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# Photogeneration and recombination of charge carriers in LEDs: related organic materials

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This paper deals with the question of how charge carriers in conjugated polymers and their oligomeric counterparts can be photoexcited and how they recombine. It is intimately tied to the question concerning the magnitude of the exciton binding energy  $\Delta E_{\text{exc}}$ . Studies of fluorescence quenching by large electric fields indicate that  $\Delta E_{\text{exc}}$  must be about 0.4 eV. Geminate e-h pairs formed by field assisted dissociation of singlet excitons act as precursors for photoconduction. Another source of photo-generated charge carriers (holes) is dissociation of excited states at an electrode. It gives rise to a photocurrent action spectrum that is symbatic with absorption. Recombination of charge carriers is in accord with the Langevin formalism implying a mutual capture radius determined by the range of the coulombic potential.

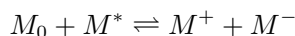
## 1. Introduction

To generate a pair of charge carriers in a molecular crystal requires the energy  $E_g = I_g - A_g - (P^+ + P^-)$ , where  $I_g$  is the gas phase ionization energy,  $A_g$  is the gas phase electron affinity and  $P^+$  and  $P^-$  are the polarization energies of the molecular radical ions in the solid phase.  $E_g$  can be identified with the adiabatic bandgap. For crystalline anthracene  $I_g = 7.4$  eV,  $A_g = 0.5$  eV and  $P^+ + P^- \approx 2.8$  eV, implying that  $E_g \approx 4.1$  eV.  $E_g$  exceeds the energy of a singlet exciton (3.1 eV) by roughly 1 eV. As a consequence, intrinsic photoconduction starts at photon energies no less than about 4 eV (Pope & Swenberg 1982). A singlet exciton can contribute to photoconductivity only in the presence of an acceptor to which the exciton can transfer one of its constituent charges at no expense of energy, the remaining charge being more or less free to follow an external applied field. Appropriate acceptors can be a metal contact with a suitably located Fermi level, a surface layer with either low lying lowest unoccupied molecular orbital (LUMO) or high lying HOMO, or molecular sensitizers present in the bulk of the material in the form of a deliberately added dopant or an inadvertant impurity. In these cases photoconductivity starts at the absorption edge of the material. If charge carriers are created in the course of excited state dissociation at the contact the action spectrum of photoconductivity is symbatic with absorption and provides information concerning the exciton diffusion length (Pope & Swenberg 1982).

Photoconductivity in molecular crystals is in accord with the above ideas while some conjugated polymers behave differently. Those that do follow the above principles are polydiacetylenes. Owing to their extremely short lifetime, singlet excitons cannot contribute to photoconductivity. It starts about 0.5 eV above the absorption

edge and marks onset of intrinsic photoionization (Pakbaz *et al.* 1994). However, in fluorescent systems such as the polyphenylenevinylenes (PPV) (Hörhold & Helbig 1987) and polythiophenes (Binh *et al.* 1992), in which singlet excitons live for some 0.1–1 ns, photoconductivity already starts at the absorption edge. This has been considered as evidence in favour of the notion that the exciton binding energy is of order  $kT$  only, implying the appropriateness of the one-electron semiconductor band picture for the description of the excited states (Pakbaz *et al.* 1994). On the other hand, there is abundant evidence, both experimental (e.g. Bässler *et al.* 1995) and theoretical (Chandross *et al.* 1994; Shuai *et al.* 1994; Conwell & Mizes 1995; Rice & Gartstein 1995) that the elementary excitations in fluorescent conjugated polymers of the PPV-type are, in fact, neutral excitons with a binding energy ranging between 0.2 and 0.9 eV.

One can view the above problem also from the standpoint of chemical equilibrium. Whether the equilibrium



is on the left or right side,  $M_0$ ,  $M^*$  and  $M^\pm$  being neutral, photoexcited, and charged forms of a conjugated polymer/oligomer, depends on the free energy of the reaction. It is obvious that for a photovoltaic device to be efficient photoionization must not require extra energy. On the other hand, organic light emitting diodes (LEDs) would not work unless recombination of a pair of charge carriers was an exothermic process involving reactants with coulombic capture cross-section. Studying how photoexcitations can dissociate into charge carriers and what the principles are that govern their recombination will therefore provide an answer to the question concerning the binding energy of a photoexcited state in conjugated systems. Resolving this question is fundamental to understanding whether or not conjugated polymers differ from conventional molecular solids as far as their opto-electronic properties are concerned as well as for the design of efficient photoelectronic devices such as LEDs or solar cells.

The present paper focuses on three topics: (i) electric field induced fluorescence quenching as a way to estimate the energy it costs to dissociate an excited state; (ii) cw-photoconductivity; and (iii) a conceptual framework for charge carrier recombination in random organic solids.

## 2. Photoluminescence quenching by electric fields

If an exciton is dissociated by an electric field, it can no longer contribute to luminescence. The ionization of weakly bound Wannier excitons in inorganic semiconductors by electric fields has been studied extensively at low temperatures. It manifests itself in a broadening of the absorption line and its eventual disappearance with increasing field strength. Typical values of the excitonic binding energy  $\Delta E_{\text{exc}}$  are of order 10 meV implying critical fields of the order of a few  $\text{kV cm}^{-1}$  for exciton ionization.

To dissociate an excited singlet state of a conjugated polymer requires field-assisted transfer of one of the constituent charges to a neighbouring chain or chain segment. To first order approximation, this would occur if the gain in electrostatic energy,  $eE\Delta z$ , compensated for the energy expense for the charge transfer in zero field. For  $\Delta z = 10 \text{ \AA}$  and  $E = 2 \times 10^6 \text{ V cm}^{-1}$ ,  $eE\Delta z = 0.2 \text{ eV}$  is estimated. If exciton binding energies were of that order of magnitude, one would expect PL quenching to occur

in electric fields in excess of  $1 \text{ MV cm}^{-1}$ . The above simple argument underestimates  $\Delta E_{\text{exc}}$  since formation of an e-h pair on chains, only  $10 \text{ \AA}$  apart, costs only a fraction of the coulombic binding energy.

PL quenching experiments were performed with films of poly-(phenyl-*p*-phenylenevinylene) (PPPV) doped into polycarbonate (PC) (Deussen *et al.* 1995) as well as with an oligomeric model compound, tris(stilbene)amine (TSA) doped into polycarbonate, and different polystyrene derivatives (Deussen *et al.* 1996). TSA was chosen because it contains stilbene substituents resembling the PPV repeat unit and it absorbs in the same spectral region as PPPV does. The samples were prepared in sandwich configuration between indium tin oxide (ITO) and aluminium (AL)-contacts (as commonly used for electroluminescence studies). To minimize current flow the devices were operated under 'reverse' bias, i.e. with ITO being negative. Fluorescence quenching, or relative reduction  $\Phi$ , is experimentally determined as  $\Phi(E) = (I(0) - I(E))/I(0)$ , where  $I(0)$  and  $I(E)$  are the fluorescence intensities at zero bias and with a field  $E$  applied to the sample, respectively, normalized to the intensity of the incident excitation light.

The spectral dependence of  $\Phi$  is shown in figure 1 for PPPV. Analogous results were obtained for TSA. In both cases  $\Phi$  is independent of excitation wavelength except at the very absorption tail where  $\Phi$  drops to zero in the case of PPPV and can even become negative in the case of TSA. 'Negative' quenching efficiency means that the PL intensity increases in the presence of an electric field. It is due to the Stark shift of the absorption spectrum which causes the optical density of the sample to increase at the absorption tail. The quenching efficiency depends on both the concentration of the active sites and the electric field (figure 2).

Experiments were also performed in a time-resolved fashion (Deussen *et al.* 1996). They showed that the quenching effect is not instantaneous but occurs with time constants of order  $1 \text{ ps}^{-1}$  in the case of PPPV and of order  $10 \text{ ps}^{-1}$  in the case of TSA blends. This rules out an interpretation of the effect in terms of a field-induced redistribution of oscillator strength, e.g. via opening of a charge transfer transition, and indicates that PL quenching is a consequence of the action of the electric field on the excited state of a chromophore.

The concentration dependence of  $\Phi$  testifies to the intermolecular nature of the quenching process. Since only charge transfer responds to an electric field, it is therefore straightforward to attribute photoluminescence quenching to the dissociation of a neutral singlet exciton on a chromophore, which can be a segment of a PPPV chain or a TSA molecule, into an e-h pair residing on adjacent chromophores. From the fact that in PPPV the quenching efficiency is independent of concentration for PPPV concentrations greater than 30% and starts decreasing below, while in TSA it decreases continuously upon dilution, one can conclude that in PPPV both interchain and intrachain dissociation processes are operative. Apparently, charge transfer processes between two segments of the same chain render even an isolated polymer coil, to a certain extent, self-sufficient, and allow for exciton dissociation into a geminately bound e-h pair.

The quenching efficiency is virtually constant within the inhomogeneously broadened absorption spectrum including its vibronic replica. A decrease is seen only at the very absorption tail. This indicates that the actual quenching step does not occur until any vibrational or electronic excess energy has been dissipated. From photoluminescence studies with sub-picosecond time resolution (Kersting *et al.* 1993), it is known that vibrational cooling in PPPV occurs within 100 fs. Subsequent electronic

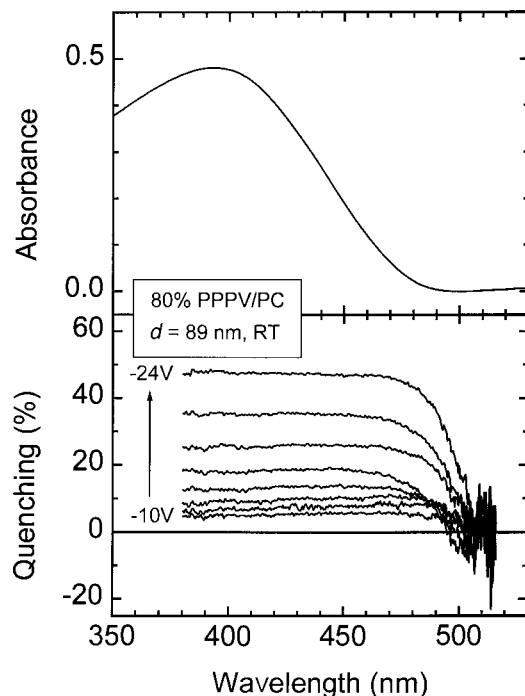


Figure 1. Absorption spectrum (top) and spectral dependence (bottom) of the fluorescence quenching in an 89 nm thick 80:20 poly(phenylphenylenevinylene):polycarbonate film sandwiched between ITO and Al-electrodes. The parameter is the applied (reverse) voltage.

relaxation of the vibrationally cold singlet exciton within the manifold of states—segments of a PPV chain that differ with regard to effective conjugation length and, concomitantly, in transition energy or TSA molecules sitting in a statistically varying environment—is a dispersive rate process, the fastest steps occurring on a 1 ps time scale.

The pronounced field dependence of PL quenching (figure 2) and the magnitude of the electric fields that are necessary for a significant reduction of PL intensity, indicate that the excited state must have a binding energy  $\Delta E_{\text{exc}} \gg kT$ . Monte Carlo (MC) simulations of the field dependence of PL quenching give a good fit to experimental data for values of  $\Delta E_{\text{exc}} = (0.4 \pm 0.1)$  eV (Deussen *et al.* 1996). They take into account: (i) spectral relaxation in a Gaussian DOS while migrating incoherently within the manifold of hopping states; (ii) capture by non-radiative traps; (iii) radiative decay; and (iv) field-assisted exciton dissociation.

The efficiency of field quenching of the excited state of TSA depends on the matrix and increases in the series tert-butyl-polystyrene, polystyrene, chloro-polystyrene. This concurs with the increase of the net dipole moments (0, 0.4 and 1.7 D, respectively) indicating that increasing polarity facilitates e-h pair formation from a molecular  $S_1$  state.

### 3. Photoconduction

Photoconduction is an important, though not always unambiguous, signature of optical ionization in a solid. In a classic semiconductor, the dominant optical transition is a valence to conduction band transition. Due to the joint effects of the weak

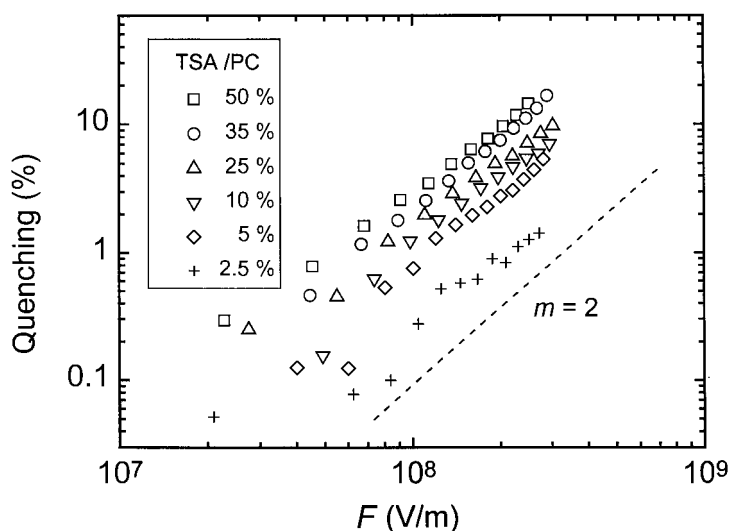


Figure 2. Concentration dependence of the electric field induced photoluminescence quenching efficiency for trisilbeneamine:polycarbonate diodes parametric in electric field ( $T = 77$  K).

binding energy of Wannier-type excitons, and mean carrier free paths being in excess of the coulombic capture radius, the resulting e-h pairs are free. The quantum efficiency for optical charge carrier formation  $\psi_{PC}$ , defined as the number of carriers generated per absorbed photon, is near-unity within the entire absorption range and independent of temperature and electric field.

In conventional molecular solids photocarrier generation is a two step process. There is a fast, optical process generating geminate charge carrier pairs that can subsequently dissociate via temperature- and field-assisted diffusion within the mutual coulombic well. The latter process is tractable within the framework of Onsager's theory for geminate pair dissociation in the presence of an infinite sink that accounts for e-h collapse being an exothermic process. There is abundant evidence that, by and large, this formalism describes charge carrier generation both in molecular crystals (Pope & Swenberg 1982) and in systems like molecularly doped organic photoconductors (Borsenberger & Weiss 1993).

The primary event that generates a geminate e-h pair can either be direct charge transfer or autoionization of an excited molecular state with sufficient energy. Since in neat molecular solids the energy required to produce a geminate pair exceeds the energy of a molecular singlet state, intrinsic photoconduction starts above the absorption edge, the energy off-set being a crude measure of the energy it costs to transfer one charge from a molecule excited to its  $S_1$  state to the LUMO or HOMO of a neighbouring molecule. Photoconduction action spectra coincident with absorption spectra are only observed if there is a sensitizer present to which the excited molecule can transfer either an electron or a hole at no expense of energy. Such processes usually occur at the surface of molecular solids with metal electrodes, sensitizing dye layers, or oxidation products that can act as electron acceptors. The surface nature of that process implies that only those excitations that diffuse towards the surface during their lifetime  $\tau_0$  can contribute. Solution of the diffusion equation indicates that this fraction is  $I_d/(I_d + \alpha^{-1})$ ,  $I_d = (D\tau_0)^{1/2}$  being the diffusion length and  $\alpha^{-1}$  the penetration depth of the incident light. In that case, the action spectrum is symbiotic with the absorption and the efficiency of the process increases with the

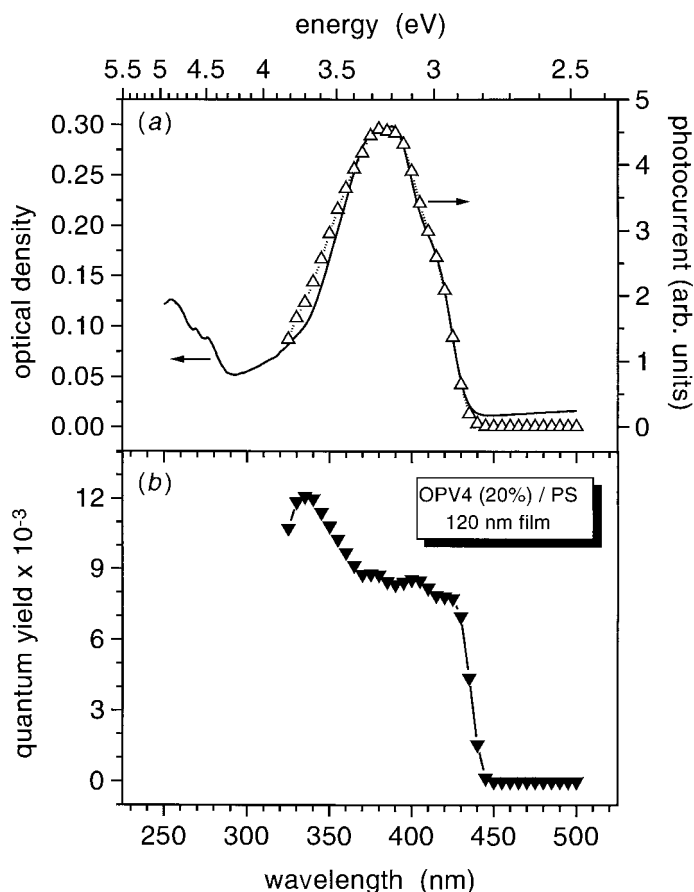


Figure 3. (a) Absorption and photocurrent action spectra of a 120 nm thick OPV:PS film. The photocurrent was measured upon irradiating through the positively biased ITO electrode ( $E = 1.7 \times 10^5 \text{ V cm}^{-1}$ ,  $T = 298 \text{ K}$ ). (b) Quantum yield of photocarrier production calculated on the premise that absorption within a 2 nm thick interfacial OPV layer contributes to the photocurrent.

diffusion constant  $D$ . By this token, it is more efficient in single crystals than in random media. In the case of no exciton diffusion, the number of excited surface states is directly proportional to the absorption spectrum.

Sensitized photoconduction can also occur if the sample contains dopants, inadvertently present or deliberately added, that can act as an electron or hole acceptor. In that case, an excited state of the bulk material can dissociate into a pair of charges, one being trapped at the sensitizer, the other one being more or less free to contribute to photoconductivity. However, to establish steady state conditions requires that the detrapping of the trapped carrier, or its neutralization by injected carriers, is efficient enough to prevent build-up of an internal space charge. Another source of extrinsic photoconductivity is ionization of defects. For this to occur, the LUMO/HOMO of the defect must be above (below) the conduction (valence) band of the bulk material.

Intrinsic photoconduction, on the other hand, depends on the fraction of the incident photons that are absorbed,  $1 - \exp(-\alpha L)$ ,  $L$  being the sample thickness, and the probability  $p$  of their dissociation. In addition to being a function of temperature

and electric field,  $p$  will also depend on photon energy because the formation of a geminate e–h pair requires more energy than formation of an exciton.

The crucial problem we wanted to address by performing cw-photoconduction experiments is to decide whether the coincidence of absorption and photoconduction often found in PPVs is due to an extrinsic or an intrinsic process. The answer is intimately tied to the magnitude of the energy of a geminate interchain e–h pair—synonymously called indirect exciton or charge transfer state—relative to the energy of an on-chain exciton. On average, the energy of the former cannot be less than that of the latter because otherwise no fluorescence from on-chain excitons should be observable.

Photoconduction experiments were performed on optically thin (about 100 nm) spin cast as well as optically thick (7–9  $\mu\text{m}$ ) solution cast films of the oligophenylenevinylene (OPV) containing four phenyl-rings blended with polystyrene (PS). Oligomers are profitably used in such a study since they can be purified extensively, have a well defined structure, and their properties resemble closely those of their polymeric counterparts (Schmidt *et al.* 1995). The samples were sandwiched between ITO and Al-electrodes. This configuration ensures that bimolecular charge recombination is kept at a minimum as evidenced by the linear intensity dependence of the photocurrent. Under these circumstances the latter is a measure of the number of carriers generated as a function of photon energy, electric field and temperature.

Figure 3 shows the photocurrent and absorption spectra of a 120 nm thick OPV:PS sample upon irradiation from the positively biased ITO-side. Under reversed polarity the photocurrent was more than two orders of magnitude less and could barely be discriminated from the dark current. Normalizing the photocurrent to the number of absorbed photons gives the yield spectrum. It features a sharp rise at the absorption edge followed by a plateau and finally an increase at a photon energy approximately 0.5 eV above the  $S_1 \leftarrow S_0(0-0)$  absorption edge. The field dependence reproduces as a straight line if plotted on a  $\log i_{\text{ph}}$  versus  $E^{-1}$  scale (figure 4).

The strong polarity dependence of the photocurrent in the thin OPV sample argues against volume photoionization. Excitation occurs homogeneously throughout the entire volume and trapping effects, if occurring, had to effect photogeneration in a symmetric way. The polarity dependence proves that the photocurrent is dominated by optical injection from the positively biased ITO contact, any volume dissociation of excited states being of minor importance if occurring at all. Injection must result from the transfer of an electron from an excited OPV molecule at or near the interface to the ITO. This process is exothermic for molecules in immediate contact with the ITO while for non-nearest excited OPV molecules it is impeded by an energy barrier which basically reflects the energy gap between the LUMO of a neutral molecule and that of an excited molecule whose HOMO is only singly occupied. Since that energy barrier has to be penetrated by tunnelling an increase of the primary excited state energy will facilitate excited state dissociation. This provides an explanation for the increase of the yield at photon energies of about 0.5 eV above the absorption edge. Although this energy is close to the exciton binding energy, estimated on the basis of photoluminescence quenching studies, we are reluctant to consider photocarrier action spectra as being a direct way of measuring  $\Delta E_{\text{exc}}$ . The reason is that  $\Delta E_{\text{exc}}$  is, by definition, the energy needed to dissociate a molecular excited state into a pair of radical cations and anions at infinite distance inside the bulk material. However, upon excited state dissociation at an electrode a hole is generated close to its twin in the electrode and subsequent full dissociation is an endothermic process involving temperature and field assisted diffusion.



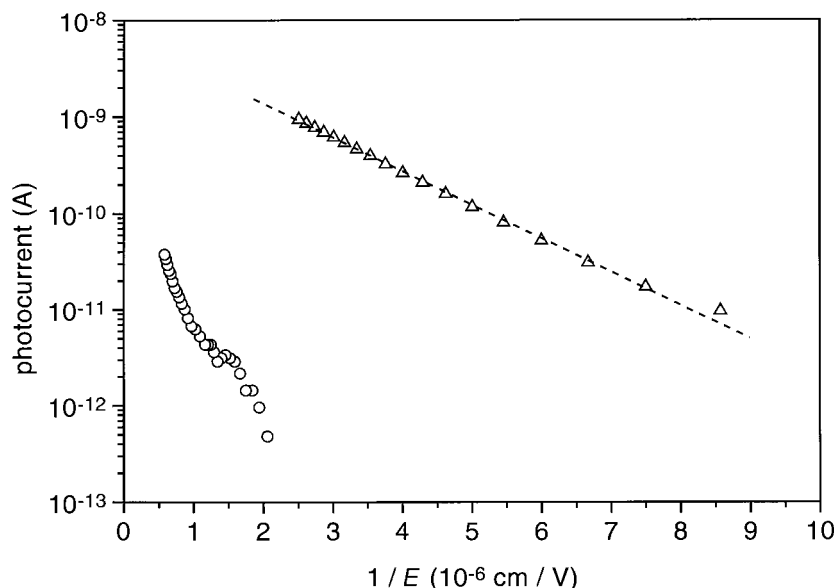


Figure 4. Field dependences of the photocurrent measured with a 120 nm thick OPV:PS sample upon irradiating through the positively biased ITO electrode (triangles) and with a 7  $\mu\text{m}$  thick film upon irradiating through the positively biased Al-contact (circles).

The latter process should be tractable within Onsager's theory of geminate pair dissociation. A recent Monte Carlo simulation (Gartstein & Conwell 1996) for a disordered system showed that its field dependence is virtually identical to that which has been observed (figure 4) and the temperature dependence is very weak, again in agreement with experiment. This demonstrates that excited state dissociation at an ITO electrode provides the essential contribution to the photocurrent. Its spectral signature being the symbatic relation between absorption and quantum yield. This process is much less efficient at an Al-electrode because of both excited state quenching by the metal electrons and chemical modification of the interface.

Basically the same photoionization phenomenon is observed upon irradiating a thick OPV:PS film through a positively biased ITO electrode. However, the phenomenology of photoconduction changes significantly upon reversing the polarity and irradiating through a semitransparent, positively biased Al-contact. To generate a photocurrent of comparable magnitude requires an electric field that is larger by more than a factor of two, and the yield spectrum, defined as the number of charges collected per absorbed photon, is flat within the main portion of the  $S_1 \leftarrow S_0$  absorption band and features peaks at the low/high energy side (figure 5). In conjunction with the polarity dependence of the photocurrent noticed with the 120 nm sample, and drawing upon the fluorescence quenching studies reported above, it is straightforward to assign it to volume photoionization of excited states in the presence of a high electric field. The e-h pairs that are created by the field-induced dissociation of an  $S_1$  state must act as precursors for intrinsic photoconduction. The photocarrier yield must then be the product of the primary field dependent yield  $\psi_0$  and the escape probability of the pair from their mutual coulombic attraction.  $\psi_{\text{esc}}$  can be recovered from the photocurrent by considering the  $E^2$ -dependence of primary dissociation. Figure 6 shows a plot of  $\psi_{\text{esc}}$ , determined in that way, as a function of the applied field. It is compared to the prediction of three-dimensional Onsager

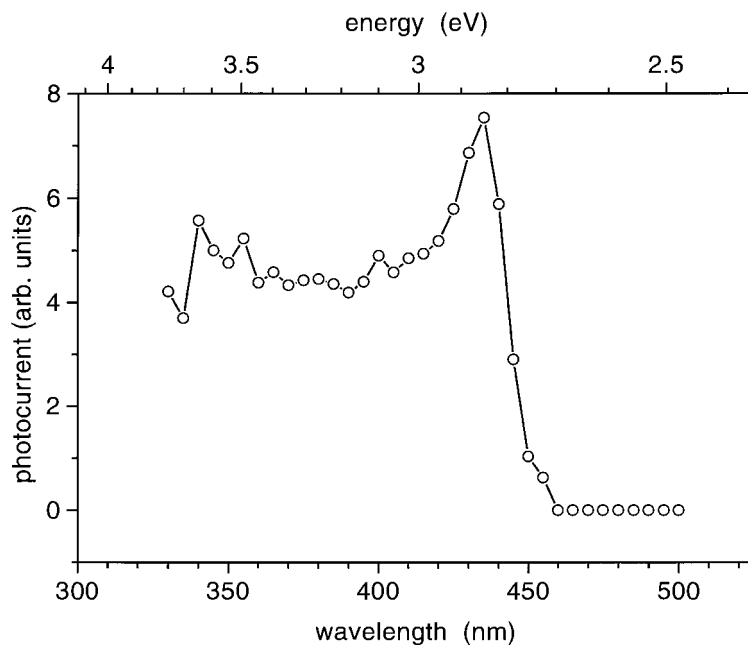


Figure 5. Photocurrent action spectrum of a 7  $\mu\text{m}$  OPV:PS film upon exciting through a semitransparent positively biased Al-electrode ( $E = 1.3 \times 10^6 \text{ V cm}^{-1}$ ,  $T = 298 \text{ K}$ ).

theory on the premise of either a fixed initial pair distance of 10  $\text{\AA}$  and an exponential distribution of initial pair distances (Borsenberger & Weiss 1993). The intention of this comparison is not to suggest quantitative agreement—which cannot be expected since Onsager’s treatment is based upon a spherically symmetric initial pair distribution which cannot be established if the primary event is field assisted—but to demonstrate qualitative consistency.

The low energy peak of the yield spectrum is likely to be caused by detrapping of charge carriers in the volume of a bulk sample while the high energy peak indicates an increase of the photoionization yield at higher energies in agreement with what has been observed in molecular crystals.

#### 4. Charge carrier recombination

In organic solids, charge carrier recombination can be described on the basis of the Smoluchowski theory for bimolecular reactions predicting the bimolecular rate constant to be

$$\gamma = 4\pi R(D_+ + D_-), \quad (4.1)$$

$R$  being the distance at which the particles interact. In the strong scattering limit  $R$  has to be identified with the coulombic radius

$$r_c = \frac{e^2}{4\pi\epsilon\epsilon_0 kT}, \quad (4.2)$$

because oppositely charged carriers approaching each other to a distance  $r_c$  will fall into their mutual coulombic funnel and release the energy gained into the heat bath (Langevin case). Inserting (4.2) into (4.1) and making use of the Einstein relation

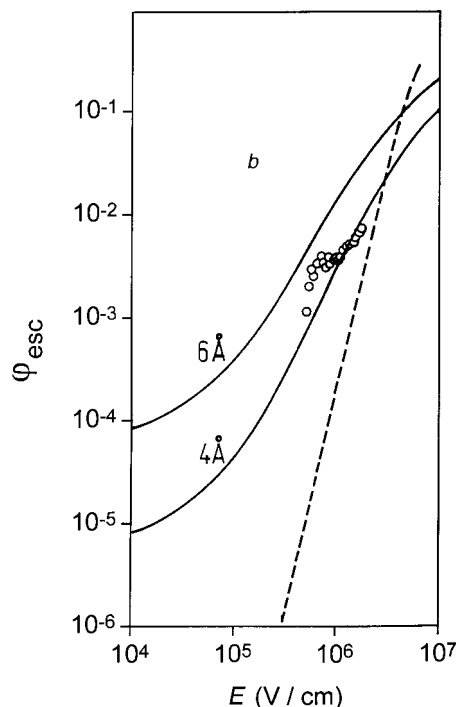


Figure 6. Theoretical three-dimensional Onsager plots for an exponential distribution of the initial pair distances (characterized by the parameter  $b$ ) and for a  $\delta$ -shaped initial pair distribution  $r_0 = 10 \text{ \AA}$  (curve). The data points are extracted from the photocurrent measured with the  $7 \mu\text{m}$  sample upon  $\text{Al}^+$  excitation by normalizing the photocurrent to the number of exciton quenching events. (For details see text).

$eD = \mu kT$  yields

$$\frac{\gamma}{\mu} = \frac{e}{\epsilon\epsilon_0}. \quad (4.3)$$

It is valid as long as the carrier mean free path is much less than  $r_c$ , as it is in molecular crystals, and implies that recombination is diffusive rather than ballistic.

Since no theory is currently available to treat the random walk of a pair of charges in an energetically roughened landscape with superimposed long ranged Coulomb interactions, a Monte Carlo simulation study has been conducted to model bimolecular charge recombination under this premise (Albrecht & Bässler 1995). A test sample with cubic symmetry and periodic boundary conditions containing point sites to represent the segments of a conjugated polymer was set up by computer. A stationary positive charge was positioned inside the sample. Negative charge carriers were started at variable positions within a boundary plane and allowed to migrate, via hopping, towards the exit contact under the action of a bias field. The simulated quantity was the recombination probability of the injected charge. Variation of the binding energy of an e-h pair was taken into account by considering a truncated coulomb potential

$$V(r) = \begin{cases} -e^2/4\pi\epsilon\epsilon_0 r, & r > na, \\ -e^2/4\pi\epsilon\epsilon_0 na, & r \leq na, \end{cases} \quad (4.4)$$

$a$  being the intersite distance and  $n \geq 1$  an integer. The quantity  $V(r = na)$  is

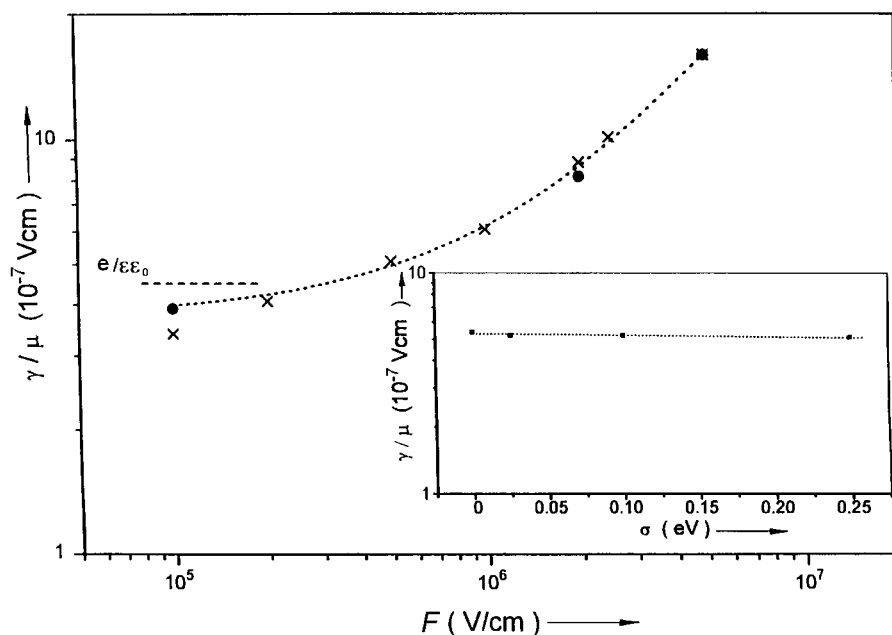


Figure 7. Dependence of the  $\gamma/\mu$  ratio on electric field for  $\sigma = 0.1$  eV. Crosses refer to  $T = 350$  K, circles to  $T = 250$  K. The inset illustrates the independence of  $\gamma/\mu$  of the width  $\sigma$  of the density of states ( $F = 5 \times 10^5$  V cm $^{-1}$ ;  $T = 350$  K).

identified with the exciton binding energy  $\Delta E_{\text{exc}}$ . By considering the competition between diffusion and drift, one can show that the effective recombination cross section  $q^{\text{eff}}$  of the stationary charge is related to  $\gamma/\mu$  via

$$\gamma/\mu = q^{\text{eff}} F. \quad (4.5)$$

Plots of  $\gamma/\mu$  and  $q^{\text{eff}}$  as functions of the electric field  $F$  are shown in figure 7, while the variation of  $q^{\text{eff}}$  with exciton binding energy  $\Delta E_{\text{exc}}$  is presented in figure 8. It is obvious that  $q^{\text{eff}}$  is constant for  $\Delta E_{\text{exc}} > 0.2$  eV but decreases sharply as  $\Delta E_{\text{exc}}$  decreases. This means that under the condition  $\Delta E_{\text{exc}} \leq kT$ , the probability for recombination of a pair of charge carriers in a LED should be almost two orders of magnitude less than what it is in a conventional molecular solid. This would be prohibitive for efficient polymeric LEDs and at variance with the maximum observed quantum yields observed so far.

## 5. Concluding remarks

Photoluminescence quenching as well as photoconductivity studies support the notion that the primarily optically excited states in conjugated polymers/oligomers of the PPV type are neutral excitons. To dissociate them into pairs of free radical cations and anions requires an energy of about 0.4–0.5 eV. This energy, defined as the exciton binding energy, is comparable to that in polydiacetylenes. There are two essential differences between both types of conjugated systems. One is that in the PDAs the short exciton lifetime (less than 1 ps) precludes their dissociation. The other relates to the structural order present in single crystalline specimens. This permits the detection of an optical transition to a delocalized conduction band state

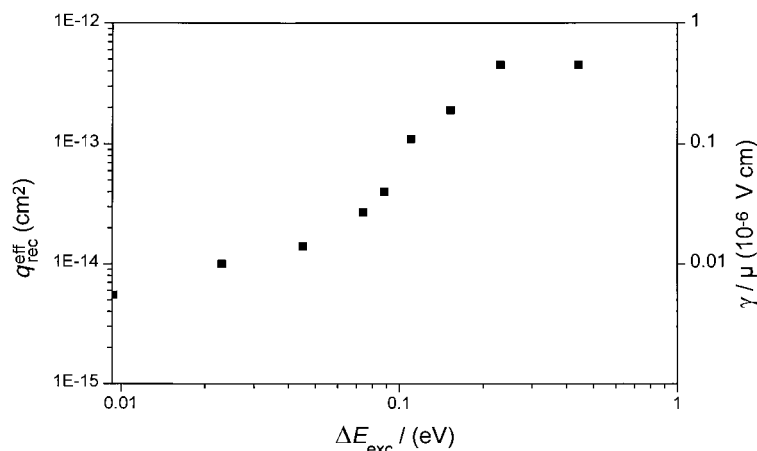


Figure 8. Variation of the effective recombination cross section of a charge carrier at an electric field of  $10^6 \text{ V cm}^{-1}$  as a function of the exciton binding energy  $\Delta E_{\text{exc}}$ .  $\gamma/\mu$  is related to  $q_{\text{rec}}^{\text{eff}}$  via equation (4.5).

via electroabsorption spectroscopy (Weiser 1992) and, concomitantly, allows determination of the exciton binding energy directly. In the more or less disordered PPVs, and their oligomeric counterpart structures, photoionization of a singlet exciton is always a multi-step process. The first one of these is the rapid transfer of one of the charges comprising the exciton to an acceptor, which can be an electrode or a dopant molecule, or to a bulk molecule if the electric field is large enough to compensate for the energy deficit. The thus formed geminate pair can subsequently dissociate via field and temperature assisted diffusion as described by Onsager's theory. Whether or not off chain e-h pairs can be generated by a direct optical transition at an appropriate transition energy needs to be clarified. The electro-optic properties of conjugated polymers and their oligomeric counterparts is, thus, very similar to that of 'classic' molecular solids, the main difference being that the exciton binding energy is only about 0.5 eV as compared to 1 eV in molecular crystals. This reduction is related to the larger exciton radius, borne out by electroabsorption studies.

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## References

- Albrecht, U. & Bässler, H. 1995 Langevin-type charge carrier recombination in a disordered hopping system. *Phys. Stat. Sol. B* **191**, 455.
- Bässler, H., Brandl, V., Deussen, M., Göbel, E. O., Kersting, R., Kurz, H., Lemmer, U., Mahrt, R. F. & Ochse, A. 1995 Excitation dynamics in conjugated polymers. *Pure Appl. Chem.* **67**, 377.
- Binh, N. T., Gailberger, M. & Bässler, H. 1992 Photoconduction in poly(3-alkylthiophene) I. Charge carrier generation. *Synth. Met.* **47**, 77.
- Borsenberger, P. M. & Weiss, D. S. 1993 *Organic photoreceptors for imaging systems*. New York: Marcel Dekker.
- Conwell, E. M. & Mizes, H. A. 1995 Photogeneration in conducting polymers. *Synth. Met.* **69**, 613.

*Phil. Trans. R. Soc. Lond. A* (1997)

- Chandross, M., Mazumdar, S., Jeglinski, S., Wei, X., Vardeny, Z. V., Kwock, E. W. & Miller, T. M. 1994 Excitons in poly(paraphenylenevinylene). *Phys. Rev. B* **50**, 14 702.
- Deussen, M., Scheidler, M. & Bäessler, H. 1995 Electric field induced photoluminescence quenching in thin film light emitting diodes based on PPV. *Synth. Met.* **73**, 123.
- Deussen, M., Haring Bolivar, P., Wegmann, G., Kurz, H. & Bäessler, H. 1996 Electric field induced photoluminescence quenching in molecularly doped polymer LEDs. *Chem. Phys.* **207**, 147.
- Gartstein, Yu. N. & Conwell, E. M. 1996 Field-dependent thermal injection into a disordered molecular insulator. *Chem. Phys. Lett.* **255**, 93.
- Hörhold, H. H. & Helbig, M. 1987 Poly(phenylenevinylene)s—synthesis and redoxchemistry of electroactive polymers. *Makromol. Chem. Macromol. Symp.* **12**, 229.
- Kersting, R., Lemmer, U., Mahrt, R. F., Leo, K., Kurz, H., Bäessler, H. & Göbel, E. O. 1993 Femtosecond energy relaxation in  $\pi$ -conjugated polymers. *Phys. Rev. Lett.* **70**, 3820.
- Pakbaz, K. Lee, C. H., Heeger, A. J., Hagler, T. W. & McBranch, D. 1994 Nature of the primary photoexcitations in poly(arylene-vinylene)s. *Synth. Met.* **64**, 295.
- Pope, M. & Swenberg, C. E. 1982 *Electronic processes in organic crystals*. Oxford: Clarendon.
- Rice, M. & Gartstein, Yu. N. 1995 Excitons and interband excitations in Polyphenylenes. *Synth. Met.* **73**, 183.
- Schmidt, A., Anderson, M. L., Dunphy, D., Wehrmeister, T., Müllen, K. & Armstrong, N. R. 1995 Photoelectron and optical spectroscopic investigations of the electronic structure of oligo(*p*-phenylenevinylene)s in the solid state. *Adv. Mat.* **7**, 722.
- Shuai, Z., Brédas, J. L. & Su, W. P. 1994 Nature of photoexcitations in poly(paraphenylenevinylene) and in oligomers. *Chem. Phys. Lett.* **228**, 301.
- Weiser, G. 1992 Stark effect of the one-dimensional Wannier excitons in polydiacetylene single crystals. *Phys. Rev. B* **45**, 14 076.

### Discussion

M. SCHOTT (*Groupe de Physique des Solides, Université Paris, France*). (1) Concerning the question about the efficiency of charge carrier recombination in double injection, this will depend on the transport properties of the injected carriers. If the mobilities are small enough—the usual case in molecular systems—so that the mean free paths are much smaller than the e–h distance at which the pair binding energy is *ca. kT*, the theory of recombination in dense gases (Langevin) applies, yielding the universal relation between recombination cross section and mobility given by Professor Bäessler. In this case, and in a situation of double injection at contacts, it can be shown that almost all carriers may recombine inside the material (Lampert & Mark 1980; Torpey 1984). The concentration of carriers of one type at their exit contact is very small, the electron and hole densities are different almost everywhere in the material, and space charge is present. If, however, the mean free path is large, as in ‘usual’ semiconductors, the Langevin recombination theory does not apply and recombination becomes less efficient. The limiting case, opposite to the Langevin one, would be that of a sample filled by an injection plasma, almost electrically neutral almost everywhere; then, only a small fraction of the carriers do recombine inside the material (Lampert & Mark 1980; Parmenter & Ruppel 1959). This situation is unlikely to be of importance in molecular and polymeric materials.

(2) Field ionization of an exciton at high electric fields is a possibility. I would like to point out that an exciton can also be quenched by interaction with a charge carrier, be it free or trapped. Since the carrier survives the interaction, usually as a free one, the same carrier is able to quench several excitons. If both excitations are fairly localized, one can think in terms of Förster-type transfer, leading to a quenching range of 1–2 nm. This type of exciton quenching in the presence of an

electric field may depend on the field direction, via the charge carrier concentrations, which depend—among other parameters—on the currents injected at the electrodes.

One may conjecture that the process might lead to a decrease of electroluminescence efficiency at very large fields (i.e. large currents).

S. BARTH. (1) Our recent studies of charge carrier recombination in random media employing the Monte Carlo simulation techniques confirmed that the Langevin description is valid in hopping systems of arbitrary degree of disorder (Albrecht & Bässler 1995*a*). As the mean free paths of the carriers increase and as the coulombic potential becomes screened, the rate of bimolecular charge carrier recombination decreases (Albrecht & Bässler 1995*b*).

(2) At large currents, one observes polarity-dependent fluorescence quenching, which may well be caused by charge carrier exciton annihilation.

#### *Additional references*

Albrecht, U. & Bässler, H. 1995*a* *Phys. Stat. Sol. B* **191**, 455.

Albrecht, U. & Bässler, H. 1995*b* *Chem. Phys.* **199**, 207.

Lampert, M. A. & Mark, P. 1980 *Current injection in solids*. New York: Academic.

Parmenter, R. H. 1959 *J. Appl. Phys.* **30**, 1548.

Torpey, P. A. 1984 *J. Appl. Phys.* **56**, 2284.