is the highest value ever reported for a conjugated polymer. A comparison of the absolute singlet and triplet exciton quenching yields a singlet exciton binding energy of approximately 0.38 eV. The delayed fluorescence in the above polymer is known to be caused by bimolecular triplet annihilation, which has been further substantiated using electric-field quenching experiments. Further, earlier experiments, which seem to verify the geminate pair origin for the delayed fluorescence of the laddertype polymer poly(para-phenylene) (MeLPPP), are discussed and re-evaluated using the above polyfluorene derivative.

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INTRODUCTION

The generation of charge carriers after optical excitation is the key parameter for efficient solar cells and light detectors based on conjugated polymers. Furthermore, a thorough understanding of the dissociation mechanism will almost certainly yield information about the reverse process, charge-carrier recombination, and as such the design rules for an advanced generation of electroluminescent polymer light emitting diodes.

Albeit not completely settled, a consensus has emerged regarding the general mechanism of photogeneration of charge carriers in conjugated polymers. Several independent studies have come to the conclusion that strong electric fields dissociate the relaxed singlet exciton.[1–4] Here, the electric field is a necessary requirement, probably in conjunction with the intrinsic energetic disorder, to overcome the singlet exciton binding energy. Apart from such direct singlet dissociation, depending on the experimental conditions, several further generation pathways may be operative as well. For example, high-excitation doses leading to fast bimolecular singlet annihilation[2,5,6] or a substantial excess energy[1] may further increase the charge-carrier generation probability.

In contrast to the vast number of studies on the singlet exciton, very little is known about electric-field-induced triplet exciton dissociation. Of course the main reason for this is that the triplet eludes simple observation, unlike the fluorescence for the singlet exciton, but requires time-resolved and sensitive detection techniques in combination with a low temperature. Under these conditions, Sinha *et al.* studied the phosphorescence of a polyfluorene derivative under weak electric bias fields.[7] The observed quenching of the delayed emission was attributed to triplet exciton-polaron quenching. The phosphorescence observed in methyl-substituted poly-para-phenylene (MeLPPP) has been investigated under strong electric-field conditions by Schweitzer *et al.*[8] Although these authors claim the opposite, the presented data clearly show an approximately 20% quenching of the phosphorescence intensity.

Intimately linked with the phosphorescence quenching, as well as the singlet exciton dissociation, is the question of the origin of the commonly observed delayed fluorescence, i.e., triplet-triplet annihilation versus geminate pair recombination. Here it is generally assumed that the dissociation process of a singlet exciton into free charge carriers is a sequential process, which initially leads to the formation of a metastable Coulombically bound pair of charge carriers.[8–11] This assumption is mainly based on luminescence studies under applied electric fields using MeLPPP, where a spike in the delayed fluorescence intensity accompanies the switchoff of a strong electric field in the microsecond time domain after pulsed excitation.[12] This observation was interpreted in terms of field-stabilized geminate pairs, which, again, collapse into singlet excitons once the external field is turned off. Interestingly, in this material delayed fluorescence is also observed in the absence of any stimulating electric field during excitation.[13,14] This zero-field delayed fluorescence is as well significantly quenched by applying a (delayed) electric field, which was interpreted as a signature of the geminate-pair-recombination mechanism.

Until now, similar electric-field quenching experiments on polyfluorene derivatives have not been performed, although these should be interesting because the delayed fluorescence in these materials originates from triplet-triplet annihilation rather than geminate-pair recombination.[7,15,16] One would expect that the different origin of the delayed fluorescence is also reflected in the electric-field dependence. Thus, here we study the influence of electric fields on the "delayed" singlet excitons using time-resolved spectroscopy and compare the results with both the prompt fluorescence and the transient triplet-absorption quenching under the same applied electric fields. The combined analysis shows an agreement only with the bimolecular triplet-annihilation framework, but interestingly, the strength of the observed quenching effects can also account for the earlier experiments on MeLPPP.

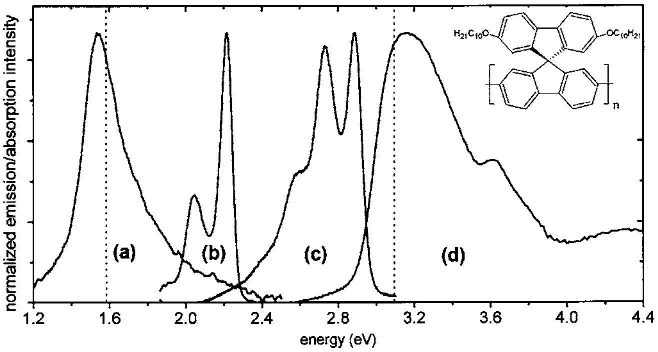

FIG. 1. These graphs show the transient triplet absorption (a), phosphorescence (b), prompt fluorescence (c), and absorption spectra (d) of the polyspirobifluorene under investigation, see inset for chemical structure. The dashed lines indicate the excitation and the transient absorption probe energies, respectively.

EXPERIMENTAL

Throughout, we used common electroluminescent devices based on the blue emitting polyfluorene derivative polyspirobifluorene [(PSF) see inset of Fig. 1 for chemical structure] as the active layer. Such spiro materials are especially suited for studies on the photophysics of conjugated polymers as they are chemically inert against backbone oxidation.[17] Therefore, we investigate pure conjugated polymer effects and avoid any influences of keto defects, which have derogated a significant number of recent publications. The fabrication of the permanently sealed devices has been described elsewhere.[18]

A continuous wave 400 nm laser diode module, featuring a turnoff time shorter than 5 ns, was employed to optically excite the polymer close to the absorption edge (compare Fig. 1), thereby avoiding large excess energies, which may lead to hot charge-carrier formation.[1] Furthermore, our highest excitation density, 30 $\mathrm{mW/cm^2}$, is orders of magnitude below the singlet-singlet-annihilation threshold, which excludes this potential source of charge-carrier generation as well.[6] In order to avoid electroluminescence, all electric fields were applied in reverse bias mode using a 100 W pulsed current source. All experiments (apart from the absorption spectra shown in Fig. 1) were performed at 20 K using an optically and electrically accessible closed cycle helium cryostat.

The total triplet exciton density was probed close to the maximum of its corresponding transient absorption spectrum using a 785 nm laser diode module (compare Fig. 1). This probe beam was focused onto the active area of the device, reflected by the Ba/Al cathode, passed through an appropriate cutoff filter to reject any sample emission, detected by a Si photodiode combined with a 200 MHz transimpedance amplifier and monitored by a 1 GHz oscilloscope. A digital delay generator was used to bring the variable optical excitation pulse and the variable electrical-field pulse in any desired temporal order to each other. The experiment was repeated with a frequency of 0.2 Hz in order to allow for a sufficient triplet decay between the subsequent excitation pulses [triplet lifetime at 20 K ~ 1 s (Ref. 15)] and at least 100 excitation pulses were accumulated for one dataset. In doing so, changes in the transient absorption ($\Delta T/T$) of 10^{-4} with a temporal resolution of 10 ns could be measured. However, the time to apply an electric pulse is limited by the (voltage-dependent) RC time constant of the device (at 20 K for 2×10^6 V/cm $\tau_{RC}\sim 50$ ns).

Finally, the delayed fluorescence has been probed using a fast and sensitive setup based on a gated charge-coupled device (CCD) camera that monitors the spectrally dispersed sample emission as a function of time. Details for this setup are given elsewhere.[19]

RESULTS AND DISCUSSION

Figure 1 shows several basic spectra of the polymer under investigation including transient absorption ($T_1\rightarrow T_n$), (electro-) phosphorescence ($T_1\rightarrow S_0$), prompt (electro-) fluorescence ($S_1\rightarrow S_0$), and absorption ($S_1\leftarrow S_0$). All data are consistent in spectral shape and energetic position with other polyfluorene derivatives and earlier investigations on polyspirobifluorene, respectively.[7,15,16,19–21]

First the influence of an applied electric field on the triplet exciton was investigated. After optical excitation, triplets in conjugated polymers are formed due to inter-system-crossing (ISC) in a sequential process from the initially excited singlet excitons; with an efficiency for PSF of 6.0%.[22] In order to avoid mutual effects due to electric-field quenching of the parent singlet excitons, the triplets were probed *after* all singlet excitons had naturally decayed. Of course, such experiments are only possible if the triplet lifetime is sufficiently long, which is why the measurements are performed at low temperature (20 K). Under such conditions the triplet lifetimes of conjugated polymers are typically of the order of one second.[16,19,21] Then, both the triplet emission and the transient absorption are available as tools to probe the triplet exciton. However, since the time resolution of the phosphorescence detection is only about 10 ms, and these measurements are made pointwise, i.e., they are time consuming,[19] for the present purpose probing the transient triplet absorption is deemed the superior method.

Four typical transients of the triplet absorption, during and after excitation of the singlet manifold at 400 nm, are shown in Fig. 2. Common for all these data sets is the triplet accumulation during the initial photoexcitation pulse, which was chosen to be 600 μs. Here, the initially linear rise of the triplet density becomes limited by bimolecular triplet annihilation, which eventually leads to a saturation of the triplet density. This triplet accumulation in the framework of annihilation will be discussed in detail in a forthcoming publication. For the moment, attention is focused on the triplet decay *after* photoexcitation. Considering the radiative triplet lifetime of polyfluorene, ~1 s, the rapid, nonexponential decline of the triplet density (~80% in 1 ms) in the absence of any electric field is almost exclusively caused by triplet annihilation. Once an electric field is applied then the remaining triplet population rapidly (by about 50% in 50 μs) decreases even faster, which clearly proves that the triplet exciton, like the singlet, can be directly quenched by an electric field. In other words, a combination of bimolecular an-

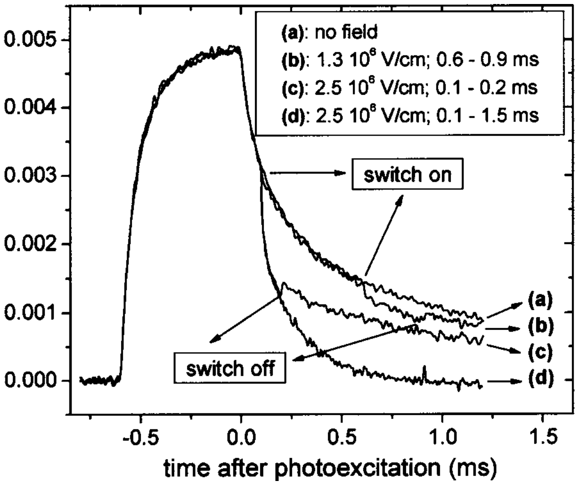

FIG. 2. Compendium of time-resolved transient triplet absorption graphs where delayed (with respect to the end of the excitation pulse) electric fields were applied as indicated. Photoexcitation was provided from −600 μs until time zero.

nihilation and triplet exciton dissociation causes the observed depletion of the triplet reservoir in the presence of an applied bias field. At this point it is not easy to quantitatively disentangle bimolecular annihilation from monomolecular dissociation. Here, the monomolecular electrical-field-driven depletion of the triplet reservoir also causes a mutual decrease of the bimolecular triplet annihilation efficiency, which itself possesses a complicated dispersive time dependence.[19] In that case, curve (a) of Fig. 3 (no electric field) cannot be considered as a true reference curve for the other cases. Nevertheless, for the highest applied fields, the triplet density approaches zero only after about 1 ms, compare curve (d) of Fig. 2, which contrasts the initial fast decay of 50% in 50 μs. Thus, qualitatively spoken, the triplet dissociation occurs over a rather long time but initially with higher efficiency. These experimental observations may find a convincing explanation in terms of the triplet exciton dipole moment alignment. Once the electric field is applied to the sample, then the fraction of the triplet excitons that has its dipole moment more parallel to the bias field will immediately dissociate and show up as rapid quenching. During their migration through the sample[19] also the remaining triplet population may change the direction of their dipole moments parallel to the applied bias field, which then causes the observed quenching in the longer time scale. Quantitatively, this scenario implies that the observed time-dependent triplet density will depend on the electric-field strength and the migration efficiency plus a contribution from the still ongoing diffusion-activated bimolecular triplet annihilation. In consequence, any meaningful quantitative analysis to disentangle true field effects from migration-activated effects is too demanding, considering that already the natural decay of the triplet density due to triplet triplet-annihilation without any additional electric field is a complex (in general unknown) function of the time (based on dispersive triplet migration) and excitation density.[19] As an alternative explanation, we cannot exclude that the long time quenching is caused by triplet exciton-polaron quenching caused by leakage currents at these rather high applied fields.

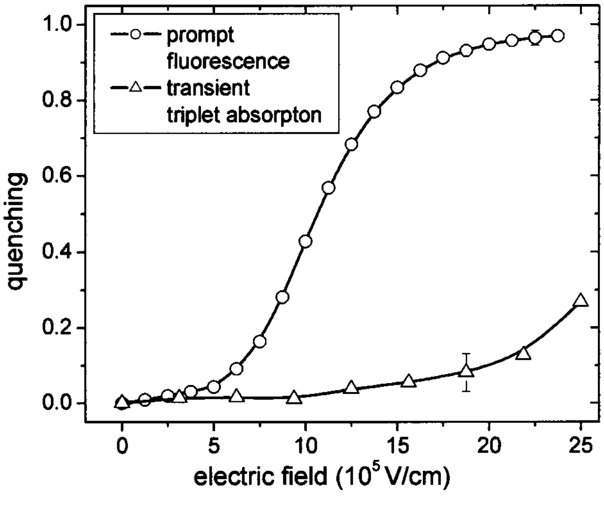

FIG. 3. Comparison of the singlet (probed by fluorescence) and triplet exciton (change in the transient absorption at the end of a 100 μs delayed-applied 10 μs pulse) quenching on electric-field strength. Error bars are indicated in both graphs and the quenching is defined in the text.

Next, attention is focused on the most striking feature of Fig. 2, which is a clear recovery of the triplet density once the electric field is turned off again. For example, in curve (c), at the end of the electric pulse (at 0.2 ms) the triplet density is quenched to about 48% of the reference curve without field, but then shows a sharp rise to reach 57% again. Such effects are always observed provided a proportion of the triplet density was quenched during the electric-field pulse, i.e., for sufficiently strong electric fields. Though qualitatively clearly observed the effect is, however, too weak to allow for a rigorous systematic examination. Potentially these observations may be explained by assuming a sequential process for the triplet exciton dissociation into charge carriers, whereby the initial step involves the field-dependent formation of a metastable geminate pair with triplet character (^{3}GP).

$$T \leftrightarrow {}^3\mathrm{GP} \rightarrow \mathrm{P}^+\mathrm{P}^-$$

Evidence for the existence of such pairs in polyspirobifluorene has recently been provided using thermally stimulated emission.[23] These pairs may either fully dissociate into free charge carriers ($\mathrm{P}^+\mathrm{P}^-$) or, especially if the stabilizing electric field is turned off, collapse into a triplet exciton again. Indeed, such a framework is generally assumed for the field-driven singlet exciton dissociation in conjugated polymers.[9,10] Alternatively, this increase in triplet density may be caused by nongeminate charge-carrier recombination, whereby the charge carriers may, for example, be left over from the triplet exciton dissociation and have not been swept out of the device. In this hypothetical case, one expects a simultaneous delayed fluorescence spike once the electric field is switched off. However, as shall be shown below, this is not observed. Thus, nongeminate pair recombination seems unlikely.

The induced quenching of the singlet and the triplet excitons are shown in Fig. 3 as a function of the applied electric field. The singlet exciton was commonly probed by its fluorescence. Here the sample was optically excited for 2 μs, with the latter pulse being symmetrically imbedded into a 20 μs electrical pulse. Under such pulsed conditions, the sample withstands considerably higher electric fields compared to common cw experiments.

First, it may be helpful to see the data for the triplet exciton quenching in the light of earlier phosphorescence quenching experiments by Sinha *et al.*[7] These authors observed virtually complete phosphorescence quenching by applying electric fields as low as 2×10^5 V/cm, which contrasts to the 10 times higher fields needed in the present study. Interestingly, at 2×10^5 V/cm, one does not observe singlet exciton quenching either, so one would not expect that the stronger bound triplet undergoes electric-field dissociation at such field strength and this is consistent with Fig. 3. In line with other experimental observations, Sinha *et al.* assigned their decrease in phosphorescence intensity to triplet exciton-polaron quenching, whereby the polaron density remains from the electrical excitation pulse. Such a polaron density is not expected for the optical excitation used here. Therefore, the main difference, apart from the time resolution, between Sinha *et al.* and the present experiments, is the different excitation source. With photoexcitation used here, we are more likely to observe true electric-field-induced triplet exciton dissociation, which we find requires considerably higher fields.

Next, we compare the absolute singlet and triplet exciton quenching under identical conditions, which yields the singlet exciton binding energy. However, in our case this can only yield a rough estimate as the absolute triplet quenching depends, as a consequence of the aforesaid migration, on the length of the applied electric-field pulse. In fact for an unambiguous comparison one would need immobile singlet and triplet excitons or at least that both excitons on average sample the same number of sites within the polymer film. This, however, is unrealistic because during its significantly longer lifetime, the triplet samples more sites within the polymer film as compared to the singlet exciton, which has recently been demonstrated using an intrinsically doped polyfluorene derivative.[24] Nevertheless, here the best compromise might be to only probe the (arbitrarily chosen) fast component of the triplet quenching. To do so, a 10 μs electric pulse was applied 100 μs after the end of the photoexcitation pulse and measurement of the quenching of the transient absorption intensity at the end (excluding the recovery effect) of this 10 μs pulse was made. We state again that this method only yields an estimate of the triplet quenching relative to the singlet as both types of excitons may not be exposed to the electric field under identical conditions during their lifetimes. Nevertheless, in both cases, the quenching parameter, Q, was conventionally estimated using

$$Q(E)=\frac{I(0)-I(E)}{I(0)},$$

where $I(E)$ represents the measured fluorescence (respectively transient absorption) signal with the electric field E being applied to the sample. Usually, studies on the electric-field-induced quenching of the photoluminescence of conjugated polymers yielded a maximum quenching of 30 to 40%.[3,4,8,11,12,14,25,26] For MeLPPP, Tasch *et al.* report a field-induced quenching of 76%, but the samples used exhibit strong signs of keto defects.[27] Unlike the commonly used pulsed laser sources, these authors employed a Xe lamp as the continuous excitation source. This technique avoids large instantaneous photocurrents during the short photoexcitation pulse, which may lead to the sample's break down. Similarly, our continuous photoexcitation for 2 μs enables us to dissociate nearly all singlet excitons—the last measured point corresponds to 97% fluorescence quenching (compare Fig. 3). To our best knowledge, this represents the highest electric-field-induced fluorescence quenching ever reported for conjugated polymers. The shape of the curve is consistent with earlier findings on small organic molecules, and basically reflects the projection of the randomly distributed exciton dipole moments in the direction of the applied field.[28]

Apparent from the lower curve in Fig. 3, the triplet as compared to the singlet exciton is much less susceptible to electric-field-induced quenching, which is expected. Here at very high fields of 2.5×10^6 V/cm an instantaneous triplet quenching of about $\sim$25% is observed.

From these measured absolute singlet and triplet exciton quenching values, an estimate for the singlet exciton binding energy is calculated. We assume virtually identical excitons, which are only distinguished by their different energy. Then, in order to form free charge carriers, the triplet exciton needs to overcome the sum of the singlet exciton binding energy and the electron correlation energy. Using such a simple framework allows one to compare the field strength at identical quenching and then work out the singlet exciton binding energy. Employing the maximum triplet quenching from Fig. 3 and a singlet-triplet-splitting of 700 meV (compare Fig. 1), the singlet exciton binding energy is obtained as 380 meV, which is comparable to several reported values (see Ref. 29 and references therein), but this might be a coincidence given the uncertainties of the absolute triplet quenching and the simplicity of the model.

Next, the influence of an electric field on the delayed fluorescence is examined. Recall, in polyfluorene derivatives including polyspirobifluorene this emission is caused by triplet-triplet annihilation,[15,16] consequently one probes the mutual quenching of the parent triplet excitons and the actually observed (delayed) singlet excitons. The gated CCD camera based set up is used for the detection of weak delayed fluorescence signals. Thus, unlike the transient absorption traces shown above, the results of pointwise measurements are presented. Three representative decays as a function of time of the delayed fluorescence following a 600 μs optical excitation pulse are shown in Fig. 4 on a double logarithmic scale. Consistent with recent findings, the decay of the delayed emission is described by a power law with a slope of -1, which has its origin in the dispersive migration of the triplet excitons at low temperature.[19] As expected, the delayed fluorescence intensity decreases once an electric field is applied and, at least for moderate fields, completely recovers after the turn off of the field. The marginally lower delayed fluorescence recovery for the

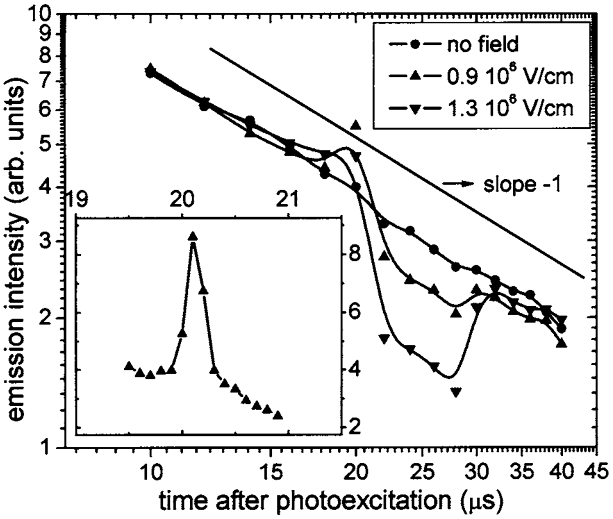

FIG. 4. Double logarithmical presentation of the spectrally integrated delayed fluorescence versus time with superimposed electric-field pulses as indicated. The light integration time for the luminescence was 1 μs and the excitation was provided by a 600 μs optical pulse prior to time zero. The straight solid line is a guideline for an algebraic decay with slope −1. The inset magnifies the time around the switch on of the electric field in a linear fashion and was measured using 100 ns detection width.

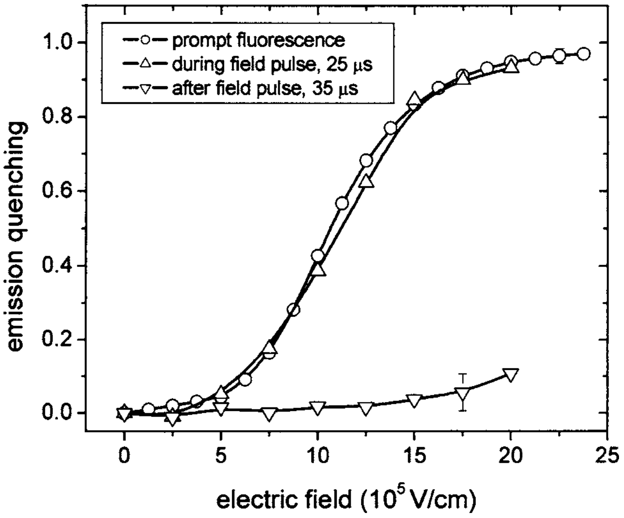

FIG. 5. Dependency of the quenching of the delayed fluorescence on field strength, during and after application of a delayed electric pulse under conditions as in Fig. 4. For the purpose of comparison, the prompt fluorescence quenching from Fig. 3 is included as well. Also shown (solid circles) is the delayed fluorescence intensity from 20.2 to 20.3 μs after excitation as a function of electric field.

1.3 MV/cm curve agrees with the onset of the triplet quenching as shown in Fig. 3.

Qualitatively, any recovery as such is only consistent if the observed delayed fluorescence stems from a secondary process (triplet-triplet annihilation), whereby the reservoir (the triplet exciton density) is much less affected by the electric field, which is fully consistent with the electric-field-induced singlet and triplet exciton quenching shown in Fig. 3. If we considered charge carriers to be the species being quenched, then the electric field would directly act on the source of the delayed fluorescence as it separates the geminate pairs. At odds with the experimental observations, no recovery after turnoff of the field is expected for this scenario. For a more quantitative insight, in Fig. 5, the dependency of the quenching of the delayed fluorescence intensity on the field strength during and after the electric pulse is compared with that of the prompt fluorescence. Clearly, during the field pulse the quenching of the delayed fluorescence closely follows that of the prompt emission, thus the reduced-delayed fluorescence intensity is mainly a consequence of the dissociation of the delayed-created singlet excitons. Likewise for the transient triplet absorption (compare Fig. 3) a quenching of the delayed fluorescence after the electric-field pulse is switched off is only observed at very high fields. Consistent with earlier findings, during or after the electric-field pulse no changes in the delayed fluorescence spectra have been observed, which always remains identical in spectral shape and position to the prompt fluorescence spectrum.

Thus, these delayed fluorescence quenching results are consistent and can, in line with previous findings, be explained by triplet-triplet-annihilation. However, one observation does not fit this framework. Once the electric field is turned on, we always observe a short spike in the delayed emission intensity. This is clearly seen in the inset of Fig. 4, where a short (100 ns) gate width has been used in order to trace this spike with sufficient time resolution. No such effect is observed once the field is turned off again. The fluorescence-like emission intensity features a sublinear dependence on excitation dose. However, this phenomenon, which is not expected within triplet-triplet-annihilation, may not be an intrinsic, i.e., general, property of conjugated polymers because it is completely lacking in another polyfluorene derivative that we have investigated as well under similar conditions. In consequence we shall not overestimate the significance of this rather weak emission ($\leqslant 1\%$ of the overall integrated delayed fluorescence intensity), which may be related to some kind of impurity site.

In a remarkable experiment Schweitzer *et al.* observed a strong spike in the delayed fluorescence intensity immediately following the turnoff of a bias field, which was applied *during* the pulsed photoexcitation.[12] Here the authors invoked singlet dissociation into field-stabilized geminate pairs, which then regenerate a singlet exciton once the field is turned off again. Within this study, singlet exciton dissociation efficiencies up to 97% were observed. Potentially some of these singlets are not fully dissociated but remain as geminate pairs, then one expects a similar spike in the delayed fluorescence intensity once the electric field is switched off as observed by the above authors. Thus, we set out to repeat the experiments by Schweitzer *et al.* using a wide range of bias fields during photoexcitation (up to 2.5×10^6 V/cm) that were switched off at various delay times after excitation, covering the whole range from 10 ns to 1 ms. Optical excitation in these experiments was provided either by the continuous wave laser using 2 μs pulses or (as in the original experiments) a truly pulsed laser source [355 nm, 170 ps, Nd-yttrium-aluminum-garnet (YAG) laser]. However, regardless of the experimental conditions, we did not observe any increase in the delayed emission intensity once the electric bias field was turned off. These results either suggest a fundamental difference between MeLPPP and polyspirobifluorene, which is unlikely, or that the actual device architecture or the purity level of the polymer are important parameters for the outcome of this experiment. Considering the latter possibility, keto defects[30] are known as electron traps.[31] In the presence of an electric bias field, those electrically charged defect sites together with their corresponding holes may well constitute a counter potential, which then collapses once the stabilizing field is switched off. Indeed, such an internal counter field, though on a longer time scale, has been observed for the archetypical conjugated polymer poly(para-phenylene vinylene).[32] Similarly, these authors attributed deep carrier traps associated with degradation sites as the origin of the internal counter field. Owing to the complicated synthesis,[33] MeLPPP possesses a large density of keto defect sites, which are always visible as an unstructured yellow emission in any delayed emission spectra.[13,14] On the other hand, due to the spiro linkage between the side groups and the polymer backbone, keto defects are virtually absent in polyspirobifluorene. Another difference in the two experiments is the different cathode material of the devices, aluminium in the above cited work versus a low work function barium/aluminium alloy in our study. Again space charge layers are conceivable in the case of aluminium cathodes due to a poor matching of the lowest unoccupied molecular orbital (LUMO) and Fermi level. The present, negative outcome of the experiment certainly proves that the enhanced-delayed fluorescence after electric-field-induced prompt fluorescence quenching is not a general intrinsic property of conjugated polymers and, therefore, cannot be compelling evidence for the intermediate formation of geminate pairs.

In view of these findings, we revisit the experimental observations that lead to the conclusion that geminate pairs are the origin of the (zero-field) delayed fluorescence in MeLPPP rather than triplet-triplet-annihilation. From our point of view, there are three main findings, which at first glance seem to be consistent only with geminate pairs; all other characteristics, including for example the decay kinetics, can be interpreted both within the geminate-pair and the triplet-triplet-annihilation picture.

First, the delayed fluorescence intensity is linearly dependent on excitation dose, which is at odds with bimolecular triplet annihilation.[14] However, this linear rise is in fact accompanied by a square-root rise for the prompt fluorescence.[14] This sublinear behavior is caused by singlet-singlet annihilation,[6] which occurs on a short time scale (ps) compared to the singlet lifetime.[2,5] Thus, only the surviving singlet exciton density can lead to triplet formation via slow intersystem crossing. Therefore, the delayed fluorescence is in fact quadratically dependent on the (surviving) singlet density, which is consistent only with bimolecular triplet-triplet annihilation.

Second, the delayed fluorescence is efficiently quenched by an applied bias field,[8,13,14] with a reported maximum quenching of ~70% at 2×10^6 V/cm. This value is consistent with the singlet exciton quenching (either prompt or delayed) shown in Fig. 5. Thus, this is not proof for the geminate-pair picture either. Unambiguous evidence for the origin of the delayed fluorescence would be whether or not the quenched-delayed fluorescence recovers after the electric field is switched off again as it does in the present study. This, however, has not been tried so far.

Third, the delayed fluorescence in MeLPPP has been observed in frozen solution.[34] Provided that the polymer chains are matrix isolated under such experimental conditions, then this observation suggests a monomolecular origin of the delayed fluorescence, which is consistent only with the geminate-pair picture. However, we have recently demonstrated that polymer chains in frozen solutions can by no means be considered as isolated, because cluster formation occurs and consequently one probes the bulk.[19]

On the whole, there is no hard evidence to support the notion that geminate-pair recombination dominates the delayed fluorescence of MeLPPP. Of course this does not exclude the existence of these pairs, especially if high-excitation doses give rise to singlet-singlet annihilation.[6] Also the very weak thermally stimulated delayed luminescence several seconds after the photoexcitation eludes a description by bimolecular-triplet annihilation.[35] However, all previous measurements on polyfluorene and these new measurements on pristine polyspirobifluorene suggest that the delayed fluorescence of all conjugated polymers, including MeLPPP, is dominated by triplet-triplet annihilation.

CONCLUSIONS

The present investigation is a further confirmation for triplet-triplet annihilation as the origin of the delayed fluorescence in polyfluorene derivatives. It was shown that the field-induced decrease of the delayed fluorescence intensity closely follows that of the prompt fluorescence. Direct triplet exciton dissociation requires about three times higher electric fields compared to the corresponding process for singlet excitons, which yields an estimate of the singlet exciton binding energy of ~0.4 eV. Evidence is provided that the triplet exciton dissociation, similar to the singlet, is a sequential process, which initially involves the formation of a metastable geminate pair.

Though there is a very small unidentified delayed fluorescence contribution, the delayed fluorescence is clearly dominated by triplet-triplet annihilation. This certainly holds true for polyfluorenes and polyspirobifluorene, but may as well apply for the often investigated MeLPPP as the current experimental evidence to support the geminate-pair picture is vague.

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