PHYSICAL REVIEW B **73**, 125202 (2006)

Exciton dissociation by a static electric field followed by nanoscale charge transport in PPV polymer films

Hikmat Najafov and Ivan Biaggio
Department of Physics and Center for Optical Technologies, Lehigh University, Bethlehem, Pennsylvania 18015, USA

Ta-Ko Chuang and Miltiadis K. Hatalis
Department of Electrical and Computer Engineering and Center for Optical Technologies, Lehigh University, Bethlehem, Pennsylvania 18015, USA

(Received 27 January 2006; published 29 March 2006)

The simultaneous study of the electric-field dependence of the photoluminescence and the photoinduced charge transport in the phenyl-substituted Super Yellow PPV derivative shows that charge carriers are created indirectly through field-induced ionization of excitons, and allows the identification of a free-carrier mobility larger than $\sim 3\times 10^{-6}$ cm^2 V^{-1} s^{-1} that is valid for transport over a few nm during an apparent free-carrier lifetime of $\sim$50 ns. The time dynamics of the photoluminescence and its temperature-quenching behavior indicate the presence of two species of excitons, which can be interpreted as intrachain and interchain excitons.

DOI: 10.1103/PhysRevB.73.125202 PACS number(s): 78.66.Qn, 71.35.Aa, 72.80.Le, 73.50.Gr

The nature of the photoinduced generation of charge carriers in conjugated polymers has been the subject of an intense discussion[1–6] that is complicated by the variety of excitonic states in polymers and the influence of interchain interactions.[4] To investigate the main question of whether photoexcitation results in localized excitons or directly leads to mobile charge carriers, one can study luminescence[1,2] and photocurrent[2,6] as a function of the applied electric field, but to get more conclusive results it is necessary to simultaneously measure the time dynamics of luminescence and photocurrent and relate them to each other. In this paper, we do so on a nanosecond time scale after illumination with picosecond pulses. We obtain the required time resolution in a standard polymer light emitting diode (PLED) configuration by measuring the time dynamics of the charge accumulated on the electrodes, instead of the photocurrent.

It is important to be able to investigate these fundamental effects in finished, encapsulated PLED devices that are protected from the environment, so that any material properties derived from the experiments directly apply to the special geometries used in real devices. One example of this is the fact, typical of dispersive charge transport, that mobility values determined by time-of-flight over distances of the order of several micrometers do not necessarily apply to the films used in PLEDs, which can be less than 100 nm thick.

The polymer we investigated is Covion Super Yellow (SY),[7] a phenyl-substituted poly phenylenevinylene (PPV) derivative.[8–10] It is the luminescent layer in a top-emitting PLED structure encapsulated in an inert gas atmosphere. An Al/Ni/ITO (1000 Å/500 Å/500 Å) anode is followed by a hole transporting layer of polyethylenedioxythiophene-polystyrenesulfonic acid (PEDOT) (800 Å), a light emitting layer of SY-PPV (600 Å), a cathode made of electron-beam-evaporated aluminum (50 Å), and a sputtered ITO film (800 Å) as the current-carrying layer. We generally investigated active areas of the order of 0.4 cm^2. For the observation of the photoluminescence, the sample was excited every 100 ms by a 30 ps long laser pulse at an energy density of 1.7 μJ/cm^2 and at a wavelength of 440 nm, near the maximum of the absorption spectrum of SY-PPV. The dynamics of the photoluminescence PL(t), detected at its peak emission wavelength of 546 nm and at longer wavelengths, was measured by a high speed photodetector ($\sim$1 ns response time) attached to a digital oscilloscope sampling at a rate of 2 GHz/s and averaged 150 times. Different electric fields were applied to the PLED contacts in the reverse bias direction and the change in the potential drop over the PLED was monitored on the oscilloscope with an RC time constant of the circuit larger than 1 ms. This integrated pulsed photoconductivity (IPP) setup[11,12] ensured that the voltage change measured on the oscilloscope was proportional to $S\Delta Q(t)/C$, where $\Delta Q(t)$ is the photoinduced surface-charge density that is deposited on the contacts, S is the illuminated area, and $C=30$ nF is the capacitance of the PLED.

Figure 1 shows PL(t) and $\Delta Q(t)$ for different applied voltages. As shown in the inset, the time dynamics of PL(t) is characterized by a fast response I_0^{PL} comparable to the time resolution of our detection system, and by a weaker luminescence I_1^{PL} that lingers at later times. This delayed portion of the luminescence has a noticeably different behavior with applied field when compared to the peak of the photoluminescence curve, which does not change much at lower fields. The photoinduced charge $\Delta Q(t)$ grows exponentially in time, with a time constant $\tau=50\pm 3$ ns. Since this time does not depend on the magnitude of the applied field, it is not due to a time-of-flight effect over the thickness of the polymer film and we associate it with a limited carrier lifetime, probably caused by trapping of the moving charge carriers at unidentified states.

Figure 2 shows the electric field dependence of the final steady-state value $\Delta Q^{\infty}=\Delta Q(0.2\ \mu\mathrm{s})$ of the accumulated charge and of the intensities I_0^{PL} and I_1^{PL} measured at the peak of the luminescence transient and in the time interval around 5 ± 2 ns indicated in the inset of Fig. 1, respectively. There is a very clear correlation between the quenching of the luminescence and the growth of charge transport. The final sur-

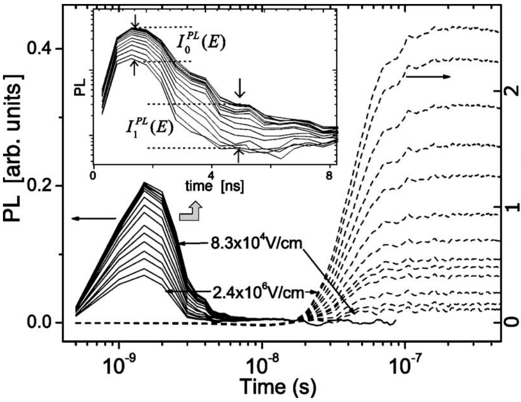

FIG. 1. Temporal variation of the luminescence PL(t) (solid curves) and accumulated charge $\Delta Q(t)$ (dashed curves) at different applied fields shown with a step of 1.5×10^5 V/cm in the range of $(8.3\times 10^4)-(2.4\times 10^6)$ V/cm. The inset shows the time dynamics of PL(t) with instantaneous $[I_0^{\mathrm{PL}}(E)]$ and delayed components of the luminescence $[I_1^{\mathrm{PL}}(E)]$.

face charge density is given by $\Delta Q^{\infty}(E)=ne\mu\tau E/(Sd)$, where e is the unit charge, n is the total number of excitons that are ionized to produce mobile charge carriers, μ is the mobility of the majority carriers, $\tau=50\pm 3$ ns is the carrier lifetime determined above, and d is the thickness of the photoconducting film. Assuming that the photoinduced excitons either decay radiatively or they are ionized to generate the mobile charge carriers, n must be proportional to $1-I^{\mathrm{PL}}(E)/I^{\mathrm{PL}}(0)$ and we can expect the accumulated charge to be given by

$$\Delta Q^{\infty}(E)=N^{p}\left[1-\frac{I^{\mathrm{PL}}(E)}{I^{\mathrm{PL}}(0)}\right]e\mu\tau E, \qquad (1)$$

where $N^{p}=n/(Sd)$ is the average density of photoinduced excitons. The solid curve in Fig. 2 is the prediction of Eq. (1). The photoluminescence quenching predicts the charge generation very well at lower fields. The deviation observed at fields higher than 3.1×10^6 V/cm could be ascribed to a field-dependent mobility or to additional ionization of more strongly bound nonradiative excitonic states or trapped carriers that becomes possible at higher fields. The good agreement between the data and Eq. (1) is very clear proof that luminescence quenching is directly connected to charge-carrier generation and that charge carriers are excited indirectly through field-induced ionization of the exciton that is responsible for the luminescence emission.

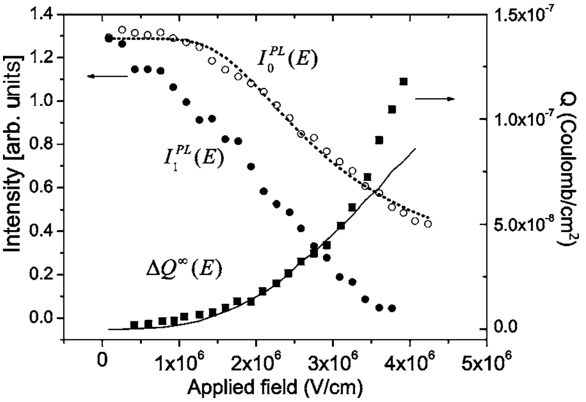

FIG. 2. Electric-field dependencies of the accumulated charge $\Delta Q(\infty)$ (solid squares) and of the intensities of instantaneous I_0^{PL} (open circles) and delayed components I_1^{PL} (solid circles) of the luminescence, and their reproduction with Eqs. (1) and (3) (solid and dotted curves, respectively).

The correlation between photoinduced luminescence and charge transport allows us to obtain a good estimation of a lower limit for the mobility by extracting N^{P} from the number of photons in the laser pulses and the absorption constant $\alpha=1.2\times 10^5$ cm^{-1} that we determined for the illumination wavelength. With this absorption constant, excitons are photoexcited over the whole film thickness of $d=60$ nm and their average density is given by $N^{p}\approx F\phi[1-\exp(-2\alpha d)]/(h\nu d)$, where $F=1.7$ μJ/cm^2 is the fluence of the laser pulses, ϕ is a quantum efficiency for exciton generation, which should be close to unity at the wavelength we are using, and the factor of 2 accounts for the reflected pulse. At electric fields below 3×10^6 V/cm we obtain $N^{p}\approx 4.8\times 10^{17}$ cm^{-3} and $\mu/\phi=3.3\times 10^{-6}$ cm^2 V^{-1} s^{-1}. Assuming $\phi=1$, we obtain a good lower limit for the mobility because we explicitly took into account the field-dependent ionization rate of the photoinduced excitons. This mobility is an order of magnitude higher than that reported in most other PPV derivatives, for example in MEH-PPV,[13,14] even though it is still much lower than the high values reported in Ref. 15. The lower reported values are probably affected, apart from the difference in materials, also by the dispersive nature of charge transport, which reduces the apparent mobility when transport is measured on larger length scales. Since the electron mobility in PPV polymers is normally very low ($\sim 10^{-9}$ cm^2 V^{-1} s^{-1}),[14] we assign our mobility value to holes. The drift length obtained with the above mobility is of the order of 5 nm at 3×10^6 V/cm, which is significantly smaller than the thickness of our polymer film, consistent with the fact that we did not observe a transit time effect.

We now analyze the field-induced quenching of the photoluminescence. Since we found that the quenching is due to field-induced ionization, it must depend on the potential with which the exciton is bound. To obtain more information on the binding energy of the excitons that we photoexcite, and use it to understand the field-induced quenching observed in Figs. 1 and 2, we performed photoluminescence experiments at various temperatures. The sample was mounted on a temperature-controlled hot plate and the homogeneity of the temperature was additionally checked with a chromel-alumel thermocouple attached to the sample surface.

Figure 3 shows $\mathrm{PL}=I_0^{\mathrm{PL}}+I_1^{\mathrm{PL}}$ and the temperature dependence of its time integral between 300 and 600 K (inset). Both the fast and delayed components I_i^{PL} $(i=0,1)$ of the luminescence can be described by a Mott-like temperature dependence of the kind $I_i^{\mathrm{PL}}(T)=I_i^{\mathrm{PL}}/[1+A_i\exp(-E_i/k_BT)]$,[16] but $I_1^{\mathrm{PL}}(T)$ does not saturate at low temperatures, so that the data in Fig. 3 can be well fitted by

$$I^{\mathrm{PL}}(T)=\frac{I_0^{\mathrm{PL}}}{1+Ae^{-E_0/k_BT}}+I_1^{\mathrm{PL}}(\infty)e^{E_1/k_BT}. \qquad (2)$$

The instantaneous response $I_0^{\mathrm{PL}}(T)$ becomes strongly temperature-dependent at high temperatures between 500 and

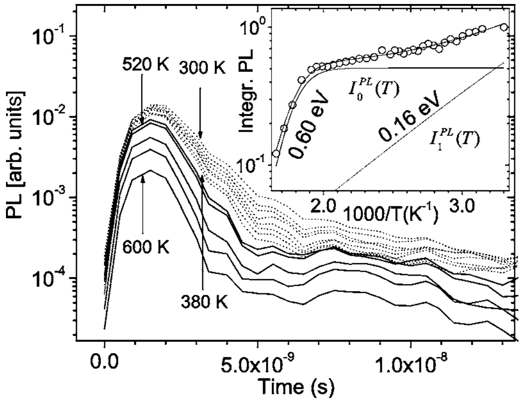

FIG. 3. PL(t) in temperature intervals of 300–380 K (dotted curves) and 520–600 K (solid curves) and the temperature dependence of its time integral (inset, open circles) reproduced with Eq. (2) (solid curve).

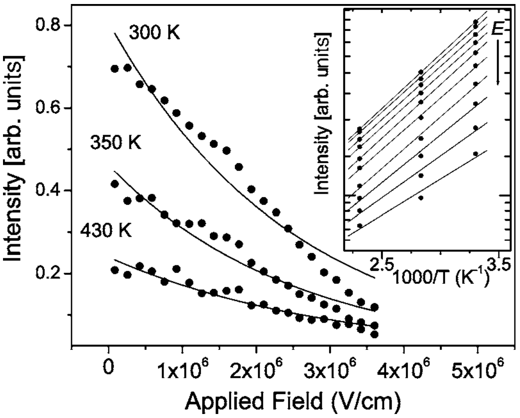

FIG. 4. Electric-field dependence of the intensity of the delayed component of the luminescence I_1^{PL} at three different temperatures in the range where the high-temperature quenching does not yet appear (solid circles). The solid curves are an approximation based on the simple model discussed in the text. The inset shows the same data for constant electric field increments in an Arrhenius plot.

600 K as described by a thermal activation energy $E_0 = 0.6 \pm 0.1$ eV, while the delayed response $I_1^{\mathrm{PL}}(T)$ has a weaker, smoother temperature dependence that is already clearly visible at temperatures in the 300–380 K range and that is thermally activated with $E_1 = 0.16 \pm 0.05$ eV. We conclude that the two activation energies we observed are related to two temporally separated processes and reflect the existence of a second excitonic species with an independent quenching mechanism. For all thermal measurements we used a polymer encapsulated in inert gas atmosphere, which avoids oxidation effects. Also, the photoluminescence data retraced themselves over several heating-cooling cycles, confirming the absence of any irreversible changes in the polymer above the glass-transition temperature, which is about 450 K in SY-PPV.[17] The fact that the glass transition does not influence the photoluminescence process is also seen by the absence of abrupt changes in the photoluminescence intensity around the glass-transition temperature, as can be seen in the inset of Fig. 3.

The higher activation energy of $E_0 = 0.6 \pm 0.1$ eV, which is the only parameter that we derive from measurements above the glass-transition temperature, can be assigned to the thermal ionization energy of an exciton on a polymer chain. This interpretation relies on the assumption that this energy is not significantly influenced by the glass transition, and that the luminescence quenching that we observed is not strongly affected by a possible temperature-dependent nonradiative recombination rate. The latter point can be argued in terms of simple considerations based on a linear coupling configuration coordinate diagram, typical vibronic energies, and the excitation and emission spectra; this would give a thermal activation energy for nonradiative recombination of the order of several eV. But the interpretation of the observed quenching as thermal ionization is also supported by the fact that a potential barrier of 0.6 eV separating the bound excitonic state from the unbound state of the charge carriers is consistent with the observed field-induced quenching of the fast luminescence component I_0^{PL}. In fact, its electric-field dependence can be very well fitted with a simple one-dimensional model for tunneling through a parabolic potential barrier,[19]

$$I_0^{\mathrm{PL}}(E) = I_0^{\mathrm{PL}}(0)\left[1 + b\exp\left(\frac{-\pi}{2\sqrt{2}}\frac{\sqrt{m}E_0^{3/2}}{\hbar eE}\right)\right]^{-1} \tag{3}$$

with only the reduced mass m and the preexponential factor b as free parameters. The dotted curve in Fig. 2 corresponds to Eq. (3) with $m = 0.2$, which is of the correct order of magnitude for the reduced mass of excitons in PPV and may account for tunneling parallel- and perpendicular to the chain configurations.[20] The activation energy of $E_0 = 0.6$ eV is in the range of those observed in PPV-derivatives in general, and it is close to that reported by Martin *et al.* ($\sim 0.8 \pm 0.15$ eV) for MEH-PPV.[18]

We now turn to the interpretation of the lower activation energy of $E_1 = 0.16 \pm 0.05$ eV that we observed at lower temperatures. In contrast to the I_0^{PL} component of the luminescence, the field dependence of the longer-lived luminescence, I_1^{PL}, cannot be reproduced with a tunneling description even approximately, with any value of the energy barrier. However, we saw that the activation energy $E_1 = 0.16$ eV gradually decreases with the applied field by measuring the luminescence at three temperatures spread over the low-temperature range where the high-temperature quenching of the I_1^{PL} component does not yet occur. The results are shown in Fig. 4. To avoid any uncertainties associated with possible morphological changes in the polymer above the glass-transition temperature, we chose the three temperatures used for the data in Fig. 4 to be well below the glass-transition temperature of 450 K.[17] The data can be modeled using the second term in Eq. (2), with the activation energy E_1 modified by the addition of an electrostatic energy ea_0E over a length scale a_0, as in $E_1(E) = E_1 - ea_0E$, or by a Poole-Frenkel expression of the form $E_1(E) = E_1 - \gamma k_B T\sqrt{E}$.[21] Both models have only one adjustable parameter and both give an equally good agreement with the data. As an example, Fig. 4 gives a fit with the former model using $a_0 = 1.2$ Å. Alternatively, using the Poole-Frenkel expression leads to a γ coefficient of the order of 10^{-3} (cm/V)$^{1/2}$, as expected for charge-carrier hopping in polymers.[13] The delayed luminescence has been assigned to interchain excitons in PPV and its derivatives.[5,23–25] Interchain excitons are also known as spatially indirect excitons due to the chain aggregation,[24] and they could be related to an additional photoinduced absorption band commonly observed in PPV and its derivatives at ~1.4 eV.[24,25] The question arises if the delayed luminescence that we see in SY-PPV can also be assigned to an interchain exciton. The main argument against such an interpretation would be that the observed 0.16 eV activation energy is significantly smaller than the thermal equivalent of the optical absorption of ~1.4 eV,[24,25] which can be estimated to be of the order of ~0.85 eV from the frequency dependence of the dielectric function.[27–29] However, Yan *et al.*[26] observed identical luminescence spectra at short (110 ps) and longer times (20 ns) after excitation, showing that the interchain exciton can transform back into a regular exciton. The delayed photoluminescence that we measured can be assigned to an interchain exciton if the energy of $E_1 = 0.16$ eV is interpreted as the activation energy of the *transformation process* between interchain and intrachain excitons. This transformation can happen by hopping of a charge from one chain to another, and we found that the field dependence of E_1 can be understood by the change in electrostatic potential over a distance of the order of angstroms, which does correspond to the expected value for the interchain distance (~4 Å) (Ref. 22) or, as mentioned before, by a Poole-Frenkel description as is normally used to describe hopping transport.

In conclusion, we have shown that photoexcitation in SY-PPV primarily results in intrachain excitons with an activation energy of 0.6 eV, and that mobile charge carriers are only created later, by field-induced ionization of this exciton that happens through tunneling through the potential barrier of its binding potential. These observations are different from earlier findings in PPV where a direct carrier photoexcitation was claimed[2] and agree with the indirect-excitation picture described in Ref. 1. By quantitatively taking into account the amount of carriers generated by field-induced ionization, we could easily derive a good estimation of the free-carrier mobility that is valid for transport over distances of the order of a few nm. We have shown that the mobility in our SY-PPV sample was certainly larger than 3×10^{-6} cm^2 V^{-1} s^{-1}.

We thank Covion Organic Semiconductors GmbH, Frankfurt, Germany, for the Super Yellow polymer.

---

[1] R. Kersting, U. Lemmer, M. Deussen, H. J. Bakker, R. F. Mahrt, H. Kurz, V. I. Arkhipov, H. Bässler, and E. O. Göbel, Phys. Rev. Lett. **73**, 1440 (1994).

[2] D. Moses, H. Okumoto, C. H. Lee, A. J. Heeger, T. Ohnishi, and T. Noguchi, Phys. Rev. B **54**, 4748 (1996).

[3] *The Nature of Photoexcitations in Conjugated Polymers*, edited by N. S. Sariciftci (World Scientific, Singapore, 1997).

[4] B. J. Schwartz, Annu. Rev. Phys. Chem. **54**, 14172 (2003).

[5] I. B. Martini, A. D. Smith, and B. J. Schwartz, Phys. Rev. B **69**, 035204 (2004).

[6] E. Hendry, J. M. Schins, L. P. Candeias, L. D. A. Siebbeles, and M. Bonn, Phys. Rev. Lett. **92**, 196601 (2004).

[7] H. Spreitzer, H. Becker, E. Kluge, W. Lreuder, H. Schenk, R. Demandt, and H. Schoo, Adv. Mater. (Weinheim, Ger.) **10**, 1340 (1998).

[8] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, and P. L. Holmes, Nature (London) **347**, 539 (1988).

[9] R. H. Friend, D. D. C. Bradley, and P. L. Holmes, Phys. World **5** (11), 42 (1992).

[10] D. Braun and A. Heeger, Appl. Phys. Lett. **58**, 1982 (1991).

[11] A. Tapponnier, I. Biaggio, M. Koehler, and P. Günter, Appl. Phys. Lett. **83**, 5473 (2003).

[12] H. Antoniadis and E. A. Schiff, Phys. Rev. B **46**, 9482 (1992).

[13] L. Bozano, S. A. Carter, J. C. Scott, G. G. Malliaras, and P. J. Brock, Appl. Phys. Lett. **74**, 1132 (1999).

[14] A. J. Breeze, Z. Schlesinger, S. A. Carter, and P. J. Brock, Phys. Rev. B **64**, 125205 (2001).

[15] J. M. Warman, G. H. Gelinck, and M. P. de Haas, J. Phys.: Condens. Matter **14**, 9935 (2002).

[16] N. F. Mott, Proc. R. Soc. London, Ser. A **167**, 384 (1938).

[17] L. Edman, M. Pauchard, D. Moses, and A. J. Heeger, J. Appl. Phys. **95**, 4357 (2004).

[18] S. J. Martin, H. Mellor, D. D. C. Bradley, and P. L. Burn, Opt. Mater. (Amsterdam, Neth.) **9**, 88 (1998).

[19] S. M. Sze, *Physics of Semiconductor Devices* (John Wiley & Sons, New York, 1981).

[20] P. Gomes da Costa and E. M. Conwell, Phys. Rev. B **48**, 1993 (1993).

[21] J. Frenkel, Phys. Rev. **54**, 647 (1938).

[22] E. M. Conwell, J. Perlstein, and S. Shaik, Phys. Rev. B **54**, R2308 (1996).

[23] H. A. Mizes and E. M. Conwell, Phys. Rev. B **50**, R11243 (1994).

[24] M. Yan, L. J. Rothberg, E. W. Kwock, and T. M. Miller, Phys. Rev. Lett. **75**, 1992 (1995).

[25] M. Yan, L. J. Rothberg, F. Papadimitrakopoulos, M. E. Galvin, and T. M. Miller, Phys. Rev. Lett. **72**, 1104 (1994).

[26] M. Yan, L. J. Rothberg, F. Papadimitrakopoulos, M. E. Galvin, and T. M. Miller, Phys. Rev. Lett. **73**, 744 (1994).

[27] K. Lehovec, Phys. Rev. **92**, 253 (1953).

[28] J. Fink, N. Nücker, B. Scheerer, A. vom Felde, H. Lindenberger, and S. Roth, in *Electronic Properties of Conjugated Polymers*, Springer Series in Solid-State Sciences Vol. 76 (Springer, Berlin, 1987), p. 79.

[29] T. P. Nguyen and V. H. Tran, Mater. Sci. Eng., B **31**, 255 (1995).