What determines the mobility of charge carriers in conjugated polymers?

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In a conjugated polymer, the mobility of charge carriers is not a well-defined coefficient of a particular material as it is in an inorganic crystalline semiconductor but depends on the time domain of detection. On a time-scale of typically 100 fs, the on-chain mobility is ultra-high and controlled by the electronic band width of the polymer chain. When a carrier hits a chain imperfection, subsequent mesoscopic on-chain motion is retarded and controlled by intrachain disorder to which the chain environment contributes. Macroscopic transport commences after a time when interchain carrier jumps become rate limiting. It is routinely probed by time-of-flight experiments and can be rationalized in terms of random walk within a rough energy landscape. Experimental signatures of the various modes of transport are discussed.

Keywords: time-resolved photoconductivity; hopping transport; conjugated polymers

1. Introduction

The response time of an optoelectronic device depends on how fast the charge carriers move in a given electric field. The notion has been that in random organic solids, notably polymers, the mobility of charge carriers is many orders of magnitude less than that in crystalline semiconductors. This is a major obstacle against their wide-scale application. The obvious reason for the low mobility is disorder. Randomness of the structure on a molecular scale implies roughening of the energetic landscape in which the charge carriers move. As a result, thermal excitation and relaxation processes become a bottleneck for transport (Arkhipov et al. 2006). However, disorder-controlled processes must depend on the length-scale of the elementary transport event. In a 20 μm thick photoreceptor of a photocopier, the length-scale is controlled by the macroscopic sample dimension, i.e. charge carriers explore the entire energetic territory of the sample. This is no longer valid if the spatial carrier displacement upon applying a high-frequency electric field becomes comparable with the length-scale of a typical potential well.

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in the energetic landscape. In this case, the charge carrier mobility must become a time-dependent quantity and should exceed the asymptotic value. Similarly, transport should be affected by the presence of charges in the device when the tail states of the distribution of states (DOS) will be filled and/or the latter can be altered. Altogether, this demonstrates that the mobility of charge carriers in a random organic solid is not a well-defined material parameter as it is in a crystalline inorganic semiconductor but depends on the length of motion, on the temporal observation window and on the sample morphology. In this article, basic elements of hopping transport of charge carriers in random organic solids and recent advances for the class of conjugated polymers will be discussed followed by a survey of phenomena occurring at short time-scales when nanoscopic effects of transport become important and a discussion of transport in the presence of homo- or heterocharges in the device.

2. Macroscopic charge transport in conjugated polymers

The conventional concept of charge transport in a random organic solid, e.g. a molecularly doped polymer or a molecular glass, rests on the notion that a charge carrier hops from site-to-site of an empty DOS of Gaussian profile with variance $\sigma$. If the carrier is initially generated randomly within the DOS, it tends to relax towards tail states. On average, the probability density of occupied states (ODOS) is also a Gaussian with variance $\sigma$ yet displaced by an energy $\sigma^2/kT$ relative to the centre of the DOS (Movaghar et al. 1986; Bässler 1993). Subsequently, thermally activated transport commences. The majority of those carrier jumps starts from the upper portion of the ODOS towards states close to the so-called transport energy (Grünewald & Thomas 1979; Arkhipov et al. 2001). Since the ODOS shifts to lower energies at lower temperatures, the average activation energy for a jump is itself temperature activated. This implies that the charge carrier mobility features a temperature dependence of the form $\mu(T) = \mu_0 \exp[-(2\sigma/3kT)^2]$. The numerical factor in the exponent can be calculated by stochastic random walk theory (Arkhipov et al. 2001, 2006) or by effective medium theory (Movaghar et al. 1986; Arkhipov et al. 2006). It depends on the system dimension; for a three-dimensional system, it is $\approx 2/3$. Usually, an electric field raises the mobility because it lowers the activation barriers. It turns out that the field dependence of $\mu$ resembles that of the Poole–Frenkel (PF) model albeit for different reasons. Note that the PF model requires that a trap is charged when empty whereas in the hopping theory they are assumed neutral. Ignoring site correlation and using Miller–Abrahams transition rates, the predicted $\mu(T, F)$ dependence in an intermediate field regime is

$$\mu(T, F) = \mu_0 \exp \left[ -\left( \frac{2\sigma}{3kT} \right)^2 \right] \exp C_0 \left[ \left( \frac{\sigma}{kT} \right)^2 - \Sigma^2 \right] \sqrt{F}.$$ 

$C_0$ is a numerical constant. For a site separation of 0.6 nm, $C_0 = 2.9 \times 10^{-4}$ (cm V$^{-1}$)$^{1/2}$. $\Sigma$ characterizes the degree of positional disorder of the hopping sites (Bässler 1993). Introducing site correlation alters the coefficient of the $T$ and $F$ dependence somewhat while the general functional dependence is retained (Novikov et al. 1998).

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A generic phenomenon of transport in a random solid is the dispersion of the carrier release times of a localized carrier and, concomitantly, the transit time of charge carriers on their way between generation and discharge at the exit electrode (Scher & Montroll 1975). It is caused by the relaxation of charge carriers until quasi-equilibrium is attained (Movaghar et al. 1986). If the relaxation time $t_{\text{rel}}$ exceeds the transit time, the carriers cannot equilibrate before their discharge at the electrode. Therefore, the displacement current due to the motion of an initially spatially narrow sheet of carriers decreases with time and does not settle to a constant plateau value. In this case, the transit time is no longer a measure of the carrier mobility as a material parameter (Borsenberger et al. 1992). This is a frequently encountered problem in experimental studies notably if the sample contains inadvertent traps.

There is abundant verification of the disorder concept as applied to molecularly doped polymers, molecular glasses and also conjugated polymers (Arkhipov et al. 2006). More recently, hole transport has been studied in the family of spirobifluorene polymers and copolymers (Laquai et al. 2006a, b; figure 1). This is a technologically interesting class of materials because the spiro linkage prevents the formation of incipient dimers that can act as charge and exciton traps (Salbeck et al. 1997). They are photochemically stable and have a convenient spectral window when used in organic light-emitting diodes (OLEDs). A special feature of that work is that (i) charge carriers were not generated intrinsically but via sensitized injection from a 10 nm thick perylene diimide (PDI) layer inserted between the aluminium counter electrode and the sample (indium tin oxide (ITO) electrode; Markham et al. 2002) and (ii) the sample thickness was only 1–2 $\mu$m, i.e. one order of magnitude less than

Figure 1. Chemical structure of the investigated polyspirobifluorene polymers. The contents of each unit are for the spirobifluorene homopolymer 1 ($x=0$, $y=0$, $z=0$), for the spirobifluorene–anthracene copolymer 2 ($x=0.1$, $y=0$, $z=0$), for the spirobifluorene–TAD 3 ($x=0$, $y=0.1$, $z=0$) and for the spirobifluorene–carbazole ($x=0$, $y=0$, $z=0.1$).
commonly used in time-of-flight (TOF) studies. This method of charge generation has two major advantages: (i) injection occurs right at the interface thus avoiding any spreading of the carrier packet due to finite penetration of light inside the sample thus allowing the use of thinner samples and (ii) the position of the highest occupied molecular orbital (HOMO) of the sensitizer is close to that of the polymer. This enables energy selective injection into the transport DOS and reduces the degree of dispersion of TOF signals substantially, even at lower temperatures.

Before discussing the dependence of the hole mobility as a function of temperature, electric field and type of polymer, a set of TOF signals for a polyspirobifluorene–anthracene sample will be discussed, as shown in figure 2. The characteristic features are: (i) except a RC-dependent signal at $t=0$, there is almost no short-time tail of the displacement current before it settles to a plateau value, (ii) the TOF signal is non-dispersive even at $T\leq 253$ K, and (iii) above 300 K, a cusp evolves that is independent of light intensity and cannot therefore be ascribed to space charge effects. The origin of the cusp is shown in figure 3. If carriers are either generated randomly or at higher site energies within the DOS, they will relax towards the quasi-equilibrium energy centred at $\sigma^2/kT$. This relaxation gives rise to a time-dependent initial displacement current that approaches the plateau value before the carriers exit the sample. If carriers are injected energy selectively into the lower states of the DOS already, relaxation is suspended and the current should be time independent. However, if injection occurs at an energy below the quasi-equilibrium energy, the carriers have to be excited thermally to that energy. During this ‘heating time’, the current must increase. Thus, a cusp appears when the equilibration time becomes comparable to or larger than the transit time. It must

Figure 2. Representative TOF transients for polymer 2 (polyspirobifluorene–anthracene) at $T=343$, 323, 293 and 253 K at constant electric field. A cusp develops at higher temperatures. At lower temperatures, the tail of the transient signal lengthens, a signature of dispersive transport.
appear at higher temperatures because the energy of the ODOS is raised at higher temperatures. Consequently, more thermal energy is needed to raise the ensemble of carriers from the generation level to the transport level. A related phenomenon should occur at lower temperatures: under non-selective generation, dispersive transport occurs whenever charge carriers cannot settle to the quasi-equilibrium before reaching the counter electrode. An experimental signature of this fact is that the temperature dependence of the carrier mobility, inferred from the kink from the displacement current in a double logarithmic $j(t)$ plot, must become weaker beyond a certain critical temperature $T_c$ where the transition from non-dispersive to dispersive transport occurs. However, upon injection to the quasi-equilibrium energy, there is no dispersive transit feature anymore yet the temperature dependence of $\mu$ must decrease at $T_c$ because further carrier relaxation at $t \leq t_r$ is absent. Therefore, energy selective injection via a sensitizing layer is an operational tool to greatly reduce dispersive features of transport. The experiments described previously thus confirm the premises of the Gaussian disorder model if applied to conjugated polymers. Figure 4 shows the field dependence of the hole mobility in polymer 1 at various temperatures. The temperature dependence of $\mu$, extrapolated to zero electric field, as well as the slope parameter $\beta$ of the $\ln \mu$ versus $F^{1/2}$ dependence against $(\sigma/kT)^2$ are shown in figures 5 and 6, respectively. The results are consistent with the disorder formalism. The constant $C_0$, which depends on the charge carrier hopping distance, turns out to be $3.5 \times 10^{-4}$ (cm V$^{-1}$)$^{1/2}$. Considering that in the simulation the hopping distance was assumed to be only 0.6 nm, this is also in agreement with the simulation value $C=2.9 \times 10^{-4}$ (cm V$^{-1}$)$^{1/2}$. It is worth noting, however, that when plotting the zero-field mobility

Figure 3. Representation of the energetic situation of the DOS at (a) room temperature $T_1$ and at (b) a higher temperature $T_2$ assuming a constant energy of injection $E_{\text{inj}}$. In (a), the holes are injected close to their equilibrium energy $\varepsilon_\infty$. Transport of charges can occur immediately. In (b), the holes are injected into the tail of the occupied density of states (ODOS); therefore, they have to reach transport sites closer to the centre of the ODOS before transport can occur. This process may cause the cusp that can be observed at higher temperatures.
on an Arrhenius scale one would end up with a straight line yielding an activation energy of 0.28 eV and a prefactor mobility of $6.6 \times 10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ while the prefactor mobility of polymer inferred from a $(1/T)^2$ plot is $2.9 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$.

Figure 4. Variation of hole mobility $\mu_H$ with electric field $F$ and temperature $T$ of homopolymer 1. The lines represent linear fits to the experimental data.

Figure 5. Semilogarithmic plot of the zero-field mobility against $1/T^2$ for homopolymer 1. The line is a linear fit to the data for temperatures higher than 233 K.

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On the other hand, the kink in the ln $\mu$ versus $(1/T)^2$ plot at the predicted temperature below where the charge carriers no longer reach quasi-equilibrium is a consistency test for the disorder model. This is a warning example that a $\mu(T)$ plot alone is an insufficient criterion for choosing a certain transport model.

It turns out that the hole mobility in the poly(spiro-9,9-bifluorene) homopolymer is one order of magnitude lower than that of the well-investigated poly(9,9-dioctylfluorene) (PFO), although the width of the DOS of the latter is higher (103 meV) than that in the former (86 meV). Since in the former the prefactor mobility is usually low as well, this indicates that the rate-limiting step in transport is interchain hopping. Obviously, the presence of the spiro linkage decreases the electronic overlap parameter of adjacent hopping sites. An analogous conclusion has been inferred from hole transport studies in methyl-substituted ladder-type poly(phenylene) (MeLPPP). Extrapolating the weak temperature dependence of the hole mobility to $T/\infty$ yields a prefactor mobility of $3 \times 10^{-3} \text{cm}^2 \text{V}^{-1}\text{S}^{-1}$. Considering the exceptionally weak disorder, this result can only be accounted for by weak interchain coupling.

The results demonstrate that neither anthracene nor carbazole introduced into the polymer chain changes the hole transport properties of alkoxy-substituted spiro copolymers significantly, since both comonomers do not act as traps for holes. This allows the tuning of the optical properties without changing the transport features in devices, e.g. OLEDs. Of course, anthracene and carbazole units interact with neighbouring spiro units and can effectively build concerted transport sites with a concentration of 50% or more if one takes into account an effective conjugation length of at least five repetition units, but this kind of interaction does not seem to influence the transport properties significantly. The result further indicates that in those materials hole transport is non-dispersive and unaffected by inadvertent impurities that could act as traps.
3. Charge transport in confined geometries

There is a huge difference between the mobility of charge carriers in conjugated polymers estimated on the basis on the on-chain transfer matrix element and, concomitantly, the electronic width of the transport bands on the one hand and the mobility values inferred from time-of-flight studies on the other hand. Since the band widths are predicted to be several electron volt wide, i.e. comparable with valence and conduction bands in crystalline inorganic semiconductors, the mobility should be on the order of $10^3 \text{ cm}^2 \text{ Vs}^{-1}$, i.e. 6–9 orders of magnitude larger than experimentally measured. The obvious reason of this discrepancy is related to the spatial scale on which transport occurs. It is reasonable to assume that, in principle, transport is fast as long as it is not affected by intrinsic or extrinsic scattering and/or localization. The ideal systems to test this conjecture are crystalline polydiacetylenes (PDAs), notably perfect PDA chains embedded in a crystalline lattice (Schott 2006). Employing the electroreflection method, Weiser & Möller (2002) analysed the reflection feature approximately 0.5 eV above the excitonic absorption edge in terms of the Franz–Keldysh effect acting on the otherwise hidden valence to conduction band transition. They came up with an effective electron mass of approximately $0.05m_e$, in agreement with theoretical calculations (van der Horst et al. 2001). This would translate into an electron mobility of approximately $10^3 \text{ cm}^2 \text{ Vs}^{-1}$. So far, nobody has ever confirmed this prediction. Employing various methods, there is consensus that the macroscopic mobility of, presumably, electrons in crystalline PDA is greater than 1 cm$^2$ Vs$^{-1}$ along the chain axis and a factor of $10^{-2}$–$10^{-3}$ lower perpendicular to it (Zuilhof et al. 2001). However, this value refers to macroscopic samples. In order to obtain information on the on-chain electron motion, one had to rely on analogous spectroscopic studies on excitons. Recently, the Schott group studied the photoluminescence of single PDA chains in an unreacted crystalline matrix. Using microphotoluminescence imaging, Dubin et al. (2006) measured the steady-state fluorescence from a single chain of a PDA with urethane pending groups, the so-called red phase of BCMU-type PDA. By generating an interference pattern from the light emitted from two spatially well-separated sections of a single chain, the authors could prove that the excited state associated with this emission exhibits quantum coherence which extends over the entire chain, to a distance of tens of micrometres. The measured width of the Lorentzian-type fluorescence line (0.5 meV at 10 K) translates into a dephasing time on the order of 1 ps whereas the exciton lifetime is approximately 100 ps which, by the way, argues against self-trapping as a generic feature of any conjugated polymer. This result is directly connected with the question on the origin of dephasing of an optical excitation in a conjugated polymer. In a non-crystalline conjugated polymer, such as derivative of polyphenylenevinylene (MEH-PPV), the phase coherence time of an optical excitation is as short as 100 fs (Milota et al. 2004; Dykstra et al. 2005). This strongly suggests that dephasing is due to scattering at static or dynamic chain imperfections rather than a generic property of conjugated polymers in general.

Since the optical excitation in conjugated polymers is a Wannier-like exciton with a mean electron–hole separation of 1 nm (Rissler et al. 2001), it is plausible that the scattering time of charge carriers is of the same order of magnitude as that of excitons. It implies that in a disordered conjugated polymer it is determined by static and/or dynamic deviations of the chain topology rather
than by coupling to optical phonons and vibrations. In this context, it is instructive to estimate the time–length scale of the displacement of a charge carrier immediately after generation. Using the Einstein ratio $eD = \mu kT$, one arrives at a mean square displacement of a charge carrier of $\langle x^2 \rangle^{1/2} = (2Dt)^{1/2}$ of 20 nm (60 nm) for a scattering time of 100 fs (1 ps). This has to be compared with the structural correlation length of a chain, the so-called effective conjugation length. Usually, although not well founded, it is inferred from the dependence of the energy of a singlet excitation as a function of the length of oligomers. A conservative estimate is less than 10 nm. Reversing the argument, it is plausible that an excitation, an exciton or a charge carrier, with a diffusion coefficient $D = \mu kT/e = 25 \text{ cm}^2 \text{ s}^{-1}$ is scattered by structural imperfections after approximately 100 fs. In order to detect the ‘true’ mobility of charge carriers unaffected by defect scattering, one had, therefore, to generate free charges and monitor their motion on a time-scale of 100 fs.

Pioneering work on time-resolved probing of charge carrier motion along the chain of a conjugated polymer has been performed by the Delft group using the time-resolved microwave conductivity (TRMC) technique (Gelinck & Warman 1996). Charge carriers are generated by 0.5–50 ns long 3 MeV electron pulses from a Van der Graaff electron accelerator. The transient microwave conductivity is inferred from the decrease of the microwave, typically 30 GHz, power reflected by the cell. Once the number of carriers generated is known, their mobility can be calculated. It turns out that under phase-insensitive detection the mobilities for a variety of conjugated polymers in solution right at the end of the generating electron pulse are approximately $10^{-3}–10^{-1} \text{ cm}^2 \text{ Vs}^{-1}$ (Grozema et al. 2005). This is comparable or somewhat larger than the prefactor mobilities calculated by extrapolating the temperature dependence of the mobility measured by employing the time-of-flight technique. The obvious conclusion is that in TOF studies the rate-limiting step is interchain hopping of carriers while the microwave conductivity is controlled by intrachain motion. More recently, the Delft group extended their work by analysing the real and imaginary part of the complex conductivity (Prins et al. 2006a). The real part of the mobility corresponds to the velocity of charge carriers in phase with the oscillating electric field, i.e. the motion of carriers before they hit a scattering boundary. Since that time is on the order of 100 fs, i.e. almost two orders of magnitude shorter than 30 GHz radiation reaches its maximum amplitude, the real part of the conductivity underestimates greatly the ‘free’ carrier motion. The imaginary part represents the out of phase motion hindered by disorder. In a hypothetical infinite PDA chain, it would be zero. In their current work, Prins et al. (2006a) investigated MeLPPP with chain repeat lengths varying from 13 to 54 in frozen solution and measured a value $\mu = 30 \text{ cm}^2 \text{ Vs}^{-1}$ for long chains. They compared this value with that of isolated chains in solution and obtained a spectacular value of 600 cm$^2$ Vs$^{-1}$ (Prins et al. 2006b). Note that in MeLPPP covalent bridging within the polymer chain ensures planar geometry. Accordingly, there are no torsions or disruptions of the backbone, different from the situation in other conjugated polymers, such as poly-phenylenevinylenes (PPV) and polythiophenes (PT). The results indicate: (i) that in a perfect chain the on-chain mobility is, indeed, as high as expected on the basis of the calculated low effective electron mass, (ii) in frozen solution, the statically disordered chain environment reduces the mobility by a factor of 20, and (iii) the TOF mobility is...
completely controlled by interchain hopping. In non-planar systems like derivatives of PPV and PT, both static and dynamic deviations from perfect chain topology will have a major impact on the microscopic on-chain mobility. Nevertheless interchain disorder effects are by far more important than on-chain localization effects.

4. Charge transport in systems with finite concentration of charge carriers

The disorder concept to rationalize charge transport in a random organic solid is based upon the notion that a charge carrier migrates within an entirely empty DOS. If bottom states are already filled, the occupational density of states must change. It is conceptionally obvious that the activation energy required for a carrier to reach the transport energy will decrease as the quasi-Fermi level is raised and, concomitantly, the carrier mobility should increase. This case is realized in field-effect (FE) transistors and under the condition of space charge limited current flow (Tanase et al. 2005). However, there is a counteracting effect. Extra charges will introduce randomly distributed coulombic centres. They will cause potential fluctuations that contribute to the already existing energetic disorder. Early on, the effect of randomly distributed spatially fixed charges on the original Gaussian DOS has been simulated. It turned out that those potential fluctuations give rise to DOS broadening featuring an exponential tail (Silver et al. 1989). It is arguable whether or not this is the reason for the ubiquitously observed exponential band tails in amorphous inorganic semiconductors.

Recent interest in those problems has been stimulated by the work on charge transport in doped organic semiconductors and on organic FE transistors. Shimotani et al. (2005) compared the hole mobility in poly(3-hexylthiophene) (P3HT) polymer films as a function of carrier concentration measured in both the FE transistor mode and under electrochemical doping. The latter method implies the introduction of counterions in order to maintain charge neutrality, while in the...
FE mode the injected homocharges are inside the transport layer while the heterocharges are inside the gate electrode. It turned out that at moderate doping, say 1%, the mobility of the mobile holes injected electrochemically (EC) is two orders of magnitude smaller than the FE mobility at the same concentration of mobile holes (figure 7). A sharp rise of the mobility with the doping level was observed under EC doping, while the FE mobility features a much weaker dependence on the concentration. Earlier experimental studies of conductivity in EC-doped P3HT (Jiang et al. 2002) have shown that at low-to-moderate doping levels, the carrier mobility decreases with increasing dopant concentration, while it increases steeply at doping levels above 1% doping, as shown in figure 8. Arkhipov et al. (2005) suggested a model of hopping transport that is able to explain the (i) interaction between charge carriers and counterions in both weakly and heavily
doped disordered organic semiconductors, (ii) experimentally observed non-monotonic dependence of the mobility upon dopant concentration, and (iii) difference between mobilities under FE and EC dopings.

The model rests on the notions that the (i) charge transport can be rationalized in terms of the hopping formalism including the concept of transport energy and (ii) DOS is broadened due to randomly positioned fixed charges considering, though, that at higher concentrations their coulombic potentials overlap which leads to a re-smoothing of the energy landscape (Hulea et al. 2004). Comparing experimental and theoretical curves in figure 8 demonstrates that the model is able to recover the basic features of charge transport under EC doping, notably the decreases of the mobility at low doping followed by a steep increase beyond 1% doping owing to progressive filling of deep tail states (figure 7). It confirms that upon EC doping, the DOS of the system deviates significantly from that of an undoped sample. This is in accordance with the theory by Arkhipov et al. (2005; figure 9). The model also provides an answer to the question why the mobility under FE doping is much higher than under EC doping: under FE conditions, the roughening of the energy landscape due to countercharges is absent because they are outside of the active layer. In this case, tail-state filling is the dominant process that determines the carrier mobility.

5. Conclusions

In conjugated polymers, the mobility of charge carriers depends on the domain within which it is monitored. Ultrafast motion, determined solely by the electronic transfer matrix element, i.e. the on-chain band width, is confined to a single topologically well-ordered segment of a conjugated polymer between two chain defects or, more generally, fluctuations of the potential. This process is relevant if a charge carrier is generated by a photon with sufficient energy or by electron beam excitation. To monitor that motion directly, one has to resort
to the technique of THz probing (Hendry *et al.* 2005; Hegmann *et al.* 2006). It is experimentally demanding and data analysis is not straightforward. However, there are several though indirect observations that support the notion of ultrafast charge motion being important. They pertain to the phenomenology of optical charge carrier generation. (i) In a poly(chinoxaline) polymer, in which the repeat units are directly linked together, it has been observed that photogeneration of geminately bound electron–hole pairs occurs at an excess energy of 0.4 eV above the $S_1 \leftarrow S_0 0–0$ transition. This process is absent in a polymer in which the repeat units are electronically decoupled via an ether linkage (Hayer *et al.* 2002). This proves that the strength of electronic coupling is important and that generation of the electron–hole must be a fast process prior to any scattering event. (ii) In the alleged planar $\beta$-phase of PFO, there is a transient absorption feature attributed to polarons, probably geminately bound electron–hole pairs, generated by autoionization of singlet excitations. It is absent in disordered phase of PFO (Hayer *et al.* 2005). This is an analogous test on the importance of ultrafast carrier motion prior to scattering. (iii) In a blend of phenyloxy-phenylenevinylene copolymer and a PDI, the yield of photogeneration features a threshold effect around 10% PDI loading (Im *et al.* 2003). By measuring the field dependence of the photocarrier yield, one can conclude that the rate-determining quantity is the separation of the coulombically bound electron–hole pair that subsequently has to dissociate into a free pair of charges. This separation is most probably morphology controlled. The establishment of an internal interface seems to improve the chain structure and, concomitantly, increases the scattering length of a photogenerated charge carrier. This is highly relevant for organic photovoltaic devices, because their efficiency is proportional to the primary dissociation yield.

Once a charge carrier has encountered an on-chain scattering event, it will execute a random walk along the chain. It is controlled by static and dynamic disorders. The order of magnitude of the on-chain mobility is $10^{-2}–10^{-1} \text{cm}^2 \text{Vs}^{-1}$, i.e. comparable with the prefactor mobility in interchain transport. The method of choice is radiation-induced microwave probing. Usually, it monitors charge motion prior to any trapping. It turns out that the intrinsic on-chain mobility is, by and large, the same for electrons and holes (Prins *et al.* 2005). This is not at all surprising since motion is controlled by fluctuations of the one-dimensional potential and their effect ought to be independent of the sign of the carrier. Any asymmetry had to be accounted for efficient trapping on on-chain traps.

The rate-limiting step for bulk transport is interchain hopping. It is controlled by the energetic and spatial disorder of the hopping sites to which both the distribution of the conjugation lengths of the chain and, concomitantly, the site energies and the environment of a chain contribute. Single-bond covalent binding among hopping sites should have little effect. This explains why the carrier mobility in dendrimers is comparable with that in, for instance, molecularly doped polymers and does not significantly depend on their generation (Lupton *et al.* 2001).

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