

# Does Conjugation Help Exciton Dissociation? A Study on Poly(*p*-phenylene)s in Planar Heterojunctions with C<sub>60</sub> or TNF

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The process of exciton dissociation in organic semiconductors is the key step that needs to be understood for the realization of efficient organic solar cells.<sup>[1]</sup> A systematic optimization of solar cells requires a well-founded and detailed understanding of the mechanism of exciton dissociation and its dependence on material parameters. Consequently, it is being investigated intensely.<sup>[2–11]</sup> There is widespread agreement on the elementary steps that accompany charge carrier generation at an organic molecular heterojunction.<sup>[1,12]</sup> Light absorption creates an excited state on one molecule. This is followed by electron transfer to a neighboring molecule, which results in the formation of a more or less strongly bound metastable intermolecular state. This excited state has a strong charge-transfer character and will eventually break up into free charge carriers or lead to recombination. The central question, therefore, is how to overcome the Coulombic binding energy that prevents the final separation of the opposite charges. There are studies implying that dissociation may be favored by a higher hole mobility,<sup>[13–15]</sup> which is typically associated with a larger conjugation length and a low degree of energetic disorder.<sup>[4]</sup> On the other hand, there are also reports that in certain circumstances an increased disorder or a lower hole mobility may be preferential.<sup>[16,17]</sup> Using a set of poly(*p*-phenylene)s (PPPs) as systematic model compounds, we have investigated how the conjugation length of the chromophore affects the process of charge carrier dissociation at a molecular heterojunction. In field-dependent photocurrent measurements we find the photocurrent yield to saturate at 100% at electric fields between  $5 \times 10^4 \text{ V cm}^{-1}$  and  $1 \times 10^6 \text{ V cm}^{-1}$ . Importantly, the saturation field that is required decreases with increasing conjugation length, implying that the excited state delocalization is of crucial importance for the yield. We conclude that the rate-limiting step of the photogeneration of charges is the formation of a loosely bound (“hot”) electron–hole pair that can either be dissociated at moderate field or relax back to a tightly bound electron–hole pair.

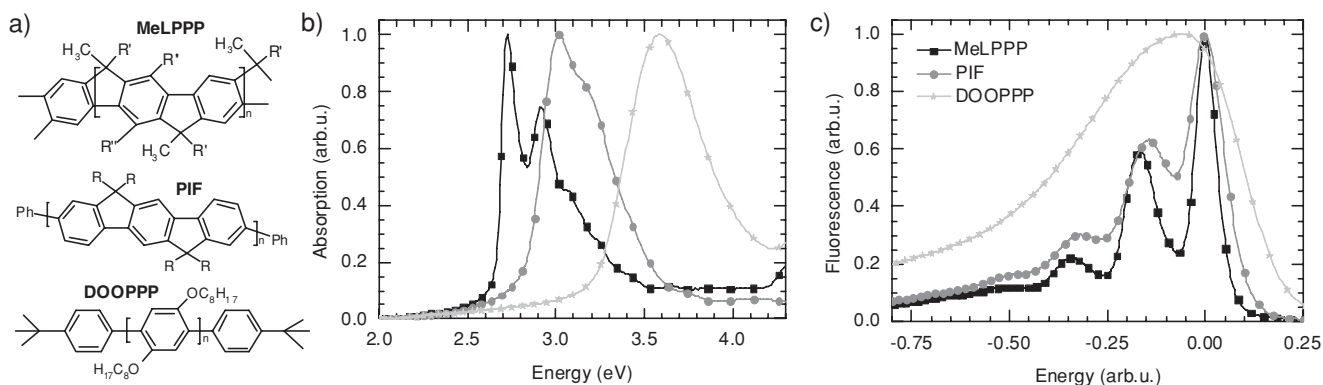
A systematic study requires changing as few parameters as possible. Therefore we chose the set of poly(*p*-phenylene)s (PPPs) shown in **Figure 1a** as a donor material system. Within this series, the polymer backbone is formed by the same chemical repeat unit, the phenylene, yet the rigidity of the backbone is varied by stiffening links. This results in an increased conjugation length and a narrower density of excited state energies from DOOPPP to MeLPPP, as evidenced by the reduced  $S_1 \leftarrow S_0$  absorption energies and the concomitantly reduced linewidth (Figure 1b). This change in linewidth is particularly obvious when the fluorescence spectra are shifted in energy such that the 0-0  $S_1 \rightarrow S_0$  coincide (Figure 1c). A Franck–Condon analysis<sup>[18]</sup> of the thin-film fluorescence spectra yields variances of 106, 45, and 28 meV for DOOPPP, PIF, and MeLPPP, respectively. We have combined these donors with two different acceptor materials, C<sub>60</sub> and trinitrofluorenone (TNF).<sup>[19]</sup> C<sub>60</sub> is a well-known acceptor, yet it has excited states at lower energies than the PPPs. For an unambiguous data analysis, we want to excite only one of the two materials at the heterojunction. Using C<sub>60</sub>, we can excite the acceptor only, however, it is not possible to excite the polymer donor without simultaneously exciting the acceptor. This can be achieved by using the strong electron acceptor TNF, as it has an onset of absorption around 3 eV, which is similar to DOOPPP and larger than PIF and MeLPPP.

For our study we employed the method of field-dependent photocurrent measurements.<sup>[8,20]</sup> We stress that this technique probes a different situation than the related field-dependent photoluminescence (PL) quenching experiment.<sup>[21,22]</sup> By PL quenching, one explores the field dependence of the recombination process. Recombination occurs from the intermolecular state when it is tightly bound. This situation is also referred to as a charge transfer state, exciplex, or tightly bound geminate pair.<sup>[11,21]</sup> In contrast, the photocurrent results from the break-up of the intermolecular state, which, immediately beforehand, will be only loosely bound. Sometimes this is termed a dark intermediate state, a polaron pair state, a hot charge transfer complex, or a weakly bound geminate pair.<sup>[5,21,23]</sup> Its weak binding energy and ultrafast split-up, on a time scale of 100 fs,<sup>[7,24]</sup> can lead researchers to disregard this intermediate state and to consider only the free carriers resulting from its dissociation.<sup>[6]</sup> The field-dependent photocurrent measurements probe the decisive process for the photogeneration of charge carriers, that is, the break-up of the weakly Coulomb bound geminate pair (GP). A priori, the experiment does not tell us whether the weakly bound intermolecular geminate pair was formed

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**Figure 1.** a) The chemical structures of the donor polymers ( $R = 2$ -ethylhexyl,  $R' = 1,4\text{-C}_6\text{H}_4$ ,  $n\text{-C}_{10}\text{H}_{21}$ ,  $R'' = -n\text{-C}_6\text{H}_{13}$ ), along with b) their absorption spectra and c) the fluorescence spectra for excitation at 3.5 eV. For comparison, the fluorescence spectra have been shifted along the energy axis so that the 0–0 transitions coincide at 0 eV.

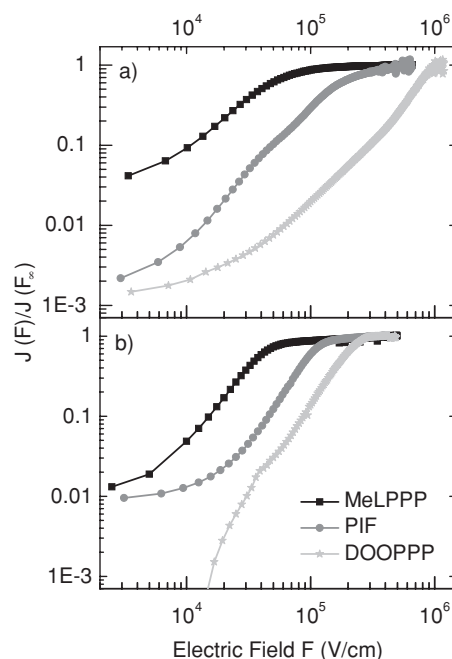
directly by electron transfer from the intramolecular excited state or whether it results from evolution via an initially tightly bound geminate pair.

For the field-dependent photocurrent measurements, a planar heterojunction geometry was chosen as device structure to avoid non-geminate recombination as much as possible. The solar cells were prepared on glass substrates in the layer structure ITO/PEDOT:PSS (35 nm)/donor polymer (40 nm)/acceptor molecule (40 nm)/aluminum, where ITO is indium tin oxide and PEDOT:PSS is poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate). The polymers were spun from chlorobenzene solution while the acceptor molecules were thermally evaporated. We note further that we employed a careful device design that ensures a homogeneous field distribution without edge effects in fully individually addressed photocells. This is an essential prerequisite for accurate measurements at high field strength.

**Figure 2** shows the photocurrent quantum yield  $J(F)/J(F_\infty)$  as a function of internal electric field  $F$  and normalized to unity at the field strength  $F_\infty$  at which the photocurrent yield saturates. To obtain the internal electric field, the open-circuit voltage was subtracted from the applied external voltage and the result was divided by the film thickness. In **Figure 2a**, the molecular acceptor  $\text{C}_{60}$  is excited, which results in electron transfer from the polymer highest occupied molecular orbital (HOMO) to the  $\text{C}_{60}$  HOMO. In contrast, in **Figure 2b** we excite the polymer donor, thus inducing electron transfer between the lowest unoccupied molecular orbitals (LUMOs) of the polymer and the TNF. In both cases, we observe the same trends. First, the photocurrent quantum yield saturates for high field strength. A quantitative analysis, taking into account the exciton diffusion length of about 10 nm inferred from a comparison of photocurrent and absorption spectra shows that the quantum yield at saturation is around 100%. This value is subject to inaccuracies regarding the exciton diffusion length. In other words, essentially all the excitations photogenerated on one compound that reach the interface split up at sufficiently high fields. Second, the electric field needed to induce this complete split-up decreases from DOOPPP to MeLPPP. In this order, the conjugation length increases and the energetic disorder decreases, as demonstrated in **Figure 1**. When using TNF as the acceptor, overall lower fields are required to dissociate all excitations

than when  $\text{C}_{60}$  is used. The fact that we observe photocurrent saturation at high fields under illumination rather than device breakdown or uncontrolled photocurrent gain is remarkable. We consider this is mostly the result of using a device geometry with an insulating patterned photopaint layer that removes any edges at the transition between polymer film and ITO electrode. This structure eliminates any high inhomogeneous fields that promote multiple or uncontrolled carrier injection, in particular under high-energy illumination. Furthermore, when  $\text{C}_{60}$  is used the exciting photon energy is low, while with TNF the saturation field strength is moderate.

What do these data reveal about the process of charge carrier separation? In a naive classical picture, following Langevin, we



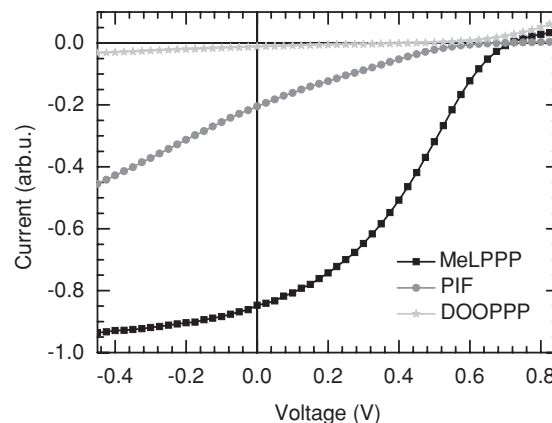
**Figure 2.** The external quantum yields of planar heterojunction devices made with MeLPPP, PIF, and DOOPPP, measured as a function of the internal field and normalized to unity at the saturation value. a) Using  $\text{C}_{60}$  as acceptor and exciting at 2.2 eV. b) Using TNF and exciting at the maximum of the polymer absorption.

may associate the binding energy of the intermolecular excited state with the Coulomb energy of two opposite pointlike charges separated at a distance  $r_{GP}$ . When the intermolecular excited states dissociate into a free electron and hole at a high field this implies that the potential energy of the electric field compensates the binding energy of the geminate pair. This is the case from a certain saturation field value  $F_{sat}$  onwards. We can use this to calculate the binding energy of the intermolecular excited state and the associated distance  $r_{GP}$ . As a basic estimate we use  $F_{sat}r_{GP}e = e^2/(4\pi\epsilon_r\epsilon_0r_{GP})$ , leading to  $r_{GP} = \sqrt{e/(4\pi\epsilon_r\epsilon_0 F_{sat})}$ , where  $e$  is the elementary Coulomb charge and  $\epsilon_r$  and  $\epsilon_0$  are the dielectric constants at the interface (taken as 3.5) and of vacuum, respectively. This results in values from 9 nm to 2 nm for the electron–hole distance and from 0.05 eV to 0.2 eV for the binding energy of the geminate pair along the series from MeLPPP to DOOPPP, as detailed in the Supporting Information. The key message to take from this is that with increasing energetic order and conjugation length, the weakly bound geminate pair is more extended and it is more loosely bound. This general observation is independent of whether the donor or the acceptor is excited.

A comparison between devices made with  $C_{60}$  and with TNF shows a lower  $F_{sat}$ , implying larger electron–hole distances, when TNF is used. This can be associated with the different energy gain that accompanies the electron transfer from the photoexcited intramolecular state.<sup>[2,25]</sup> When  $C_{60}$  is excited and the electron transfers between the HOMOs, the excess energy between the HOMO levels ranges from 1.1 eV to 0.7 eV from MeLPPP to DOOPPP. In contrast, when the polymer is excited, the electron transferring between LUMOs gains an energy of about 1.3–1.5 eV (see Supporting Information). The data in Figure 2 suggest that this larger excess energy in particular for PIF and DOOPPP reduces the binding energy of the geminate pair. In the conceptual framework of two pointlike charges, this corresponds to a larger extent of the geminate pair created when TNF is used instead of  $C_{60}$ .

Figure 2 also allows us to draw conclusions about the nature of the intermolecular state. Consider the point that electron transfer from a photoexcited intramolecular state may, in principle, result in a tightly or loosely bound geminate pair. A tightly bound geminate pair with charges separated by less than 1 nm requires an electric field exceeding  $4 \times 10^6$  V cm<sup>-1</sup> in order to overcome its Coulomb binding energy of 0.4 eV. Our experiment tells us that much lower fields are sufficient to split up the geminate pairs. Thus the geminate pairs formed by electron transfer in the presence of a high electric field must be only weakly bound and well extended. Furthermore, our experiment results in a yield around 100% at high fields. This implies there are no efficient competing processes such as energy transfer to triplet excited states or radiative or non-radiative recombination.<sup>[2,26]</sup> It follows that such processes limit the efficiency of dissociation only if the geminate pair is tightly bound, as is the case for example at low fields or when the weakly bound geminate pair relaxes.<sup>[27]</sup>

How can we use the insight gained from Figure 2 to make more efficient solar cells? For applications, it is worth noting that the field required to separate all charges also affects the fill factor, which is a critical parameter for the efficiency of solar cells. This is illustrated in Figure 3, where the current



**Figure 3.** The current density of MeLPPP, PIF, and DOOPPP in a planar heterojunction with  $C_{60}$  for excitation at 2.2 eV, as a function of applied voltage. The curves are normalized to  $-1$  at the saturation value of the photocurrent.

densities obtained for the three different polymers are normalized to negative unity at the voltage at which the photocurrent saturates. For the performance of the solar cell, the operating range between zero applied volts and the open-circuit voltage is relevant. It is evident that the fill factor strongly decreases with increasing saturation field from MeLPPP (35%) to DOOPPP (20%). A low saturation field is also required as, ideally, one would like to obtain a quantum yield of 100% at the electrical field strength that prevails at the open-circuit voltage. The essence is that the saturation field strength needs to be close to the internal field strength. This is tantamount to saying that the extent of the intermolecular excited state needs to be large. In the picture of pointlike charges, they need to be separated by distances around 10 nm. From our data this seems to be enabled by the larger conjugation length of the more ordered polymers. It is known that right after generation the charge carrier on a conjugated segment is in a highly mobile state, characterized by a low effective mass and a large coherence length.<sup>[28,29]</sup> Scattering by conformational disorder quickly reduces the mobility of the charge carrier, and the coherent motion of the carrier becomes limited to the conjugation length.<sup>[30]</sup> A long conjugation length means the hole coherently oscillates over a large segment of the polymer chain, leading to a large mean separation from the electron on the acceptor site. We therefore conclude that the realization of efficient solar cells will benefit from the use of materials that are highly conjugated and allow for effective charge carrier delocalization.

## Experimental Section

MeLPPP, PIF and DOOPPP were synthesized by the group of U. Scherf as described elsewhere.<sup>[31–33]</sup> Trinitrofluorenone (TNF) was synthesized in Bayreuth following the method of Woolfolk and Orchin.<sup>[34]</sup> Cyclic voltammetry measurements were carried out in dichloromethane and the HOMO levels were calculated relative to ferrocene.

For spectroscopic measurements, about 40 nm thick polymer films were spun from filtered chlorobenzene solution ( $7.5$  mg mL<sup>-1</sup>). The films were heated at 80 °C for 10 min. Absorption was measured with a Cary 5000 (Varian) UV-vis spectrometer. The fluorescence spectra

were recorded using a charge-coupled device (CCD) camera at room temperature with the samples in vacuum under UV-multimode (351 nm/364 nm) excitation from an Ar<sup>+</sup> laser. Photoluminescence spectra of C<sub>60</sub> and of TNF are included in the Supporting Information. For photocurrent measurements, heterojunction solar cell devices were fabricated on structured ITO-coated glass substrates. To ensure a homogeneous electric field without edge effects, a circular active area of the device was defined on top of the ITO anode using AZ 1518 photopaint from Microchemicals. The devices were then prepared by spin-coating 35 nm poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) into the active area, heating at 140 °C for 30 min, spin-coating 40 nm polymer on top of it, and heating again to 80 °C for 10 min to drive off any residual solvent. After this, we evaporated 40 nm C<sub>60</sub> (99.9% purity, American Dye Source Inc.) or TNF, followed by 80 nm aluminum.

Current–voltage curves under monochromated illumination from a 150 W Xenon lamp were measured under active vacuum at room temperature with a Keithley source-measure unit. Light intensities were recorded with a Hamamatsu S1337-33BQ photodiode. The internal electric field was calculated as  $F = (V - V_{oc})/d$ , with applied external voltage  $V$ , open-circuit voltage  $V_{oc}$  (typically between 0.5 and 0.7 V, see the Supporting Information) and active film thickness  $d$ . The photocurrent quantum yield  $J(F)$  was calculated taking into account photocurrent density of the solar cell, illumination light intensity, and the exciton diffusion length (typically around 10 nm)<sup>[35–38]</sup> derived by comparison between absorption and photocurrent spectra.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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