

## Intrinsic Photoconduction in PPV-Type Conjugated Polymers

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Steady state photoconduction experiments have been performed on thin films of derivatives of polyphenylenevinylene contacted in sandwich configuration. The use of a silicon monoxide blocking layer allows the separation of intrinsic from extrinsic photocurrents. Intrinsic photogeneration increases with electric field, temperature, and photon energy in agreement with the 3D version of Onsager's theory of geminate pair dissociation adapted to energetically random hopping systems. The thermalization distance, which determines the escape rate, increases with the effective conjugation length of the chain segments. The average energy required to dissociate a confined on-chain excitation is 0.4 eV. [S0031-9007(97)04621-8]

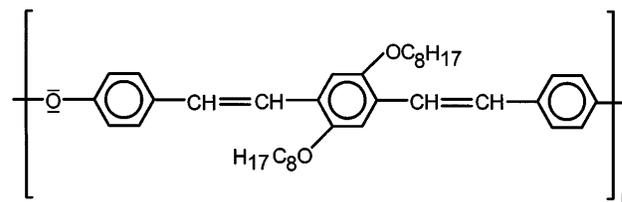
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The energy required to dissociate a singlet exciton in a molecular crystal into a pair of free charge carriers is typically 1 eV. It is for this reason that intrinsic photoconductivity starts  $\sim 0.5$  to 1 eV above the optical absorption edge. A photon of that energy is able to generate a Coulombically bound (geminate) electron-hole ( $e-h$ ) pair at some distance  $r_0$ , called the thermalization distance [1,2]. It can either dissociate into a pair of free charge carriers or recombine to form an excitonic state that may or may not decay radiatively. The trade-off between pair dissociation and recombination has successfully been modeled by Onsager's theory of geminate pair recombination [3]. An already thermalized exciton can dissociate efficiently only if it can transfer one of its constituent charges to an extrinsic acceptor—a dopant or an electrode—with appropriately located energy levels to render that process exothermic. Its twin can follow a collecting electric field at little cost of thermal energy and cause unipolar extrinsic photoconductivity, whose action spectrum is symbatic with the absorption spectrum.

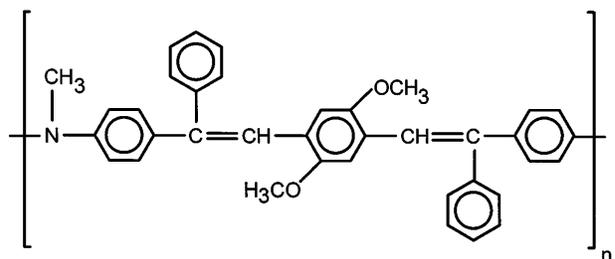
The coincidence between the onset of optical absorption and photoconductivity in conjugated polymers has been taken as evidence for the identity of optical and electrical gap in the sense of semiconductor theory [4], although there is abundant evidence for the primary optical excitations being neutral excitons rather than unbound polaron pairs [5]. Both results can be reconciled if one associates the photocurrent generated by "band gap" light to an extrinsic process. The work of Chandross *et al.* [6] on a derivative of polyphenylenevinylene (MEH-PPV) supported this hypothesis, as did recent photoconductivity work on an oligomeric model compound of polyphenylenevinylene (PPV) [7]. However, final proof requires an unambiguous separation between extrinsic and intrinsic sources of photoconductivity in conjunction with experiments delineating the dependence of the intrinsic photoionization yield  $\varphi_b$  on electric field, temperature, and photon energy in a quantitative fashion in order to identify the photoionization mechanism on the basis of func-

tional dependencies. It is of particular importance to clarify whether or not the absolute value of  $\varphi_b$ , as well as its field dependence, varies with photon energy. In molecular crystals,  $\varphi_b$  does increase with  $h\nu$  because higher photon energies facilitate the production of less tightly bound geminate pairs that, concomitantly, are more liable to subsequent dissociation, reflected by a flattening of the  $\varphi_b(E)$  dependence. No such dependence is expected if primary photoexcitations were to generate free carriers already, as is the case in semiconductors at ambient temperature. In this Letter, we present evidence for conjugated polymers to follow the predictions of Onsager's theory as far as intrinsic photocarrier generation is concerned and show that the yield depends on the effective conjugation length of the chain segments.

Cw-photoconductivity measurements have been performed on typically 100 nm thick spin coated films of two differently substituted derivatives of PPV, poly(oxy-1,4-phenylene-1,2-ethynylene-2,5-dioctyl-oxy-1,4-phenylene-1,2-ethynylene-1,4-phenylene) (PPV-ether):



and poly(methylimino-1,4-phenylene-1-phenyl-1,2-ethynylene-2,5-dimethoxy-1,4-phenylene-2-phenyl-1,2-ethynylene-1,4-phenylene) (PPV-amine):



They differ with regard to their effective conjugation length because the ether linkage interrupts  $\pi$  conjugation more efficiently than does the amino linkage as indicated by the bathochromic shift of the absorption threshold [ $20\,000\text{ cm}^{-1}$  for PPV-amine as compared to  $21\,700\text{ cm}^{-1}$  for PPV-ether (see Fig. 1)]. Site selectively recorded cw-fluorescence spectra prove that the low energy absorption tail is due to intrinsic states rather than extrinsic defects. The synthetic routes by which these polymers are made [8] guarantees a high level of purity, inaccessible with standard PPV. For this reason, one can expect defect-sensitized bulk photocarrier generation to be less important than in standard PPV. The samples were sandwiched between an aluminum (Al) and an indium tin oxide (ITO) electrode. To investigate the role of carrier injection, part of the ITO was covered by a 8–10 nm thick silicon monoxide (SiO) layer, known to block charge injection, yet—by virtue of its lower band gap and its higher dark conductivity as compared to that of the polymers [ $10^{-13}$  vs  $10^{-15}$  ( $\Omega\text{ cm})^{-1}$ —to affect discharge of carriers only marginally. To exclude any distortion of the  $j(E)$  characteristic due to residual internal space charge accumulation, photocurrents were recorded in a pointwise manner taking particular care in cleaning the sample prior to each measurement. Further experimental evidence against space charge effects being important derived from (i) the absence of significant photocurrent hysteresis effects, (ii) the strictly linear dependence of photocurrents on light intensity, and (iii) the independence of UV-excited photocurrents in PPV-amine on the presence of a SiO layer. The samples were irradiated either from the ITO side or through the semitransparent Al electrode by light from a calibrated xenon lamp. Experiments on PPV-amine were done using quartz optics.

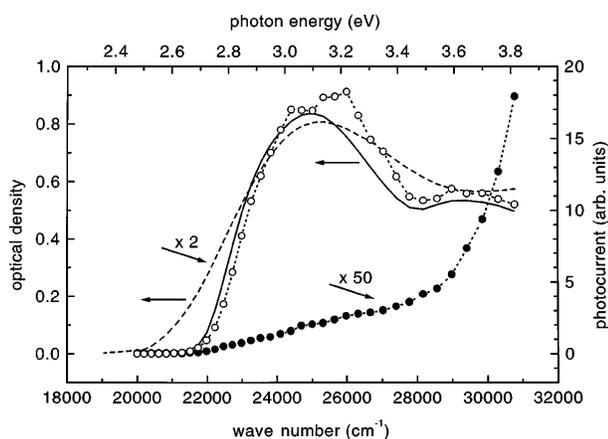


FIG. 1. Photocurrent normalized to the number of incident photons observed upon irradiating a 95 nm thick PPV-ether film through a positively biased neat ITO electrode (open circles) and an ITO electrode carrying an 8–10 nm thick silicon monoxide layer (filled circles), respectively ( $E = 2.1 \times 10^5$  V/cm,  $T = 298$  K). The full curve is the absorption spectrum of PPV-ether; the dashed curve is the absorption spectrum of PPV-amine.

Figure 1 shows photocurrents in PPV-ether, normalized to the incident photon flux, upon irradiation through either the neat ( $j_+$ ) or the SiO-covered ( $j_{+,SiO}$ ) ITO electrodes at positive bias. While  $j_+$  matches the absorption spectrum equivalent to a constant yield when normalized to the number of absorbed photons,  $j_{+,SiO}$  rises monotonously upon increasing  $h\nu$  and is 2–3 orders of magnitude less than  $j_+$ . From previous work [9], it is known that  $j_+$  has to be identified as a sensitized unipolar photocurrent arising from hole injection from ITO via electron transfer from photoexcited PPV-ether chains to the ITO electrode.  $j_{+,SiO}$  could, in principle, arise from residual photocarrier production at the SiO/PPV-ether interface or from sensitized electron injection from the back electrode. Since in both cases the same photoexcited state of PPV-ether had to act as the carrier delivering species, the action spectrum of  $j_{+,SiO}$  should have been similar to that of  $j_+$  after appropriate correction for the filter effect due to sample absorption. Since both spectra are different, we discard both explanations and attribute  $j_{+,SiO}$  to volume photoionization of PPV-ether. PPV-amine behaves differently. Except near the absorption edge, where optically stimulated hole injection from an ITO anode prevails as evidenced by the SiO-sensitivity of the photocurrent, the latter becomes independent of both polarity and the presence of a SiO layer at photon energies  $\geq 25\,000\text{ cm}^{-1}$  and exceeds the bulk photocurrent in PPV-ether by 1–2 orders of magnitude. Obviously, bulk photoionization in PPV-amine, which the photocurrent recorded at negative bias of ITO ( $j_-$ ) will be taken as a measure of, is much more efficient than it is in PPV-ether.

The field dependence of the bulk photoionization yield  $\varphi_b$ , calculated by normalizing  $j_{+,SiO}$  (PPV-ether) and  $j_-$  (PPV-amine) to the number of photons absorbed in the bulk, is presented in Fig. 2.  $\varphi_b$  is  $\ll 1$  and increases by 1–2 orders of magnitude within the field range  $10^5$ – $10^6$  V/cm. Except for  $h\nu_{exc}$  close to the absorption threshold, the slope of the  $\log \varphi_b(E)$  vs  $\log E$  curves decreases with increasing photon energy. This is a characteristic feature of photoionization involving geminate pair dissociation. Within the framework of that concept, a primarily excited state generates an intrinsic thermalized  $e-h$  pair of intrapair distance  $r_0$  with efficiency  $\varphi_{b,0}$  before losing its excess energy and before diffusing towards an extrinsic defect that may sensitize dissociation. If  $\varphi_{esc}$  denotes the fraction of pairs that escapes geminate recombination,  $\varphi_b = \varphi_{b,0}\varphi_{esc}$ . The simplest analytic expression for  $\varphi_{esc}(E, T)$  is provided by the three dimensional version of Onsager's theory premised upon the notions that (i) the system is homogeneous, (ii) the primary event generating  $e-h$  pairs is field independent, and (iii) the distribution of thermalized pairs can be described by an isotropic delta function with a discrete value for  $r_0$ , which may depend upon  $h\nu_{exc}$  [10]. Comparison between theoretical  $\varphi_{esc}(E)$  curves and experimental  $\varphi_b(E)$  data requires knowledge of  $\varphi_{b,0}$ . In Fig. 2, the relevant portions of  $\varphi_{esc}(E, r_0)$  curves, calculated for  $\varepsilon = 4$ , have been included on the premise

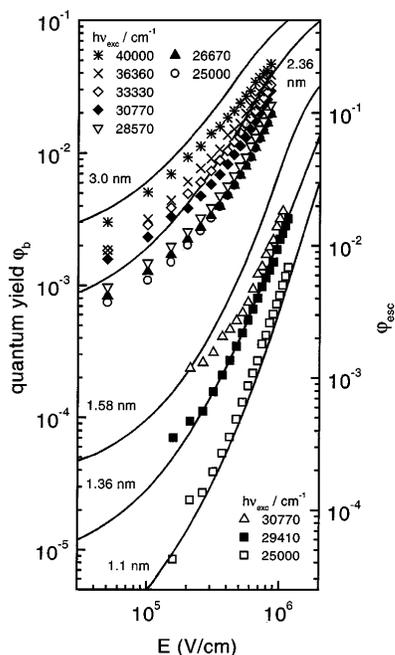


FIG. 2. Field dependence of the quantum efficiency  $\varphi_b$  for intrinsic photogeneration in PPV-amine (upper set of data points) and PPV-ether (lower set of data points) parametric in the photon energy ( $T = 298$  K). Lines represent the dissociation yield  $\varphi_b$  of geminate pairs calculated from the 3D Onsager model applying the algorithm of Ref. [11].  $\varphi_b$  and  $\varphi_{\text{esc}}$  scales are related on the premise that in experiment the primary ionization yield is  $\varphi_{b,0} = 0.2$  for both samples.

that for both samples  $\varphi_{b,0} = 0.2$ . It is obvious that the 3D Onsager theory provides at least a zero order description for the entire family of  $\varphi_b(E)$  curves. The agreement even improves upon assuming sample specific  $\varphi_{b,0}$  values,  $\varphi_{b,0}^{\text{PPV-ether}} = 0.4$  and  $\varphi_{b,0}^{\text{PPV-amine}} = 0.1$ . Under this premise, the initial pair distances  $r_0$  have been obtained by comparing experimental  $\varphi_b$  values with calculated [11]  $\varphi_{\text{esc}}$  data. The result is shown in Fig. 3 in conjunction with action spectra of intrinsic photoionization.

The Onsager formalism predicts that the  $e-h$  pair dissociation is an activated process, the activation energy  $E_a$  decreasing with increasing electric field. In the  $E \rightarrow 0$  limit,  $E_a = e^2/4\pi\epsilon\epsilon_0 r_0$ .  $r_0^{(\text{app})} = 1.05$  nm translates into an apparent zero-field binding energy of 0.34 eV. At  $E = 3.2 \times 10^5$  V/cm, it should have dropped to 0.26 eV. The temperature dependence of  $\varphi_b/\varphi_{b,0}$ , measured in PPV-ether at  $E = 3.2 \times 10^5$  V/cm, is shown in Fig. 4. It approaches Arrhenius behavior with an activation energy of  $0.25 \pm 0.02$  eV in the high temperature limit, while for  $T < 200$  K,  $\varphi_b/\varphi_{b,0}$  saturates. Consistent with the larger  $\varphi_b$  values for PPV-amine, the temperature dependence of  $\varphi_b$  is considerably weaker. Previous Monte Carlo simulations [12] have shown that such a behavior is a characteristic feature of geminate pair dissociation in hopping systems in which the density of states (DOS) function for the manifold of hopping sites is a Gaussian distribution of variance  $\sigma$ . Basically, this is a reflection of the interplay between the energetic relaxation carriers, which had ini-

tially been started at random within the DOS, suffer while migrating, and thermally activated motion required for escape from the Coulombic potential. The simulations in Ref. [12] were performed for a DOS with  $\sigma = 0.1$  eV, and a zero-field Coulombic binding energy of the  $e-h$  pair of  $e^2/4\pi\epsilon\epsilon_0 r_0 = 0.168$  eV. A good fit to the present experimental data is obtained by rescaling the simulation data to an initial pair binding energy of 0.3 eV at a field of  $3.2 \times 10^5$  V/cm. Extrapolation to  $E = 0$  on the basis of Onsager's theory yields 0.4 eV for the true average Coulombic binding energy of a geminate  $e-h$  pair in PPV-ether generated at  $h\nu_{\text{exc}} \leq 27\,300$   $\text{cm}^{-1}$ . The rescaled intrapair distance is 0.9 nm. Note that an analysis of  $\varphi(E, T)$  data obtained for a disordered system on the premise of a homogeneous medium approach, such as the classic 3D Onsager treatment without considering disorder effects, underestimates  $E_a$  values by at least about 20 percent, without affecting the functional form of  $\varphi_{\text{esc}}(E)$ , though [12].

The experiments show that the efficiency of intrinsic photogeneration is highly material sensitive. The crucial parameter is the initial distance  $r_0$  of the dissociating pair, which must ultimately be limited by the length of conjugated segments. In PPV-ether, that length is determined by the separation of the ether linkages, which is about 1.8 nm, consistent with the observation that  $r_0 \leq 1.5$  nm. In that case, the dissociating entity must be an exciton-type  $e-h$  pair confined to such a segment. The distinguishing feature between PPV-ether and PPV-amine is, obviously, the more extended  $\pi$ -conjugation system, manifest in the redshifted optical threshold. It allows a primary excitation to form a spatially less confined  $e-h$  pair, albeit with smaller yield, that is, concomitantly, more liable to field and temperature-assisted dissociation. The primary dissociating pair is, thus, identified as an on-chain excitation, while subsequent dissociation is a 3D random walk.

The present results are relevant also concerning both the definition and the magnitude of the exciton binding energy  $E_b$ . It is obvious from Fig. 3 that  $\varphi_b$  rises monotonously with  $h\nu_{\text{exc}}$ —starting near the absorption edge—and this reflects the increase of  $r_0$  rather than of  $\varphi_{b,0}$ . Notably, the results for PPV-amine indicate the absence of any feature related to higher optical transitions occurring in PPV-like systems at  $h\nu_{\text{exc}} \geq 30\,000$   $\text{cm}^{-1}$  [13]. Apparently  $r_0$  is a monotonous function of the energy of the primarily excited Franck-Condon state irrespective of its electronic parentage. Deriving a threshold for photoionization from any extrapolation of  $\varphi_b(h\nu_{\text{exc}})$  does not seem, therefore, to be an adequate way to determine  $E_b$ . Since  $E_b$  refers to the energy required to dissociate a vibrationally relaxed singlet exciton,  $E_b$  should be identified with the thermal energy it costs to create a pair of intrinsic charge carriers from excitations generated near the  $S_1 \leftarrow S_0$  0-0 band maximum. For PPV-ether, this energy is 0.4 eV, which agrees with both a theoretical estimate [14] and estimates based upon fluorescence quenching [15] and the photovoltaic response of PPV in thin film devices [16].

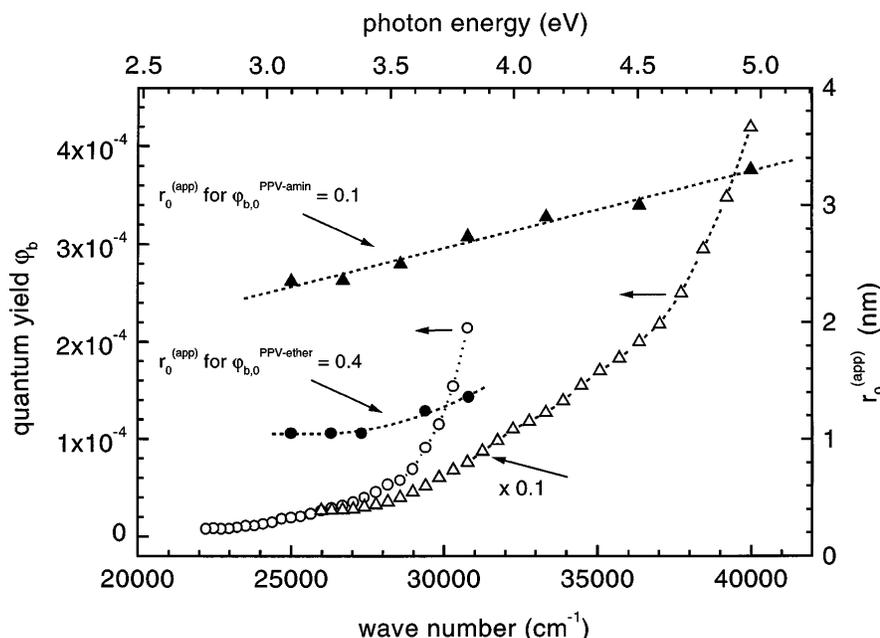


FIG. 3. Left ordinate: quantum yield for intrinsic photo-generation as a function of photon energy in PPV-ether (open circles) and PPV-amine (open triangles) ( $E = 2.1 \times 10^5$  V/cm; respectively,  $E = 2 \times 10^5$  V/cm,  $T = 298$  K). Right ordinate: apparent zero-field initial  $e-h$  pair distances for PPV-ether (full circles) and PPV-amine (full triangles) derived from the data of Fig. 2 for  $\phi_{b,0}^{\text{PPV-ether}} = 0.4$  and  $\phi_{b,0}^{\text{PPV-amine}} = 0.1$ .

In summary, the experiments prove that there is no qualitative difference between a conjugated polymer of the PPV-type and a conventional molecular solid as far as intrinsic photoionization is concerned. In both systems, it can be appropriately described by Onsager's theory of geminate pair dissociation. In quantitative terms, the distinguishing feature is that in the former the energies of an on-chain exciton and an  $e-h$  pair on adjacent chains are of comparable magnitude. This is related to the delocalization of both neutral and charged excitations

within the chain segments, whose magnitude depends on the chemical nature of the chain.

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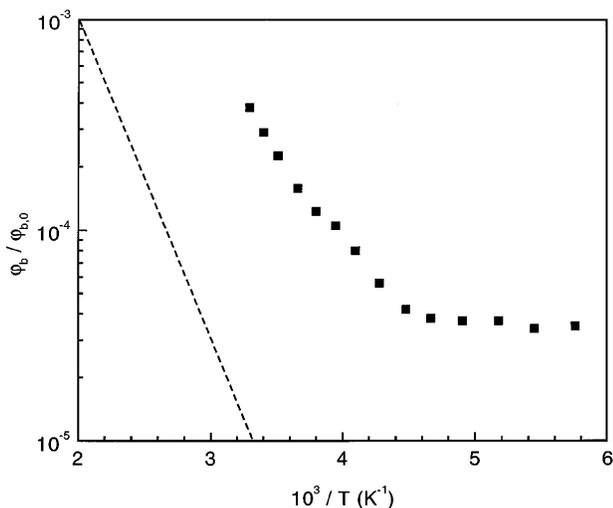


FIG. 4. Temperature dependence of the intrinsic photogeneration yield  $\phi_b$  in PPV-ether normalized to the primary yield  $\phi_{b,0} = 0.4$  ( $E = 3.2 \times 10^5$  V/cm,  $h\nu_{\text{exc}} = 27300$   $\text{cm}^{-1}$ ). The full line is the prediction of Monte Carlo simulations (Ref. [12]) for geminate pair dissociation in a hopping system whose DOS has a Gaussian width of 0.1 eV after rescaling the initial pair binding energy from 0.168 eV (simulation) to 0.3 eV (experiment). The dashed line represents Arrhenius' law for an activation energy of 0.3 eV.

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