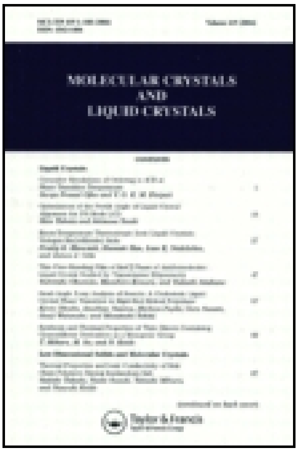

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Photogeneration and Photoluminescence Studies in Bilayer Structures Containing Poly(P-Phenylene Vinylene) and Molecularly Doped Polymers

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PHOTOGENERATION AND PHOTOLUMINESCENCE STUDIES IN BILAYER STRUCTURES CONTAINING POLY(*P*-PHENYLENE VINYLENE) AND MOLECULARLY DOPED POLYMERS

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Abstract The photogeneration efficiency for photocarriers (holes and electrons) in poly(*p*-phenylene vinylene) (PPV) is measured in the presence of high electric fields, for bilayer sandwich devices containing molecularly doped polymers (MDP) and PPV. A hole transport diamine molecule (TPD) and an electron transport malononitrile molecule (BCFM) each dispersed in polycarbonate were used to study holes and electrons respectively. By performing photoluminescence (PL) experiments in the bilayer structures and hole collection experiments in single layers without the TPD:PC overcoat, we have concluded that generation of photocarriers in PPV is mainly a *bulk mediated* process, assisted by the applied electric field, and *not* sensitized by the presence of the MDP. The electric field dependence of photogeneration suggests that photoexcitation results in a strongly correlated electron-hole pair dissociated by the electric field.

INTRODUCTION

Although there is a considerable interest in the mechanism of electronic excitation processes in poly(*p*-phenylene vinylene) (PPV),[1-6] the quantum efficiency for photogeneration of charge carriers (defined as the number of charge carriers generated per absorbed photon under the presence of an electric field) has not yet been addressed in detail. This number is an important parameter for PPV photoconducting devices and may shed light on fundamental issues related to mechanisms of photoexcitation. If, for instance, the principal optical transition in PPV is more appropriately described in terms of strongly correlated electron-hole pair (i.e., excitons or polaron-pairs),[1,7] a strong electric field dependence for the photogeneration should be observed, and photogeneration will approach unity only at high electric fields. Alternatively if a strong intersite coupling leads to the formation of weakly correlated electron-hole pairs (readily separated),[8] the photogeneration efficiency will approach unity and will be relatively insensitive to electric field effects. These two pictures while they have drawn much attention, they remain controversial.[1]

Bilayer organic photoreceptors are widely used in electrophotographic technology.[9,10] They are usually comprised of two layers consisting of an organic pigment thin layer for the photogeneration of charge and a MDP layer for the charge transport. It has been shown that these device structures can be utilized to address fundamental issues related to photogeneration of charge within the pigment layer.[9-11] This approach is particularly valuable for studying devices with a trap limited pigment layer. Thus, charge trapping can be minimized, by reducing the thickness of the pigment layer, so that collection of the photogenerated charges is facilitated via the MDP. The role of the adjacent acceptor or donor MDP on the sensitization of photogeneration of carriers has been discussed. In some cases such extrinsic sensitization has been used to support the argument that excitons are the dominant photoexcited species.[11]

We fabricated bilayer devices with PPV as the generation layer and a trap-free MDP as the charge transport layer, enabling the migration and collection of the photogenerated charge. A hole transport diamine molecule (TPD), or an electron transport malononitrile molecule (BCFM) each dispersed in polycarbonate, were used to study the photogeneration of holes and electrons respectively. A schematic of the bilayer device and the chemical structures of TPD and BCFM are shown in Fig. 1. The main purpose of this paper is to clarify the role of TPD and BCFM on the photogeneration efficiency as measured in the bilayer charge collection experiments. We also investigated the effect of TPD and BCFM on the PL (photoexcited emitting species) of PPV. We explored further the sensitizing effect of TPD on photogeneration of charge in PPV by comparing the charge collection efficiency in bilayer PPV/TPD:PC structures and single layer structures without the TPD:PC overcoat.

EXPERIMENTAL

Materials: In all experiments the PPV films were prepared from the sulfonium precursor polymer as described in a previous publication.[12,13] The hole transport molecule, N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD) (50% by weight) and the electron transport molecule, (4-*n*-butoxycarbonyl-9-fluoronylidene)-malononitrile (BCFM), (30% by weight) were dispersed in bisphenol-A-polycarbonate (PC) and poly(4,4'-cyclohexylidene-diphenylcarbonate) (PCZ) respectively, and were synthesized according to the literature procedures.[14,15]

Devices: Detailed descriptions for the fabrication of thick bilayer devices, like the one shown in Fig. 1, are given elsewhere.[12,13] Thin films of PPV (0.25 - 1 μm) were cast on ITO for charge collection experiments without the MDP. Semitransparent Al or Au electrodes were vacuum evaporated on the surface of PPV to complete the ITO/PPV/Al,Au sandwich structures. For the PL experiments thin PPV films were spin cast on 7059 Corning glass. Four sets of PPV films were prepared, each having the same thickness, ranging from 50 Å to 500 Å. Then TPD:PC and BCFM:PCZ thin films (500 - 1000 Å) were spin cast (from chloroform solution) on PPV to study their effect on the PL efficiency of PPV.

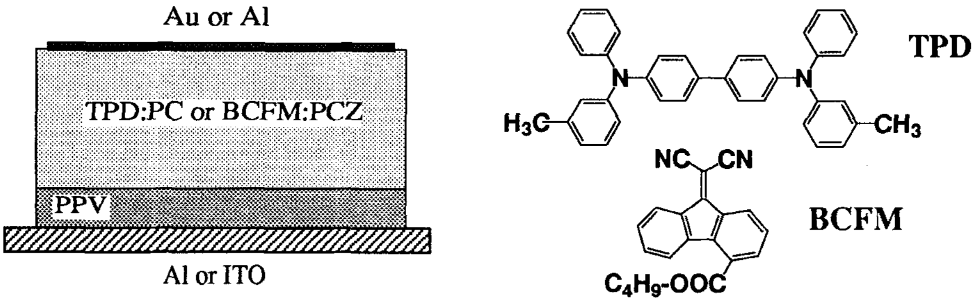

FIGURE 1 Schematic of the bilayer devices and the chemical structures of TPD and BCFM.

Measurement techniques: The charge collection in the bilayer and in single layer devices was done by using a typical time-of-flight (TOF) apparatus. The excitation light source was a pulsed (pulse width 1ns) nitrogen pumped dye laser. Wavelengths of 460 nm or 405 nm were used to establish the complete absorption of photons within PPV. The transient photocurrent induced by the applied electric field was integrated in a digital scope (integration time was ten times the transit time) to fully determined the photocharge, which was always kept smaller than $CV/20$ (C is the capacitance of the device, and V the applied voltage) to prevent screening of the applied electric field. This requirement was satisfied by keeping the absorbed photon intensity below 10^{11} photons/cm^2 per pulse. Steady state PL studies were done on Spex Fluorolog-2 spectrofruorometer where the polymer film was placed so that the emission was detected at 22.5° from the incident beam. The wavelength of the excitation source was 440 nm, with minimal absorption within TPD:PC and BCFM:PCZ. Time-resolved PL decay measurements were performed by using the time-correlated-single-photon-counting technique. The samples were photoexcited with 10 ps pulses at 380 nm. Details for the PL equipment are given in ref. 23. From the optical absorption spectra of PPV/TPD:PC and PPV/BCFM:PCZ bilayers we found no evidence of ground state charge transfer complex formation between PPV and the MDP. All measurements presented here were performed under ambient conditions.

RESULTS

Charge collection in bilayer devices

We have studied the photocarrier generation efficiency in PPV both in bilayer devices and in single layer devices by using the charge collection technique described earlier.[12,13] A compilation of all our measurements is shown in Fig. 2. The open symbols correspond to charge collection of electrons and holes measured in bilayer devices, where electrons and electrons are photogenerated within PPV and subsequently are injected into and drift

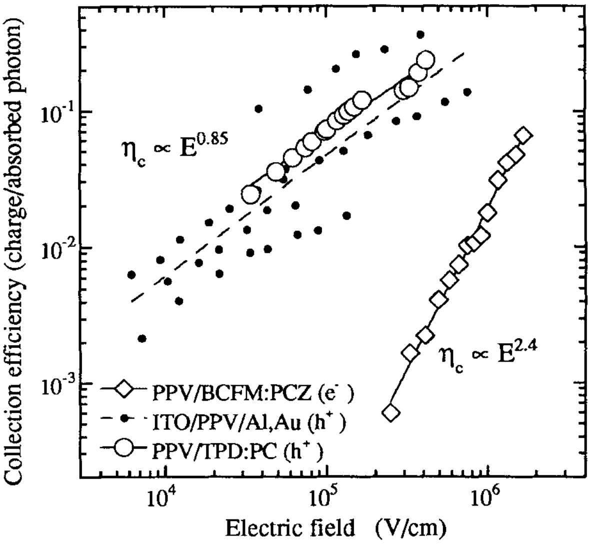

FIGURE 2 Open symbols show the electric field dependence of collection efficiency for holes (h$^+$) and electrons (e$^-$), performed in bilayer devices. Small filled circles show the hole collection efficiency from five ITO/PPV/Al,Au single layer devices. The dashed line is the average power law fit to all the data measured in single layer devices.

through the trap-free MDP under the influence of the applied electric field. The excitation wavelength of the laser flash was 460 nm to ensure negligible absorption within the molecularly doped polymers. TPD:PC or BCFM:PCZ was used for the collection of holes or electrons respectively. In these experiments the overall collection efficiency η_c is determined from the integrated TOF photocurrent and is the product of four factors: $\eta_c = \eta_g\eta_t\eta_i\eta_{tr}$; where η_g is the quantum efficiency for generation of photocarriers in PPV (the main quantity of interest), η_t the efficiency to escape trapping in PPV, η_i the injection efficiency of photocarriers through the PPV/TPD:PC (for holes) or PPV/BCFM:PCZ (for electrons) interface barrier, and η_{tr} the efficiency of photocarriers to escape trapping in the MDP layer. As seen in Fig. 2, the collection efficiency for holes exhibits an almost linear dependence upon the electric field ($\eta_c \propto E^{0.85}$), and a strong superlinear dependence ($\eta_c \propto E^{2.4}$) for electrons.

Hole transport in TPD:PC or electron transport in BCFM:PCZ is known to be trap-free;[14,16,17] therefore η_{tr} is unity for either case. The energy diagram presented in Fig. 3, based on electrochemical data (discussed in detail in an earlier publication[13]), suggests that the injection of holes and electrons into TPD and BCFM respectively, is energetically favorable especially in the presence of the electric field. Also, the lack of dispersion and time delay in the shape of electron and hole TOF photocurrent signals,[12] together with the

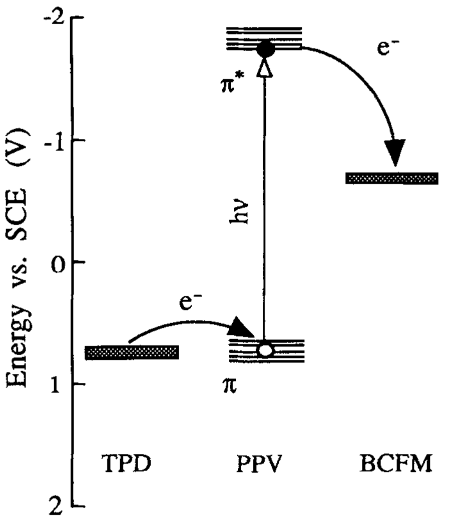

FIGURE 3 Energy diagram showing the oxidation and reduction potentials (vs. SCE) of TPD, PPV, BCFM. The proposed photoinduced electron transfer responsible for the quenching of PL is also shown.

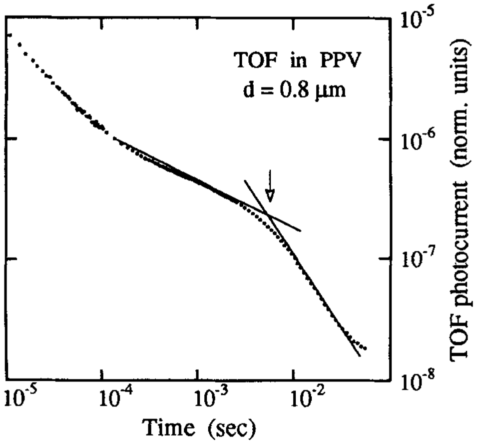

FIGURE 4 Transient photocurrent for holes in PPV showing dispersive TOF. The arrow indicates the arrival of holes in the counterelectrode corresponding to the electric field of 2×10^4 V/cm.

earlier observations of trap-free space-charge-limited (TFSCL) dark current in ITO/PPV/TPD:PC/Al bilayer structures,[18] indicates that photoinjection from PPV into the MDPs is highly efficient and close to unity ($\eta_i \approx 1$) for both electrons and holes in the two devices. As a result, the collection efficiency and its electric field dependence are, to a good approximation, solely a function of η_g and η_t for both electrons and holes. In order to further resolve the nature of photogeneration in the bilayer devices, charge collection experiments in single layer devices and the effect of electron donating (TPD) or accepting (BCFM) molecules on the PL of PPV were conducted.

TOF and charge collection in single layer devices

As shown in Fig. 4, a dispersive[19] TOF signal *for holes* can be observed in a single layer of fully converted PPV (ITO/PPV/Al, or Au), at relatively large electric fields ($>10^4$ V/cm). The TOF photocurrent transient corresponds to the drift of holes across a thin film of PPV (~ 0.8 μm) at the electric field of 2×10^4 V/cm. A laser flash of 405 nm was used to minimize the absorption depth of photons within PPV. The arrow in the figure indicates the arrival time of photogenerated holes (transit time) from which a drift mobility of about 10^{-6} cm^2/Vs is estimated. Detailed analysis of the dispersive hole transport in PPV will be published elsewhere.

The observed TOF signal in Fig. 4 indicates that at electric fields of 2×10^4 V/cm or larger, most of the photogenerated holes within PPV can be collected at the opposite electrode, thus trapping is minimized and the efficiency to escape trapping approaches unity ($\eta_t \approx 1$). An estimate[18] for the trapping mobility-lifetime product for holes in PPV ($\mu\tau \approx 10^{-9}$ cm^2/V) also confirms the fact that the range ($x = \mu\tau E$) of holes in the present experiments will be comparable to the thickness of the samples. From the above, we conclude that the collection efficiency (integrated transient photocurrent normalized with the number of absorbed photons times the elementary charge e) provides a more direct estimate of the photogeneration efficiency η_g for holes. The black circles shown in Fig. 2 correspond to the collection efficiency for five devices having different PPV thicknesses (0.2 - 1.2 μm). All the data points are within the close vicinity of those obtained in the bilayer devices. Indeed the average power law fit ($\eta_c \propto E^{0.85}$) to all of them, shown in the figure by the dashed line, is very close to the one for the bilayer device. The scatter of the data points could be attributed to different states of conversion of the PPV's used and thus the morphology of the PPV's.[20] Discrepancies in the steady state PL spectra among these five devices have also been observed. The similarity of the charge collection efficiency in single layer devices and bilayer devices, suggests that the role of TPD is like that of aluminum and gold and, furthermore, TPD may not play a major role on the photogeneration of holes. Supporting evidence for that will also be provided by the PL experiments below.

We were not able to detect a TOF signal due to *electron* transport in PPV, suggesting either a much smaller mobility for electrons or, most probably, a very high density of electron traps limiting their collection efficiency to values much lower than unity, thus setting $\eta_t \ll 1$. In fact molecular oxygen, with a reduction potential lower than that of PPV and commonly cited as an electron trap in organic molecular crystals,[21] may act as the predominant electron trap.

Photoluminescence studies

The PL spectrum of PPV measured on samples with or without the TPD:PC or the BCFM:PCZ overcoat is shown in Fig. 5(a) and Fig. 5(b) respectively. Three samples were used for this experiment where the thickness of PPV is about 55 Å. In the figure the maximum of the PL spectrum for the uncoated PPV sample was set to unity and the two PL spectra, obtained from specimen structures containing TPD:PC or BCFM:PCZ overcoats, were then normalized with respect to it. A small reduction of about 40% in the PL intensity of PPV is observed when TPD:PC thin film is used. On the other hand, BCFM:PCZ exhibits a much stronger quenching effect on the PL of PPV without altering the shape of the PL spectrum. We also found that the process of quenching was reversible. The original PL spectrum of PPV can be restored when TPD:PC or BCFM:PCZ is washed away with chloroform (cf. Figs. 5).

The quenching effect of BCFM:PCZ on the time-resolved PL decay of PPV is also demonstrated in Fig. 6. The presence of BCFM:PCZ has a dramatic effect on the PL decay dynamics of PPV. The lifetime of the emitting species in PPV is reduced at least ten times, to values below the instrumental resolution (detector response ~ 50 ps). This indicates the existence of rapid quenching process associated with an efficient

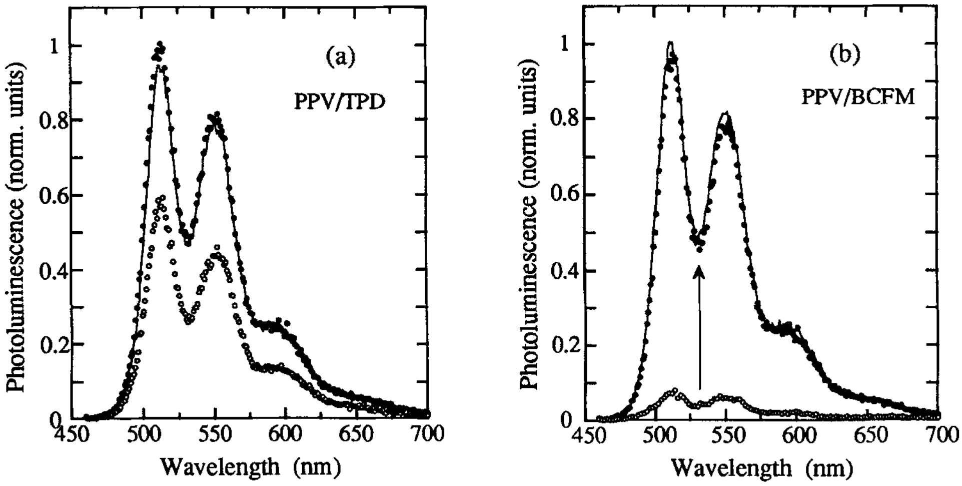

FIGURE 5 Steady-state PL of a PPV thin film of 55 Å (filled circles) as a function of emission wavelength. The PL spectra of PPV when TPD:PC (a) or BCFM:PCZ (b) is used are shown with open circles. Also shown, with continuous lines, the PL of PPV after washing the molecularly doped polymers with chloroform.

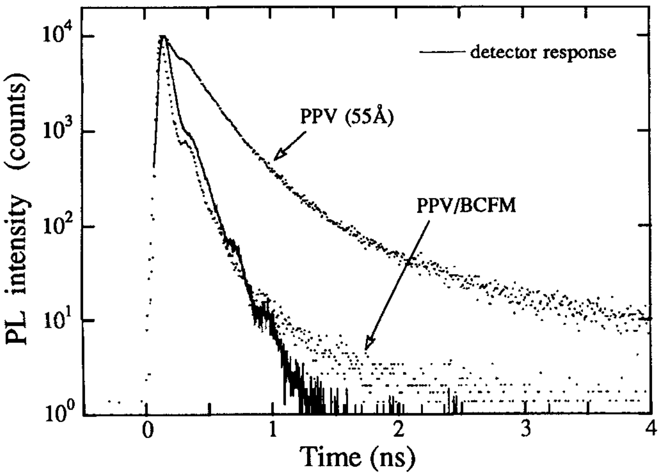

FIGURE 6 Time resolved photoluminescence for PPV and PPV/BCFM:PCZ. The response of the spectrometer is also shown.

photoinduced electron transfer shown in Fig. 3. This is analogous to the behavior of the MEH-PPV/C_{60} system.[22] Negligible lifetime changes due the presence of TPD were observed.

All the available data from the steady state PL experiments are shown in Fig. 7. In this, the quenching factor (defined as the ratio between the integrated PL spectrum of the

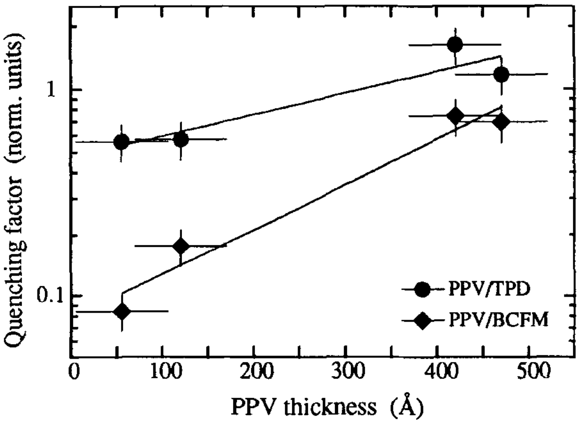

FIGURE 7 Quenching factor of the PL of PPV as a function of PPV thickness for bilayer structures PPV/TPD:PCand PPV/BCFM:PCZ.

bilayer structure to that of the PPV single layer) is plotted as a function of PPV thickness for four sets of samples. For thin PPV films the effect of TPD on the PL of PPV is much weaker than that of BCFM. This is because the acceptor molecule (BCFM) is more capable of dissociating the emitting excited species within PPV. However when thicker PPV films are used, the two quenching factors converge to unity implying the irrelevance of TPD and BCFM on the PL of PPV. The slight increase of the PL when TPD:PC is used may be due to weak exciplex formation between the excited state of PPV and the ground state of TPD. Larger enhancements have been observed in similar π-conjugated/MDP bilayer structures.[23] The thickness dependence of the PL quenching, particularly in the case of BCFM, suggests that quenching is a *surface effect* not affecting the PPV to depths more than about 200 to 300 Å. Since excitons are widely reported to be the predominant emitting species in PPV[1-3,5] this depth can be used to estimate the *diffusion length* of excitons within PPV. The above observation suggests that the majority of the excited species in the bilayer charge collection experiments will be unaffected by the presence of TPD or BCFM, since the absorption depth of the light used for photoexcitation (460 nm) is more than 2000 Å (PPV thickness was about 4000Å). Thus it appears that surface sensitization is not a major factor in the photogeneration of holes and electrons in bilayer structures, which is in agreement with the conclusion drawn from the charge collection performed on ITO/PPV/Al,Au devices.

DISCUSSION

The experimental data suggest that photogeneration of mobile holes and electrons in PPV is mostly a *bulk mediated* process. Thus the collection efficiency η_c measured in the PPV/TPD:PC device provides a direct estimate for the quantum efficiency for photogeneration of holes in PPV. The η_c for electrons as measured in PPV/BCFM:PCZ devices is the product of quantum efficiency for photogeneration of electrons (same as holes), times the efficiency to escape trapping η_t. In fact the ratio between the collection efficiency η_c for electrons and holes provides an estimate for η_t. From the data shown in Fig. 2 we get $\eta_t \propto E^{1.5}$, the nonlinear part of which might be attributed to trapping-detrapping effects and/or an electric field dependent electron mobility. Based on an average photon absorption depth of d = 2000 Å, a drift distance x is estimated (since $\eta_t \approx x/d$) to be about 100 Å for the electric field of 10^6 V/cm. Thus, only the electrons photogenerated very close to the PPV/BCFM interface will be collected.

The electric field dependence ($\eta_g \propto E^{0.85}$) of the quantum efficiency for photogeneration of electrons and holes in PPV suggests that upon photoexcitation a strongly correlated electron-hole pair is formed, and its separation is assisted by the applied electric field. The exciton is a plausible candidate for the observed electric field dependence, the binding energy of which must be larger than the thermal energy ($E_b \gg K_BT$) to explain the data. According to this picture the electric field enhances exciton dissociation, thus giving rise to mobile carriers (bipolarons, trapped carriers, etc.) and eventually quenches the PL. For example, in the simplest case, if photoexcitation produces singlet excitons with a spatial extent of about 25 Å and a binding energy of about 0.5 eV then an electric field of 2×10^6 V/cm is needed for complete dissociation ($\eta_g \approx 1$). This is in agreement with the data shown in Fig. 2. The above physical parameters are not far from those predicted by theory.[5,24]

A relatively low quantum yield for PL efficiency (at room temperature) in PPV[25,26] (< 20%) suggests, however, that the majority of photoexcited species follow nonradiative decay channels. According to this, excitons may dissociate nonradiatively at quenching sites (charged defects and/or impurities) within the bulk of the material, followed by generation of mobile species. The applied electric field can accelerate such dissociation process and result in a field dependent photogeneration. It has been recently suggested that non-emissive "spatially indirect" singlet excitons (polaron-pairs) may be formed with very high efficiency in PPV.[6,7] Dissociation of these pairs into mobile charge could be enhanced by an electric field. A weakly correlated electron-hole pair could also result in a photogeneration efficiency approaching unity, but under conditions where the electric field effects are relatively unimportant. Clearly this model cannot be a good candidate for our observations.

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