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"Hot or cold": How do charge transfer states at the donor-acceptor interface of an organic solar cell dissociate?

Heinz Bässler[1*], Anna Köhler[1,2]

1 Bayreuth Institute of Macromolecular Research, Universitätsstr. 30, Universität Bayreuth, 95440 Bayreuth, Germany

2 Experimentalphysik II (Organic Semiconductors), Department of Physics, Universitätsstr. 30, Universität Bayreuth, 95440 Bayreuth, Germany

e-mail: Heinz.baessler@uni-bayreuth.de

Abstract

Electron transfer from an excited donor to an acceptor in an organic solar cell (OSC) is an exothermic process, determined by the difference in the electronegativities of donor and acceptor. It has been suggested that the associated excess energy facilitates the escape of the initially generated electron-hole pair from their mutual coulomb well. Recent photocurrent excitation spectroscopy on conjugated polymer/PCBM cells challenged this view. In this perspective we shall briefly outline the strengths and weaknesses of relevant experimental approaches and concepts. We shall enforce the notion that the charge separating state is a vibrationally cold charge transfer (CT) state. It can easily dissociate provided that (i) there is electrostatic screening at the interface and (ii) the charge carriers are delocalized, e.g. if the donor is a well ordered conjugated polymer. Both effects diminish the coulomb attraction and assure that the in-built electric field existing in the OSC under short current condition is already sufficient to separate most the CT states. The remaining CT excitations relax

towards tail states of the disorder controlled density of states distribution, such as excimer forming states, that are more tightly bound and have longer lifetimes.

1. Introduction

The efficient conversion of sun light into electrical energy using an all-organic photocell has been a challenge for decades. Meanwhile this dream has been fulfilled. Organic solar cells (OSCs) based upon the combination of donor-acceptor materials already reached power conversion efficiency of about 10% which is a benchmark for profitable technical application. [1] [2] [3] However, this success involves a combination of rational design with trial and error, and the understanding of the underlying elementary processes is far from complete. It is indeed fortunate that OSCs are so efficient but it is unfortunate that the reason is unclear. Recall that a *power* conversion efficiency of 10% requires that the *internal* quantum efficiency - i.e. the elementary step of dissociating an optical excitation into a pair of free charges - be close to 100%. How can this be accomplished in an organic material?

Let us recall that for an inorganic solar cell, such as a silicon diode, the above question is irrelevant because (i) in a semiconductor with a dielectric constant of 11, such as silicon, dielectric screening is efficient and (ii) photogenerated electron-hole pairs escape from their screened, weak, mutual coulomb potential easily because the scattering length of the charges is large. However, in an organic solar cell (OCS) the situation is different. Since the dielectric constant is typically about 3 - 4 the coulomb energy of a photogenerated electron-hole pair (eh-pair) with a typical intra-pair separation of 1 nm is 0.4 – 0.5 eV. Furthermore, a film of organic semiconductors is held together only by van der Waals forces between its constituent elements, i.e. molecules or polymer. This implies a much weaker electronic coupling among the constituent elements compared to an inorganic semiconductor, where atoms are kept together by covalent or ionic binding. Concomitantly, it implies that the scattering length of charge carriers in organic semiconductors is comparable to the intermolecular spacing, quite in contrast to the large scattering lengths prevailing in inorganic crystalline semiconductors.

In organic solar cells, optical power conversion is therefore a sequential process involving initially a coulomb-bound eh-pair at a donor-acceptor interface that subsequently has to dissociate into a pair of free charges. The opposite charges execute a diffusive random walk within their coulomb potential and eventually escape or recombine geminately. This escape process via diffusion ought to be a thermally activated and, concomitantly, inefficient process. The pertinent question is therefore how can an eh-pair escape from its mutual coulomb potential.

It has been a plausible idea that excess energy, dissipated when an optically generated electron of the donor jumps down to the electron accepting state of the acceptor, may facilitate the escape of the eh-pair from its mutual coulomb well. This energy is determined by the electronegativities of donor and acceptor. It may be used to either populate a higher (thus “hot”) electronic state of the donor-acceptor interface that couples efficiently to electron transporting states or to generate a vibrationally “hot” charge transfer (CT) state that will subsequently thermalize thereby generating more expanded and, concomitantly, more loosely bound eh-pair. Such a hot state could avoid geminate recombination more easily than a “cold” nearest neighbor CT state. The remainding pairs would relax to form geminately bound pairs that can live for nanoseconds or even longer. [4] However, this view has been challenged recently, notably by the work by Vandewal. [5] In this perspective we outline different concepts that are currently employed to describe the dissociation of eh-pairs in donor-acceptor OSCs. We compare them to experiments and highlight their strengths as well as shortcomings with particular emphasis on the role of the excess energy of the hot CT state.

2. Concepts for photogeneration of charge carriers

2.1 The Onsager model

Before embarking on a discussion of concepts for electron-hole-pair dissociation in OSCs it appears useful to recall how Onsager solved a related problem. In his 1934 treatise he considered the thermodynamic equilibrium between free ions and coulomb bound ions of infinite lifetime in a weak electrolyte. [6] Later on he extended this work to pairs of charges that are generated optically or by high energy radiation. [7] He assumes that a photon with sufficient quantum energy ionizes a molecule, thereby creating a metastable, coulomb-bound pair of charges with intra-pair separation r_0 that is embedded in a medium with a dielectric constant of ε_r. The charges undergo a diffusive Brownian motion within the superimposed coulomb potential of the charge pair and an applied electric field. In the course of their motion they can either fully dissociate or recombine geminately on their first encounter. This is the so-called “infinite sink approximation”. Since both, recombination and dissociation, are diffusion controlled, the trade-off of both processes is independent of the diffusion constant and, concomitantly, their mobility. Onsager’s 1938 treatment yields the dissociation yield as a function of the initial intra-pair separation r_0, the angle Θ the vectors of the pair dipole, the applied electric field F, and temperature T. In the weak field limit it predicts that the yield is thermally activated and increases linearly with the electric field,

$$\varphi(F) = e^{-\frac{r_{coul}}{r_0}}\left(1+\frac{e^3F}{8\pi\varepsilon_r\varepsilon_0(kT)^2}(1+\cos\Theta)\right), \tag{1}$$

where $r_{Coul}=\frac{e^2}{4\pi\varepsilon_r\varepsilon_0 kT}$ is the coulombic capture radius.

In their seminal work, Chance and Braun showed that the intrinsic steady state photoconduction of a single component molecular crystal, such an anthracene crystal, can be explained consistently by applying Onsager’s 1938 theory. [8] From the temperature dependence of the photocurrent they derived the initial separation as a function of photon energy. They found that r_0 is 5 nm when exciting the second singlet (S_2) state of anthracene and increases to 6.7 nm when reaching the third singlet state. The important message is that the electron-hole pairs that act as precursors for free charge carriers are created by autoionization of higher excited electronic states that couple to valence or conduction band states. [9] It turns out that this not only a characteristic feature of molecular crystals but also of conjugated polymers because in both cases the energy needed to dissociate the lowest singlet state is 0.5 – 1 eV. [10] [11]

2.2 The Onsager-Braun concept

The fundamental difference between a single component molecular solid and donor-acceptor system, such as an OSC, is that (i) the energetically lowest excited state is a charge-transfer state rather than the singlet state of either the donor or acceptor. Because the charge transfer state has a finite lifetime it can make several attempts towards ultimate dissociation. Therefore Onsager's infinite sink approximation no longer applies. Recognizing that this effect is important in materials that are intentionally or inadvertently doped with electron acceptors, Braun extended Onsager's 1934 concept by introducing the lifetime of the charge transfer state as a parameter. [12] In this model the dissociation yield is determined by the trade-off between the field and temperature dependent dissociation rate $k_d(F)$ of the eh-pair localized on a donor-acceptor pair and the rate of its ultimate decay to the ground state $k_f = \tau^{-1}$, where τ is the lifetime of the charge transfer state,

$$\varphi(F) = \frac{k_d(F)}{k_d(F)+k_f} = \frac{1}{1+k_f k_d(F)^{-1}} \quad (2)$$

The theory predicts a strong field dependence rate $k_d(F)$,

$$k_d(F) = \frac{3\mu e}{4\pi\epsilon_0\epsilon_r {r_0}^3} \exp\left(\frac{-\Delta E}{kT}\right) \frac{J_1(2\sqrt{-2b})}{\sqrt{-2b}} \text{ with } b = \frac{e^3 F}{8\pi\epsilon_0\epsilon_r k^2 T^2}. \quad (3)$$

Here, J_1 is the Bessel function of order one, F is the electric field, μ is the sum of the electron and hole mobilities, $\Delta E = e^2/4\pi\varepsilon_0\varepsilon_r r_0$ is the coulomb binding energy of the electron-hole pair with initial intra-pair separation r_0.

The tacit assumption behind this treatment is that there is equilibrium between dissociation of a relaxed eh-pair and its radiative or non-radiative recombination that depends on the charge carrier mobility (eq. 3). The reason is that the number of attempts an eh-pair can make during its lifetime depends on its diffusivity, hence its mobility. Note that in Onsager's 1938 work the mobility does not enter as a parameter because the infinite sink approximation prevents any sampling of dissociation events. The free parameters in the calculation are therefore the intra-pair separation r_0 and the mobility-lifetime ($\mu\tau$) product. Note, however, that when covering a large field range, it is important to use the Bessel function J_1 rather than the frequently used approximation $(1 + b + b^2/3 + b^3/18 + \cdots)$. In passing we also note that, in the derivation of the dissociation yield, Braun considered the charges as hard core entities in the dissociation and recombination kinetics. This translates into exponential kinetics, i.e. the rate constant for the recombination process is time independent and, consequently, the concentration of the reactants decays exponentially with time. This is a simplification because the charge carriers are not hard core entities and their recombination rate depends on their separation. Wojcik and Tachyia included this effect in an amended version of the Onsager Braun formalism. [13]

The Onsager-Braun model is a stationary formalism and disregards how eh-pairs have initially been generated. It has been applied successfully to the bulk molecular donor-acceptor systems it was developed for. [14] Peumans and Forrest adapted it to a molecular bilayer donor-acceptor system. [15] Depending on the choice of the mobilities of electron and hole and assuming that the excess energy dissipates when the electron in the donor jumps to the acceptor, they were able to rationalize the experimental results. However, applying the Onsager-Braun formalism to OSCs with π-conjugated polymer-donors and C_{60} or PCBM as an acceptor, the required fit parameter, i.e. the mobility-lifetime product, is unacceptably large. [16] Moreover, the experimentally determined dissociation yield is almost independent of temperature and electric field. [10] [17] [18] This is at variance with the notion of thermally activated escape of the electron-hole-pair from its mutual coulomb potential and calls for a modification of the Onsager-Braun formalism.

2.3 The "excess energy" concept for organic solar cells

An intuitively plausible idea to explain why organic solar cells work so efficiently is that it is the excess energy dissipated in the course of the initial charge transfer process that facilitates this escape process. This excess energy is determined by the difference between the electron affinities (or ionization potentials) of donor and acceptor. One possibility is that the electron of the excited donor is transferred to the acceptor thereby creating a vibrationally hot charge transfer (CT) state. If vibrational cooling occurs faster than subsequent charge transfer (1), the excess energy is funneled into the local heat bath thus increasing the local temperature and, comcomitantly, the Boltzmann factor that controls the escape of the eh-pair from the coulomb potential. [19] [20] In the opposite case (2) the excess energy is dissipated in a series of exothermic charge transfer steps eventually creating a thermalized yet only loosely bound electron-hole-pair. Another option is that – depending on the difference of the electronegativities of donor and acceptor – a higher electronic CT -state is generated (3) that couples to charge transporting states more efficiently. This would also lead to the formation of loosely bound eh-pairs. In the extreme case, the transferred electron leaves the coulomb well ballistically (4). Those pairs that do not manage to escape from the coulomb well will relax energetically and form more tightly bound charge transfer states. They will recombine geminately or make several attempts to escape involving a Onsager-Braun type of dissociation process. The processes (1) – (4) are illustrated in Figure 1.

<Fig 1 about here>

The concept of hot CT dissociation implies that the dissociation yield should increase with excess energy, i.e. with the off-set of electronegativities of donor and acceptor. There is indeed experimental support for this notion. [21] [22] [23] [24] However, a simple estimate raises doubts about this reasoning. An efficient OSC requires a large fill factor of the cell. This implies a virtually flat current-voltage-curve near short-circuit conditions. Assuming a 100 nm thick diode and an open circuit voltage of 0.5 eV, the built-in electric field under short circuit is $5x10^4$ V/cm. Field-saturated dissociation requires that the coulomb energy of the dissociating electron-hole-pair be compensated by the existing electrostatic potential. For a diode with ε_r = 3 this translates into an average intra-pair separation of the majority of the dissociating pairs of about 8 nm, assuming a crude point-charge approximation. In this case the escape of the eh-pair had to be essentially a ballistic process. Considering that OSCs are usually disordered, this appears highly unlikely. In fact, Jackson et al. also showed that there are surprisingly weak correlations between solar cell efficiency and energy level positioning, i.e. on the open circuit voltage, and on the enthalpic offset at the donor-acceptor interface and the optical gap. [25]

The tacit assumptions underlying those concepts is that the initial charge transfer event occurs from the lowest excited singlet state of the donor. From work on molecular crystals it is known, however, that photogeneration is more efficient when a higher electronic state of the donor is excited. This process would resemble autoionization in a single component molecular crystal in which one excites a higher lying electric singlet state that couples more efficiently to charge transporting states. [9] It is conceivable that the same phenomenon applies to donor-acceptors systems also. To obtain insight into the effect of excess photon energy on the photogeneration of charges, it is instructive to recall some relevant experiments.

3. Recent experimental advances

3.1 Ultra-fast pump-probe spectroscopy

Ultra-fast pump-probe spectroscopy provides a way to monitor the generation of electron-hole-pairs from excitons initially created in either the donor or acceptor phase. The work by Herrmann et al. demonstrated that at the interface of a bilayer of either aggregated or non-aggregated P3HT with silicon singlet excitons in the donor layer dissociate into electron-hole-pairs on a time scale of 140 fs. [26] Grancini et al. conducted similar experiments on PCPDTBT/PCBM diodes. [27] They observed even shorter transfer times and, importantly, found that upon increasing the photon quantum energy from 1.65 eV to 2.55 eV the appearance time of the radical cation of the donor material decreases from about 50 fs to 20 fs. This is consistent with the work by Kaake et al. on bilayers diodes with an oligomer of a silicon-containing push-pull donor material combined with C_{60} as an acceptor. [28] The explanation for this decrease of the appearance time of the radical cations with increasing photon energy is that at higher energies charge transfer states are populated that are superimposed on the S_1-S_0 transitions and couple to acceptor states more efficiently and, thus, facilitate the electron transfer to the acceptor [29]. Those experiments demonstrate that the rate of charge transfer to an acceptor increases with electronic excess energy while vibrational excess has no effect. However, they neither prove nor disprove the notion that an excess energy can assist the *subsequent* dissociation of eh-pairs in a OSC. There are two reasons for this. (i) Conventional pump-probe spectroscopy monitors the time after which a radical cation (anion) of the donor (acceptor) is created from a neutral excitation. It does, however, not carry any information on whether the radical cation is still bound to its sibling radical anion, nor does it not carry any information on the intra-pair separation. (ii) The dissociation yield of an OSC is usually determined from the short circuit current of the diode. In the case of efficient OSCs the built-in electric field is already sufficient to dissociate almost all eh-pairs even if the primary pair generation process is facilitated by an electronic excess energy.

3.2 Monitoring the generation of electron-hole-pairs by EFISF spectoscopy

Vithange et al. monitored the charge carrier separation in a bulk-heterojunction-P3HT/PCBM diode using the technique of electric field-induced second harmonic (EFISH) generation with sub-picosecond time resolution. This method is usually employed to determine molecular hyperpolarizabilities. [30] In a centro-symmetric system, second harmonic generation of light can only occur when an electric field breaks its symmetry. This effect will be diminished when an applied electric field is shielded by photogenerated electron-hole-pairs. This shielding effect is reduced as the electron-hole-pairs expand. This allows mapping the temporal course of the dissociation events. It yields the carrier mobility and, via the Einstein relation, their diffusivity. [31] The experiments on the P3HT/PCBM diode shows that only nearest-neighbor electron-hole pairs are created at the donor-acceptor interface by charge transfer from the excited donor to the acceptor on a time scale of 100 fs yet the expansion of the electron-hole-pair occurs on a time scale of 100 ps. Figure 2 shows that in an electric field of 2.7 x 10^5 V/cm it takes 100 ps until the pairs reach an intra-pair separation of about 5 nm. This is incompatible with the notion that the escaping electron-hole-pairs are "hot" and proves that the escape process involves diffusion of vibrationally cold electron-hole-pairs. This process is kinetically dispersive because the mobility of the charge carriers decreases with time since they relax towards tails of the density of states distribution.

< Fig.2 about here>

3.3 Time-resolved electro-absorption

Another technique to temporarily resolve the expansion of a coulomb bound electron-hole-pair is electroabsorption (EA) spectroscopy. It is based upon the first order Stark effect and predicts that an oscillating electric field shifts the spectrum with an oscillation amplitude that varies quadratically with the electric field. [32] Using phase sensitive detection one can detect small spectral changes even if the absorption spectrum is much broader. Gelinas et al. applied this technique to both a small molecule and a polymeric (PCDTBT) donor-acceptor heterojunction OSC with a variable content of the fullerene PCBM as an electron acceptor. [33] They excited the donor by femtosecond light pulses and interrogated the transient electroabsorption spectra of the initial singlet exciton, the generated radical cation of the donor, as well as the ground-state-bleach signal on a time resolution of 30 fs. From the spectral shift of the EA signal as a function of the delay time they are able to monitor the early time escape process of the eh-pair. The result confirms that an initially a short ranged (1.5 nm) eh-pair is created that escapes from its mutual coulomb well by diffusion. Initially, the pair is in a coherent state. As time progresses, coherence is lost and the escape process becomes diffusive. The experiments also prove that the dissociation process is faster when the concentration of PCBM is high enough that domains are formed.

3.4 Ultra-fast monitoring of the evolution of optical anisotropy

In order to monitor the dynamics of photogenerated eh-pairs Matheson et al. employed ultra-fast pump-probe spectroscopy. They investigated how fast the initial optical anisotropy of an eh-pair is lost after creating a singlet exciton at the interface of a P3HT/PCBM diode. [34] The results indicate that a hole on the donor generated on a 100 fs time scale is localized on the same polymer chain as the precursor excitons. This confimes that the initial dissociation event is a nearest-neighbor donor-acceptor charge transfer. Depolarization dynamics reveals a fast initial hole motion on a 0.3 ps time scale followed by a slower motion up to 100 ps. Remarkably, the excess energy dissipated in the electron transfer from donor to acceptor has no measureable effect. It is an open question, though, how a nearest-neighbor charge-transfer state is able to surmount their coulomb well. The authors argue that a high charge mobility is certainly helpful, as are entropy effects. [21,35] The notion concerning the importance of entropy effects derives from the fact that the number of donor chromophores a hole can visit during its journey out the coulomb funnel increases as the separation increases. This leads to an increase of entropy and stabilizes a charge separated state relative to the charge transfer state. This implies that the Gibbs free energy contains a distance dependent contribution in addition to the coulomb energy. The conclusion that the formation of an eh-pair at a donor-acceptor interface is a short ranged event is consistent with the work of Duttan and Robey who examined the distance dependence of the exciton dissociation rate at the donor-acceptor interface. [36] To this end they performed two-photon photoemission measurements on a phthalocyanine/C_{60} bilayer assembly as a function of the thickness of the H_2Pc layer. They found that the rate for electron transfer to the second H_2Pc layer adjacent to C_{60} is by at least one order of magnitude less than that for the first layer indicating that this is a short ranged process.

3.5 Energy-selective generation of CT states in OSCs

Most relevant in the context of whether or not excess energy is helpful in the dissociation process of eh-pairs at a donor-acceptor interface is the recent work of Vandewal et al. [5] [37] These authors studied the spectral dependence of the stationary photocurrent in MEH-PPV/PC_{61}BCM and PBDTTPD/PC_{61}BM blends. The differences between both diodes are (i) that in the MEH-PPV diode the j(V) curve is strongly dependent on the applied voltage (equivalent to a poor fill-factor), while in the PBDTTPD case the j(V) dependence is almost flat, and (ii) the absorption spectrum PBDTTPD overlaps with the PCBM absorption spectrum which is not the case for MEH-PPV. The important message derived from those experiments is that the photocurrent can be generated by directly exciting the charge transfer state. It is well know that there are CT states at the interface of donor-acceptors domains in the blend. The most direct evidence comes from the studies of electroluminescence emitted from a diode under forward bias and when using appropriate hole and electron injecting electrodes . [38] [39] [40] Because of the weak electronic coupling in the charge transfer state, the oscillator strength of the $S_0 \rightarrow CT$ transition in absorption and emission is considerably less than that of the $S_0 \rightarrow S_1$ transitions of the parent compounds. Therefore the $S_0 \rightarrow CT$ transition is usually difficult to measure, notably in a thin film. The authors solved this challenging problem by measuring an inverse process, i.e. the radiative decay from the thermally relaxed CT manifold. They found that the internal quantum efficiency of photogeneration, i.e. the number of generated charges per absorbed photon, is the same when directly exciting the charge transfer transition, the donor material or, in the MEH-PPV case, the direct excitation of the PCBM acceptor (Figure 3). This proves that the essential entity that dominates photogeneration is the relaxed CT state irrespective of how it has been initially generated. Obviously, any excess energy is dissipated before the subsequent dissociation of the CT state commences. This conclusion is consistent with the work of Jailaubikov et al. on bilayers of copper phthalocynanine and C_{60}. [41] These authors combined the techniques of time resolved two-photon-generation with two-photon-photoemission from CT states to unravel the kinetics of charge transfer to monitor the relaxation of initially hot CT states. They found that the excess energy released in the course of the interfacial charge transfer is dissipated within a picosecond indicating that cooling of the initially hot CT state is faster than the subsequent dissociation of the CT state, i.e. the eh-pair.

<Figure 3 about here>

Related experiments on photogeneration were performed on blends of a poly-phenylenevinylene copolymers as a donor material and perylenediimide as an electron acceptor. [42] It turned out that the number the charge carriers generated per absorbed photon, i.e. the internal quantum efficiency, is constant within a spectral range of 2.2 eV to 3.6 eV. This proves that it neither matters if the donor or the acceptor were optically excited nor that higher vibrational states of the singlet states are accessed.

4. Parameters affecting eh-pair dissociation

4.1 The energetics at the donor-acceptor interface

The above experiments indicate that ultrafast electron transfer generates cold nearest-neighbor (or at least short-range) eh-pairs, from which dissociation takes place by diffusion of the opposite charges in their mutual coulomb potential. Once this has been accepted, the central question remains: Why can eh-pairs escape from their mutual coulomb potential so easily?. [43] One way to resolve this puzzle is to invoke a screening of the coulomb potential at the donor-acceptor interface. In the case of a bulk heterojunction this is the internal interface at the relevant domains of donor and acceptor. Owing the difference in electronegativities between donor and acceptor, it is conceivable that there is partial charge transfer at the donor-acceptor interface already in the dark that gives rise to interfacial dipoles. They are detectable via a shift of the vacuum level in a photoemission experiment. Veenstra indeed observed a level sift of 0.25 eV when depositing a thin C_{60} layer on top of a film of an oligomer of phenylenevinylene (*p*-bis((*p*-styryl)styryl)benzene). [44] More recent photoemission studies on interfaces between conjugated polymers of the poly-phenylene family and C_{60} confirmed those preliminary results. [45] They indicated that there is a drop of the electrostatic potential due to interfacial dipoles in the range of 0.1 – 0.2 eV. Since a C_{60} molecule occupies an area of about 1 nm^2, this translates into a fractional charge displacement at the donor of 0.015 – 0.030. Early on, Arkhipov et al argued that such a dipole layer should facilitate eh-pair dissociation because it partially screens the coulomb potential. [43] Theoretical concept has been elaborated further by Wiemer et al. [46] [47] Quantum chemical calculations by Avilov et al. shed light on the level shift at the interface of a strong electron donor and a strong electron acceptor. [48] They show that the formation of interfacial dipoles is governed by both charge transfer as well as polarization effects. Microelectrostatic computations on pentacene/C_{60} heterojunctions also showed that quadrupoles of pentacene contribute to permanent interfacial dipoles . [49]

4.2 The influence of disorder at the interface

Organic solar cells are usually non-crystalline. In the above conceptual frameworks for explaining electron-hole-pair-dissociation, this fact has been disregarded although it is supposedly important. The general notion is that disorder decreases the charge carrier mobility, increases the temperature dependence, and the relevant rate processes are retarded. There can be, however, an intervening effect regarding the efficiency of a dissociation event. The reason is that disorder broadens the density of states (DOS) distribution with the consequence that a charge carrier tends to relax towards tails states of the DOS distribution. Hopping theory predicts that charge carrier hopping does, on average, take place among states below the center of the DOS. This implies that a charge carrier needs, on average, less thermal energy to continue its subsequent journey than estimated when ignoring this effect. Therefore disorder may have a positive effect of the liberation of an eh-pair from its mutual coulomb potential, albeit at the expense of the rate constant of dissociation [50]. An illustration of this effect is the recent work by the Forrest group. The authors demonstrated that a controlled change of the morphology of the interface in a heterojunction OSCs with small molecules as donors alters the short circuit current and the open circuit voltage of the cell. [51] [52] The experimental system was a bilayer of a squaraine-type molecular donor and C_{60} whose morphology is modified by controlled film deposition and vapor phase annealing (SVA). “As cast” films are disordered but some order is introduced by annealing. Improved structural ordering can be achieved when a deposited squaraine film is subjected to SVA prior to C_{60} deposition. Interestingly, the annealed devices, i.e. the somewhat less ordered devices as compared to the films subjected to SVA, have the highest cell efficiencies and the highest open circuit voltages. This is an indication that some disorder can assist eh-pair dissociation, notably in a small molecule device.

4.3 The impact of delocalization on eh-pair dissociation

Although disorder at the interface may assist electron-hole-dissociation, it does not solve the problem of how to reconcile the observation that the dissociating entity is initially a “short” eh-pair, i.e. a coulomb bound CT state, with the fact that its subsequent dissociation requires little if any thermal energy, as evidenced by temperature-dependent photocurrent measurements. [53] Arkhipov et al. conjectured that delocalization of an initially quite mobile charge on a preferentially polymeric donor is helpful. [43] They parametrized the delocalization in terms of an effective mass of the mobile charge. When generating an eh-pair on conjugated polymer/C_{60} interface the electron will initially, at least temporarily, be localized at the C_{60} but the hole is delocalized within the conjugation length of the chain. This implies that the hole will execute zero point oscillations within the coulomb potential which, in a semi-classical picture, is associated with a finite zero-point oscillation energy. The energy needed for a pair to escape is therefore the energy of the charge-transfer state in the coulomb potential diminished by the energy the zero point oscillation. It can be further diminished by dark dipoles at the interface (see above). In an harmonic approximation the zero point energy of this oscillation scales inversely with the square root of the effective mass of the oscillating particle. When the hole moves away from the sibling electron, the coulomb potential vanishes and so does the zero point energy.

A rough estimate of this effect indicates that it can be important only if the effective mass of the oscillating charge is significantly less that the free electron mass. This is realized in conjugated polymers as testified by experiment and theory. An experimental probe is provided by the electrorabsorption/reflection signal of the valence to conduction band transition of isolated perfect polydiacetylene chains embedded in a monomer crystal that is located 0.5-0.6 eV above the excitonic absorption spectrum. [54] An analysis of this spectral feature in term the Franz-Keldysh theory indicates that the charge carriers move in delocalized band states with an effective mass m of 0.05 electron masses m_e. Later on van der Horst et al. showed that this value of the effective mass is recovered when solving Bethe-Salpeter-equation for the two-body Green's function. [55] It includes interchain screening of the coulomb interaction by using the bulk dielectric constant in the screened interaction. The fact that basically the same value of m/m_e have been calculated for number of (perfectly ordered) conjugated polymers (Table 1) indicates that the result is more or less universal for a perfectly ordered polymer chain. It is straightforward to assume that the effective mass should decrease with disorder and should eventually approach the value of a molecular crystal composed of small molecule.s [56]

We tested the idea whether or not delocalization has an important influence of eh-dissociation by measuring the dependence of the photocurrent as a function of the applied electric field in a series of poly-phenylene-type donor materials and C_{60} in an only 60-70 nm thick bilayer assembly. Since in a thin bilayer diode bimolecular recombination is suppressed, this field dependence reflects the balance between the escape of the eh-pair from the coulomb potential and their geminate recombination. The experimentally determined dissociation yield increases with increasing electric field and finally saturates. The saturation field, F_{sat}, is the field at which the binding energy of the eh-pair is compensated by the electrostatic potential due to the superimposed applied and built-in field. A decreasing value of F_{sat} is therefore a signature of a lowering of the binding energy.

It turns out that F_{sat} decreases is the series DOO-PPP, PF2/6, PIF, MeLPP-dimer, MeLPPP and PCDTBT. [45] It is striking that the saturation field decreases from more than 10^6 V/cm in the case of DOO-PPP to 4.4 x 10^4 V/cm in the case of MeLPPP and 3.4 x 10^4 V/cm for PCDTBT although the factional charge transfer in the dark increases by only a factor of 2 (from $\alpha = 0.014$ for Me-LPPP to 0.030 for DOO-PPP). The only parameter that changes considerably between these polymers is the optical absorption edge. While MeLPPP features a $S_1 \leftarrow S_0$ 0-0 transition near 2.7 eV, it is blue-shifted by 0.6 eV when going to DOO-PPP. This is an obvious signature of disorder. While in MeLPPP covalent bridging enforces planarization of the phenylene rings and, thus, gives rise to a large effective conjugation length, the phenylene rings in DOO-PPP are torsionally displaced. This leads to a short conjugation length, defined as the length of an ordered segment of a chain within which an optical excitation is coherent. The conjugation length can be estimated from the spectroscopically determined variation of the $S_1 \leftarrow S_0$ 0-0 transition energy as a function of the number of repeats. The exponential correlation between the blue shift of the absorption spectrum from going from MeLPPP to DOO-PPP and the increase of the saturation field of photogeneration proves that it is indeed the donor delocalization that is responsible for efficient dissociation of eh-pairs in MeLPPP/C_{60}. It is remarkable that F_{sat} increases in the series PCDTBT/C_{60}, Me-LPPP/C_{60} and DOO-PPP/C_{60} although the difference between the electronegativities of donor and acceptor increases. This is inconsistent with the notion that the driving force, quantified in terms of the electronegativity difference, has a crucial influence on the cell efficiency.

5. The Arkhipov-Baranowskii model

The notion that both delocalization and dark dipoles at the donor-acceptor interface have an important bearing on eh-pair dissociation has been cast into the Arkhipov-Baranowskii model. [43, 57] It is an analytic approach to explain the dissociation of electron-hole-pairs at the internal interface of a bilayer donor-acceptor assembly as a function of the electric field and temperature. It is essentially a continuation of the Onsager-Braun model yet taking into account the effects of delocalization and interfacial dipoles. The donor moieties are considered to be infinite parallel chains on top of an acceptor layer. It is assumed that optical excitation creates a stationary electron on the acceptor and the hole that oscillates within the coulomb potential of the sibling electron. Under the action of an electric field, oriented perpendicular to the chains, the hole executes a random walk and will eventually escape the coulomb potential or recombine geminately. The input parameters are the effective mass of the hole, the fractional charge transfer at the donor-acceptor interface in the dark, the product of the intrinsic lifetime of the eh-pair and the jump rate, the distance between the chains and the dielectric constant. The dissociation yield is determined by the trade-off between the rate of escape from the coulomb potential, tractable in terms of the Rubel approach for a one dimensional random walk, [58] and the rate of intrinsic recombination of the electron-hole-pair at the donor-acceptor interface. This is equivalent to the Onsager-Braun approach (see eq 2). We note, however, that the Onsager-Braun approach is premised on the notion that the electron-hole pair is formed by point charges. Thus, it disregards the distance dependent contribution of the kinetic energy of the hole executing zero point oscillations within an extended π-conjugated chain of a polymer or an more extended oligomer. In the Arkhipov-Baranowskii approach, this zero-point oscillation energy is explicitly included. The energy of the hole on the chain is calculated in the Arkhipov-Baranowskii model by solving the Schrödinger equation employing a harmonic approximation of the coulomb potential. In an amended version of the model the realistic potential is introduced and solved numerically. In the Arkhipov-Baranowskii model, inter-chain disorder is disregarded and intra-chain disorder is taken into account via a variable effective mass of the hole.

It has been shown that the model is able to fit the experimentally determined field dependence of the dissociation of eh-pairs in a series of poly-phenylene-type donors and C_{60} as an acceptor using realistic fit parameters. For a PCDTBT/C_{60}, MeLPPP/C_{60} and DOO-PPP/C_{60} bilayer devices the values of 0.125, 0.11 and 1.18 for m/m_e are inferred from the experimentally determined saturation fields. This correlates with the hypsochromic shift of the absorption when going to DOO-PPP and the concomitant decrease of the effective conjugation length. The fact that the values of F_{sat} for MeLPPP and PCDTBT are around 4 x 10^4 V/cm and, consequently, are comparable if lower that the built-in electric field explains that the j(V) curve of the diode is essentially flat under short circuit condition. Figure 4 illustrates the reason for this result that turns out to be crucial for the power efficiency of OSCs. It shows the evolution of the energy of an eh-pair as a function of distance of the hole from the countercharge. As m/m_e decreases that dependence flattens.

<Figure 4 about here>

Using the model advanced above allows calculating the binding energy of charge transfer state at the donor-acceptor interface. It is defined as the difference between the energy of a pair of charges at infinite separation and that of the CT state, $E_b = (I_P^D - E_A^A) - E_{CT}$, where E_{CT} is the energy needed to generate the CT state from the ground state. Figure 5 shows E_b as a function of m/m_e parametric in the dielectric constant. In the limit of complete localization, equivalent to m/m_e=10 , E_b converges to the value predicted from the point charge model. This is a gratifying consistency test for the model. E_b decreases when the effective mass decreases. For m/m_e = 0.1 and a dielectric constant in the realistic range of 3.0-4.5, E_b is predicted to be about 0.25±0.7 eV if fractional dipoles are neglected. Taking a realistic value of α=0.02, typical for MeLPPP or PCDTBT with C_{60}, for the fractional dipole strength yields E_b=0.18±0.04. The value of the binding energy can be determined experimentally, thus allowing for comparison between experiment and model. For this, the ionization potential of the donor, I_P^D, and the electron affinity of the acceptor, E_A^A, need to be known, e.g. from photoemission and inverse photoemission spectroscopy. The energy of the charge transfer state, E_{CT}, can be determined for example from the intersection of CT emission and absorption spectra or from extrapolating the temperature dependence of the open-circuit voltage to 0 K. [5, 38] With this approach, one obtains $E_b = (I_P^D - E_A^A) - E_{CT}$= (5.28-3.65) eV – 1.4 eV = 0.23 eV for MeLPPP/C_{60}, with an error of about 0.05 eV [59] We consider this agreement as an important support for the model. In passing we note a similar agreement exists for a PCDTBT/PCBM diode, and consistent values are also obtained for a DOO-PPP/C_{60} diode, where the CT state is more strongly bound as expected for a highly disordered polymeric donor with large effective mass. This is consistent with the observation that a DOO-PPP/C_{60} diode is a very poor solar cell. Efficient charge generation occurs only when an electric field of 1 MV/cm is applied.

<Fig.5 about here >

Further evidence in favor of the Arkhipov-Baranowskii model is the weak temperature dependence of the eh-pair dissociation. Early on, the missing temperature dependence of photogeneration in OSCs as well as in single compound conjugated polymers has been taken as a signature of the failure of the point charge model for explaining eh-dissociation . [10] [53] The present model provides a straightforward explanation. Figure 6 shows the calculated temperature dependence of the dissociation yield in an Arrhenius representation. Above 300 K the temperature dependence of the dissociation yield becomes weaker and ultimately vanishes when using the parameters m/m_e = 0.1 and α =0.02 for the effective mass and the fractional charge transfer at the interface, respectively. At lower temperatures conventional Arrhenius behavior is approached with activation energies that decrease with increasing electric field. When going from a system with a constant fractional dipole strength of α =0.02 but decreasing m/m_e from 1 to 0.1, the activation energy decreases from 0.35 eV to 0.12 eV. Consider that the point charge model would predict an activationn energy of 0.45 eV. Beyond a certain temperature the dissociation yield flattens and eventually becomes temperature independent because a hole can make an increasing number of attempts towards final escape although each individual jump is still thermally activated. In order to test the applicability of the model, photodissociation was studied on MeLPPP/C_{60} bilayer cells within a temperature range of 300 – 150 K (Figure 7). The fact that within a temperature range between 300 K and 150 the data can be fitted using the same set of parameters is an important consistency check for the model.

<Figure 6 and Figure 7 about here>

6. Conclusions

Let us summarize important experimental results on the eh-pair dissociation in donor-acceptors OCSs. There is consensus that neutral excitons in the donor or acceptor phase, either generated at the donor-acceptor interface or diffused towards it, undergo a charge transfer reaction on a time scale of 100 fs.. [26, 27] CT states can also be generated by direct excitation below the absorption edges of donor and acceptor. [5, 41] The initially created eh-pairs are nearest-neighbor charge transfer (CT) states [34] [30] or short ranged eh-pairs. [33] [4], independently of the way they have been generated, i.e. by exciting either the donor, the acceptor or – directly- the CT state. [5] This implies that the dissociating entities are relaxed, i.e. “cold” CT states and it does matter how much energy is dissipated in the course of the initial electron (hole) transfer. [25] [59] One cannot rule out that just after its creation an intermediate hot CT state has a higher chance for dissociation, but the overwhelming fraction of dissociation events proceed via cold CT states. Their dissociation occurs on a 100 fs to ns time scale. [30] [33] The escape of CT-state/eh-pair from the mutual attractive potential is an field assisted random walk that depends crucially of the screening of the coulomb potential by preexisting dipoles at the interface. In OSCs with π-conjugated polymers as donors, delocalization further facilitates the dissociation of the CT state / eh-pair. [45] [33] [60] Independent evidence for the importance of delocalization in conjugated polymers comes from electron spin resonance and electron nuclear double resonance experiments on P3HT:PCBM blends. Since such experiments probe the magnitude of the interaction between the spin of the unpaired electron and the magnetic moments of the protons they provide a handle on how a hole in the polymer chain is delocalized .[61]

Organic solar cells are more or less disordered systems. This implies that both the exciton states of donor and acceptor as well as CT states form distributions in energy with more or less broad tails. Usually, the separating eh-pairs can be identified with the center states of the distribution of cold yet delocalized CT states. Those electron-hole pairs, however, that do not escape from the coulomb well will eventually migrate to tails states of the distribution of states in the course of a dispersive random walk process .[62] Being more strongly localized those tail states are also more strongly bound and have a longer lifetime. They recombine geminately featuring non-exponential decay characteristics and can be revitalized by IR stimulation.[63] [64] [24] The broad distribution of the DOS results primarily from variations in polarization energy and conjugation length, both due to structural and morphological disorder. Notably in conjugated polymers there are furthermore additional morphologically controlled states that give rise to weak and red-shifted photoluminescence. This is due to specific interchain configurations that lead to excimer or H-type emissions.[65-69] Such states can also contribute to efficient dissociation.

The Arkhipov-Baranowskii model is way to describe the dissociation of "cold" CT states/eh-pairs in polymeric OSCs incorporating the effect of delocalization and electrostatic screening by interfacial dipoles. In its present version it applies to an ordered system in which one of the charges (usually the hole) is delocalized while the sibling counter charge is localized. This is certainly a simplified view and ignores the fact that in OSCs with C_{60} or PCBM as an acceptor the electron is quite mobile.[70] Gelinas et al argued that in small molecule diode there can be an ultra-fast coherent electron motion within well-ordered domains of PCBM.[33] An extension of the model might pave the way to a unified description of eh-pair dissociation in systems spanning the range from complete charge localization to full delocalization. Another timely problem relates to anisotropy of OSCs with π-conjugated polymeric donors. It is well documented that in conjugated polymers the dielectric constants parallel and perpendicular to the chain differ by about a factor of two.[71] This effect may be irrelevant in thin bilayer diodes because the polymer chains are more or less parallel to the substrate, i.e. the electric field is orthogonal to the chains. However, it could be important in bulk heterojunctions because in this case there is an arbitrary orientation of charge transfer events relative to the internal electric field.

Undoubtedly, significant progress has been made towards a unified view of photogeneration of charges in both organic and inorganic semiconductors over the last decade. It has meanwhile been recognized that dielectric screening in inorganic semiconductors has its counterpart in π-conjugated polymers in which excitons as well as charges are more or less delocalized depending on how perfect the chains are organized. In a similar way, there is electrostatic screening at the donor-acceptor interface of an OSC. The superposition of both effects, screening and delocalization, ensures that the coulomb potential of an eh-pair is effectively distorted so that the capture radius can become much less than the Langevin capture radius of an eh-pair in a material with a given dielectric constant. While there are still a number of issues to be clarified further, the present level of understanding is gratifying.

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Tables

Table 1:

Effective mass calculated by Van-der-Horst et al. [55] using the Bethe-Salpeter equation

Polymer	effective mass
Polythiophene	0.076
PPV	0.048
LPPP	0.058
PA	0.029
PDA	0.035*

*experimental value: 0.05 ±0.01 [54]

Figures

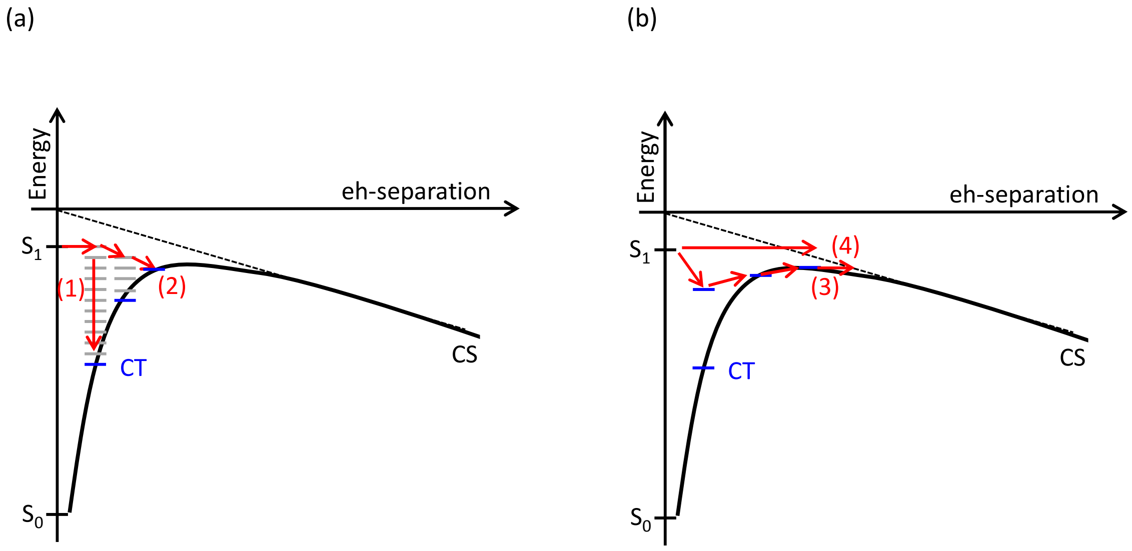

Figure 1

Schematic illustrating 4 different ways how excess energy resulting from electron transfer may assist the dissociation of the interfacial electron-hole pair. (a) The energy of a vibrationally hot CT states leads to local heating, thus increasing the Boltzmann factor for thermally assisted escape from the cold CT state (1), or thermalization via exothermic transfer steps leads to a more loosely bound CT state (2). (b) a higher-energy CT state is generated that couples more efficiently to charge separated / charge transporting states (3) or the transferred electron leaves the coulomb well ballistically (4).

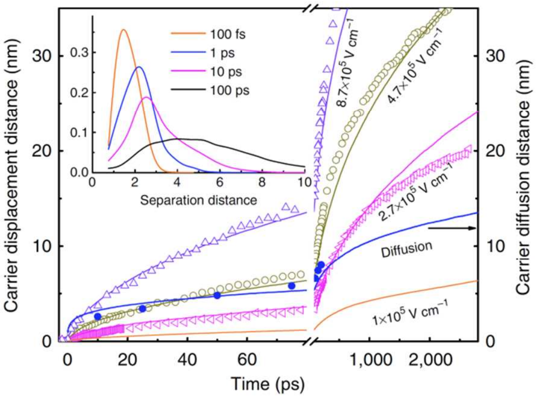

Figure 2

Time dependent separation of electron-hole-pairs generated in P3HT:PCBM bulk-hetero junction employing the EFISH technique. The parameter is the applied electric field corrected for the built-in field. The symbols and lines indicate values derived from EFISH experiment and calculation, respectively, with the blue symbols relating to a Monte-Carlo simulation. The inset shows how the distribution of the electron-hole separation evolves with time in the absence of an electric field.

From Vithanage et al. [30]

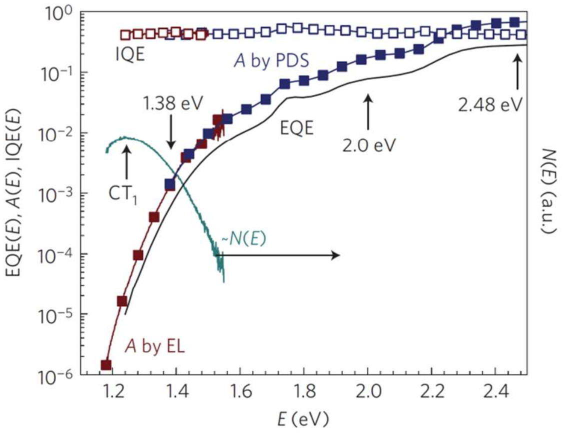

Figure 3

The internal quantum efficiency (IQE) of photogeneration in a MEH-PPV/PCBM bulk-hetero blend (open squares). The full curve is the external quantum efficiency (EQE) of the diode. A is the fraction of absorbed photons (full squares). In the spectral region of the $S_1 \leftarrow S_0$ transition (with origin close to 2.0 eV), A is inferred from the optical density. Below 2.0 eV, is measured employing photothermal deflection spectroscopy. In the low energy spectral range in which relaxed charge transfer states (CT_1) emit, A was reconstructed from the radiative decay of thermally relaxed CT states with a density of states distribution (right ordinate) centered at 1.24 eV. The energy of non-relaxed CT states is 1.38 eV.

From Vandewal et al. [5]

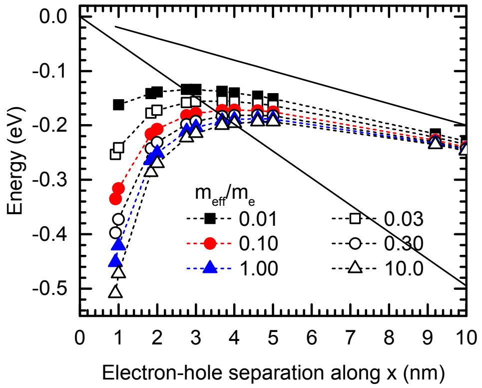

Figure 4

Calculated energy of mobile hole as a function of the distance x perpendicular to the interface where a sibling countercharge is located. The black line is the applied potential at a field of 2 x 10_5 V/cm. The binding energy at a certain distance thus corresponds to the difference between the black line and the hole energy. The parameter of the calculationis the relative effective mass of the hole. No fractional dipoles are considered here.

From Tscheuschner et al. [59]

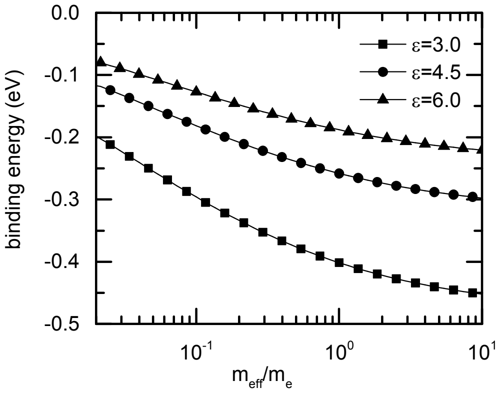

Figure 5

The binding energy E_b of an electron hole pair with inter-charge separation of 1 nm as a function of the hole effective mass for different dielectric constants ε in zero applied electric field and in the absence of interfacial dipolar screening.

From Tscheuschner et al. [59]

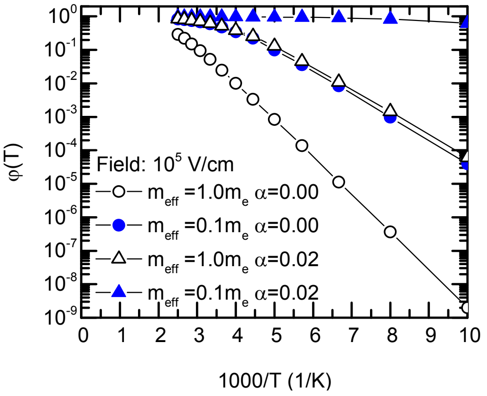

Figure 6

The calculated dissociation probability $\varphi(F)$ as a function of inverse temperature for an effective mass of 1.0 m_e (open symbols) and 0.1 m_e (full sumbols) in the absence of an interfacial dipole (circles) and for a fractional dipole strengths of α=0.02 (triangles).

From Tscheuschner et al. [59]

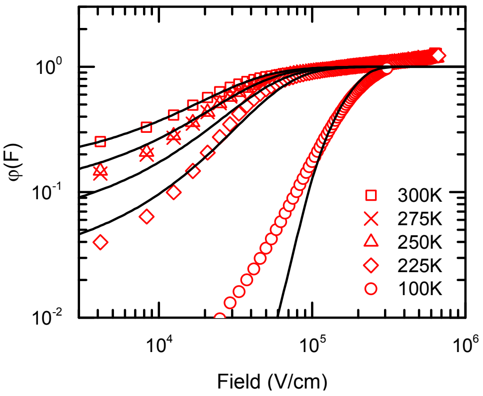

Figure 7

The photocurrent yield (red symbols), normalized to unity at the saturation field, for an organic solar cell in the layer structure ITO/MoO_3/ 30 nm MeLPPP /30 nm C_{60}/Al. Also shown is the dissociation probability $\varphi(F)$ calculated using the Arkhipov-Baranowskii formalim for an relative effective mass of m/m = 0.112, a fractional dipole strength of , α=0.0142 and $\tau\nu_0 e^{-2\gamma r_{ij}} = 2500$ for different temperatures.

From Tscheuschner et al. [59]

References

1. M. A. Green, K. Emery, Y. Hishikawa, W. Warta and E. D. Dunlop, *Progress in Photovoltaics*, 2013, **21**, 1-11.
2. A. K. K. Kyaw, D. H. Wang, V. Gupta, J. Zhang, S. Chand, G. C. Bazan and A. J. Heeger, *Advanced Materials*, 2013, **25**, 2397-2402.
3. E. T. Hoke, K. Vandewal, J. A. Bartelt, W. R. Mateker, J. D. Douglas, R. Noriega, K. R. Graham, J. M. J. Frechet, A. Salleo and M. D. McGehee, *Adv Energy Mater*, 2013, **3**, 220-230.
4. A. C. Morteani, P. Sreearunothai, L. M. Herz, R. H. Friend and C. Silva, *PHYS REV LETT*, 2004, **92**, 247402.
5. K. Vandewal, S. Albrecht, E. T. Hoke, K. R. Graham, J. Widmer, J. D. Douglas, M. Schubert, W. R. Mateker, J. T. Bloking, G. F. Burkhard, A. Sellinger, J. M. J. Frechet, A. Amassian, M. K. Riede, M. D. McGehee, D. Neher and A. Salleo, *Nature Materials*, 2014, **13**, 63-68.
6. L. Onsager, *Journal of Chemical Physics*, 1934, **2**, 599.
7. L. Onsager, *Phys. Rev.*, 1938, **54**, 554-557.
8. R. R. Chance and C. L. Braun, *J. Chem. Phys.*, 1976, **64**, 3573-3581.
9. N. E. Geacintov and M. Pope, *Journal of Chemical Physics*, 1967, **47**, 1194-&.
10. S. Barth, H. Bässler, U. Scherf and K. Müllen, *Chemical Physics Letters*, 1998, **288**, 147-154.
11. A. Köhler, D. A. dos Santos, D. Beljonne, Z. Shuai, J. L. Bredas, A. B. Holmes, A. Kraus, K. Müllen and R. H. Friend, *Nature*, 1998, **392**, 903-906.
12. C. L. Braun, *Journal of Chemical Physics*, 1984, **80**, 4157-4161.
13. M. Wojcik and M. Tachiya, *Journal of Chemical Physics*, 2009, **130**.
14. T. E. Goliber and J. H. Perlstein, *Journal of Chemical Physics*, 1984, **80**, 4162-4167.
15. P. Peumans and S. R. Forrest, *Chemical Physics Letters*, 2004, **398**, 27-31.

16. D. Veldman, O. Ipek, S. C. J. Meskers, J. Sweelssen, M. M. Koetse, S. C. Veenstra, J. M. Kroon, S. S. van Bavel, J. Loos and R. A. J. Janssen, *Journal of the American Chemical Society*, 2008, **130**, 7721-7735.

17. P. Petelenz, M. Slawik and B. Pac, *Synth. Met.*, 1994, **64**, 335-339.

18. N. Christ, S. W. Kettlitz, S. Valouch, J. Mescher, M. Nintz and U. Lemmer, *Organic Electronics*, 2013, **14**, 973-978.

19. V. I. Arkhipov, E. V. Emelianova and H. Bassler, *PHYS REV LETT*, 1999, **82**, 1321-1324.

20. D. M. Basko and E. M. Conwell, *Physical Review B*, 2002, **66**.

21. T. M. Clarke and J. R. Durrant, *Chemical Reviews*, 2010, **110**, 6736-6767.

22. H. Ohkita, S. Cook, Y. Astuti, W. Duffy, S. Tierney, W. Zhang, M. Heeney, I. McCulloch, J. Nelson, D. D. C. Bradley and J. R. Durrant, *Journal of the American Chemical Society*, 2008, **130**, 3030-3042.

23. J. D. Servaites, M. A. Ratner and T. J. Marks, *Energ Environ Sci*, 2011, **4**, 4410-4422.

24. S. D. Dimitrov, A. A. Bakulin, C. B. Nielsen, B. C. Schroeder, J. P. Du, H. Bronstein, I. McCulloch, R. H. Friend and J. R. Durrant, *Journal of the American Chemical Society*, 2012, **134**, 18189-18192.

25. N. E. Jackson, B. M. Savoie, T. J. Marks, L. X. Chen and M. A. Ratner, *Journal of Physical Chemistry Letters*, 2015, **6**, 77-84.

26. D. Herrmann, S. Niesar, C. Scharsich, A. Kohler, M. Stutzmann and E. Riedle, *Journal of the American Chemical Society*, 2011, **133**, 18220-18233.

27. G. Grancini, M. Maiuri, D. Fazzi, A. Petrozza, H. J. Egelhaaf, D. Brida, G. Cerullo and G. Lanzani, *Nature Materials*, 2013, **12**, 29-33.

28. L. G. Kaake, C. M. Zhong, J. A. Love, I. Nagao, G. C. Bazan, T. Q. Nguyen, F. Huang, Y. Cao, D. Moses and A. J. Heeger, *Journal of Physical Chemistry Letters*, 2014, **5**, 2000-2006.

29. Y. Olivier, D. Niedzialek, V. Lemaur, W. Pisula, K. Mullen, U. Koldemir, J. R. Reynolds, R. Lazzaroni, J. Cornil and D. Beljonne, *Advanced Materials*, 2014, **26**, 2119-2136.

30. D. A. Vithanage, A. Devizis, V. Abramavicius, Y. Infahsaeng, D. Abramavicius, R. C. I. MacKenzie, P. E. Keivanidis, A. Yartsev, D. Hertel, J. Nelson, V. Sundstrom and V. Gulbinas, *Nat Commun*, 2013, **4**, DOI: 10.1038/ncomms3334.

31. A. Devižis, A. Serbenta, K. Meerholz, D. Hertel and V. Gulbinas, *PHYS REV LETT*, 2009, **103**, 027404.

32. L. Sebastian, G. Weiser and H. Bassler, *Chemical Physics*, 1981, **61**, 125-135.

33. S. Gelinas, A. Rao, A. Kumar, S. L. Smith, A. W. Chin, J. Clark, T. S. van der Poll, G. C. Bazan and R. H. Friend, *Science*, 2014, **343**, 512-516.

34. A. B. Matheson, S. J. Pearson, A. Ruseckas and I. D. W. Samuel, *Journal of Physical Chemistry Letters*, 2013, **4**, 4166-4171.

35. B. A. Gregg, *Journal of Physical Chemistry Letters*, 2011, **2**, 3013-3015.

36. G. J. Dutton and S. W. Robey, *J. Phys. Chem. C*, 2013, **117**, 25414-25423.

37. S. Albrecht, K. Vandewal, J. R. Tumbleston, F. S. U. Fischer, J. D. Douglas, J. M. J. Frechet, S. Ludwigs, H. Ade, A. Salleo and D. Neher, *Advanced Materials*, 2014, **26**, 2533-2539.

38. K. Tvingstedt, K. Vandewal, A. Gadisa, F. L. Zhang, J. Manca and O. Inganas, *Journal of the American Chemical Society*, 2009, **131**, 11819-11824.

39. M. A. Loi, S. Toffanin, M. Muccini, M. Forster, U. Scherf and M. Scharber, *ADV FUNCT MATER*, 2007, **17**, 2111-2116.

40. F. Provencher, M. Sakowicz, C. N. Brosseau, G. Latini, S. Beaupre, M. Leclerc, L. X. Reynolds, S. A. Haque, R. Leonelli and C. Silva, *Journal of Polymer Science Part B-Polymer Physics*, 2012, **50**, 1395-1404.

41. A. E. Jailaubekov, A. P. Willard, J. R. Tritsch, W. L. Chan, N. Sai, R. Gearba, L. G. Kaake, K. J. Williams, K. Leung, P. J. Rossky and X. Y. Zhu, *Nature Materials*, 2013, **12**, 66-73.

42. C. Im, W. Tian, H. Bassler, A. Fechtenkotter, M. D. Watson and K. Mullen, *Journal of Chemical Physics*, 2003, **119**, 3952-3957.

43. V. I. Arkhipov, P. Heremans and H. Bässler, *Appl. Phys. Lett.*, 2003, **82**, 4605-4607.

44. S.C.Veenstra, PhD, University of Groningen, 2002.

45. C. Schwarz, S. Tscheuschner, J. Frisch, S. Winkler, N. Koch, H. Bässler and A. Köhler, *Physical Review B*, 2013, **87**.

46. M. Wiemer, A. V. Nenashev, F. Jansson and S. D. Baranovskii, *Appl. Phys. Lett.*, 2011, **99**.

47. M. Wiemer, M. Koch, U. Lemmer, A. B. Pevtsov and S. D. Baranovskii, *Organic Electronics*, 2014, **15**, 2461-2467.

48. I. Avilov, V. Geskin and J. Cornil, *ADV FUNCT MATER*, 2009, **19**, 624-633.

49. S. Verlaak, D. Beljonne, D. Cheyns, C. Rolin, M. Linares, F. Castet, J. Cornil and P. Heremans, *ADV FUNCT MATER*, 2009, **19**, 3809-3814.

50. E. V. Emelianova, M. van der Auweraer and H. Bässler, *Journal of Chemical Physics*, 2008, **128**, -.

51. J. D. Zimmerman, X. Xiao, C. K. Renshaw, S. Y. Wang, V. V. Diev, M. E. Thompson and S. R. Forrest, *Nano Letters*, 2012, **12**, 4366-4371.

52. B. Song, C. Rolin, J. D. Zimmerman and S. R. Forrest, *Advanced Materials*, 2014, **26**, 2914-2918.

53. A. Petersen, A. Ojala, T. Kirchartz, T. A. Wagner, F. Wurthner and U. Rau, *Physical Review B*, 2012, **85**.

54. G. Weiser, *Physical Review B*, 1992, **45**, 14076-14085.

55. J. W. van der Horst, P. A. Bobbert, M. A. J. Michels and H. Bassler, *Journal of Chemical Physics*, 2001, **114**, 6950-6957.

56. D. M. Burland, *PHYS REV LETT*, 1974, **33**, 833-835.

57. A. V. Nenashev, S. D. Baranovskii, M. Wiemer, F. Jansson, R. Osterbacka, A. V. Dvurechenskii and F. Gebhard, *Physical Review B*, 2011, **84**.

58. O. Rubel, S. D. Baranovskii, W. Stolz and F. Gebhard, *PHYS REV LETT*, 2008, **100**, -.

59. S. Tscheuschner, H. Bässler, K. Huber and A. Köhler, *Journal of physical Chemistry B*, in press.

60. C. Deibel, T. Strobel and V. Dyakonov, *PHYS REV LETT*, 2009, **103**, 036402.

61. J. Niklas, K. L. Mardis, B. P. Banks, G. M. Grooms, A. Sperlich, V. Dyakonov, S. Beaupre, M. Leclerc, T. Xu, L. P. Yu and O. G. Poluektov, *Physical Chemistry Chemical Physics*, 2013, **15**, 9562-9574.

62. C. S. Ponseca, A. Yartsev, E. Wang, M. R. Andersson, D. Vithanage and V. Sundstrom, *Journal of the American Chemical Society*, 2012, **134**, 11836-11839.

63. A. A. Bakulin, A. Rao, V. G. Pavelyev, P. H. M. van Loosdrecht, M. S. Pshenichnikov, D. Niedzialek, J. Cornil, D. Beljonne and R. H. Friend, *Science*, 2012, **335**, 1340-1344.

64. R. A. Marsh, J. M. Hodgkiss and R. H. Friend, *Advanced Materials*, 2010, **22**, 3672-+.

65. C. J. Collison, L. J. Rothberg, V. Treemaneekarn and Y. Li, *Macromolecules*, 2001, **34**, 2346-2352.

66. H. Yamagata, N. J. Hestand, F. C. Spano, A. Kohler, C. Scharsich, S. T. Hoffmann and H. Bassler, *Journal of Chemical Physics*, 2013, **139**.

67. O. G. Reid, R. D. Pensack, Y. Song, G. D. Scholes and G. Rumbles, *Chemistry of Materials*, 2014, **26**, 561-575.

68. F. Panzer, M. Sommer, H. Bassler, M. Thelakkat and A. Kohler, *Macromolecules*, 2015, **48**, 1543-1553.

69. B. M. Savoie, A. Rao, A. A. Bakulin, S. Gelinas, B. Movaghar, R. H. Friend, T. J. Marks and M. A. Ratner, *Journal of the American Chemical Society*, 2014, **136**, 2876-2884.

70. A. Devizis, D. Hertel, K. Meerholz, V. Gulbinas and J. E. Moser, *Organic Electronics*, 2014, **15**, 3729-3734.

71. D. Comoretto, G. Dellepiane, F. Marabelli, P. Tognini, A. Stella, J. Cornil, D. A. dos Santos, J. L. Bredas and D. Moses, *Synthetic Metals*, 2001, **116**, 107-110.

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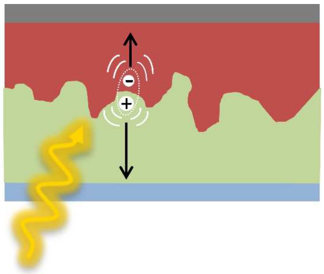

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