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Modelling exciton diffusion in disordered conjugated polymers

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ABSTRACT

We present a combined quantum-chemical and Monte Carlo approach for calculating exciton transport properties in disordered organic materials starting from the molecular scale. We show that traps and energetic disorder are the main limitations for exciton diffusion in conjugated polymers. An analytical model for exciton hopping in a medium of sites with uncorellated energetic disorder gives a quantitative description on the dependence of the diffusion length to both the energetic disorder strength and temperature. We demonstrate how traps and energetic disorder can pin down the diffusion length in conjugated polymers to values below 10 nm.

Keywords: Exciton diffusion, conjugated polymers, energetic disorder, Monte Carlo simulations, quantum-chemical calculations, analytical model

1. INTRODUCTION

During the last decade, conjugated materials have found a plethora of applications in solar cells[1,2], field effect transistors[3], light emitting diodes[4] and sensing devices[5], some of which have reached already the commercial stage. However, improving the efficiencies of those devices depends critically on the control of charge and exciton transport properties in such media. Polymeric materials are disordered in nature, either due to the preparation technique and packing or due to the presence of extrinsic chemical defects with a consequence that the transport properties of charges and excitons have not been fully understood yet. The value of the exciton diffusion length L_D, is critical as for example in solar cells determines the effective area over which exciton dissociation is efficient while in light emitting diodes the value of L_D will control the color of the device. Until now, there is a clear distinction between molecular and polymeric solids on the magnitude of the diffusion length with molecular materials[6-8] displaying L_D values at least one order of magnitude higher than the values found in conjugated polymers[9,10] that are typically below 10 nm.

Here we will argue that the limited exciton diffusion length found in polymers is not an intrinsic property but rather a physical consequence of the large values of disorder that are found in these materials. We will show that even within the weak coupling regime, where exciton transport proceeds via hoping between localized units, the diffusion length could be rather high, in the absence of trapping events and if energetic disorder is low. The aim of this paper is twofold: first to introduce a Monte Carlo (MC) model based on quantum-chemical calculations and investigate the dynamics of the motion of singlet excitons in the presence of traps and energetic disorder and secondly to apply a physical model, based on a simple analytical approach that validates the above results.

2. MOLECULAR SCALE MODELLING

The necessary ingredients for a theoretical model that has as a starting point the molecular scale, are the molecular packing and the intermolecular interactions. In our case we will present and employ such a model in a typical rigid rod fluorene polymer, polyindenofluorene (PIF) of which the photophysical properties have been extensively studied experimentally[11]. Since we are not interested here on providing exact values of the exciton diffusion length in the material, we will use simplified chain-like morphologies. A detailed description of the molecular packing via atomistic

Molecular Dynamics simulations goes beyond the scope of this paper and will be discussed elsewhere for the case of IF3 oligomers forming liquid crystalline mesophases[12]. Here we treat the polymer as a macromolecule, consisting of a number of segments of different lengths. Such assumptions on the morphology are supported by X-ray diffraction data on crystalline samples of a similar rigid rod like polymer, polyfluorene (PFO)[13], that showed hexagonal like packing of the chains. The distribution of segments is extracted by converting the absorption energy distribution of PIF to a length distribution and includes oligomers of indenofluorene of increasing size from 3 to 8 repeat units.

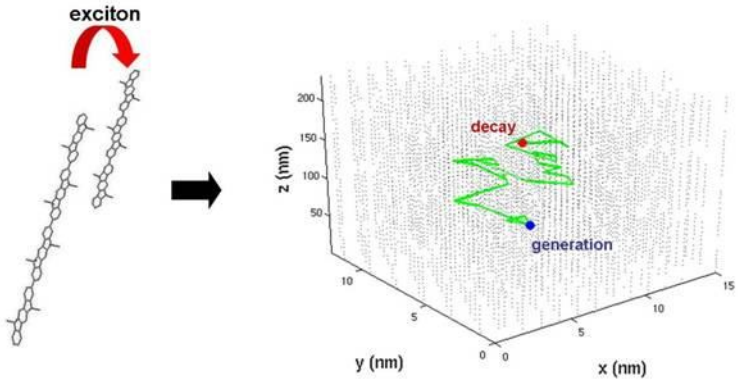

Figure 1. From microscopic transfer rates to exciton trajectories.

2.1 Energy trasfer rates

For singlet excitons in conjugated polymers, the electronic coupling between the individual subunits is much weaker than the electron-nuclear interactions. Therefore, exciton transport takes place in the weak coupling regime with excitons localised in single molecular units[14] (chromophores), transferring their excitation energy to neighboring molecules, that are in their ground electronic state, via resonant energy transfer. The rate for energy transfer between a donor D molecule and an acceptor A molecule that are separated by a distance r can be expressed on it's simple form according to Förster[15] as:

$$k_F = \frac{1}{\tau}\left(\frac{r_F}{r}\right)^6 \tag{1}$$

Where τ is the donor's radiative lifetime and r_F is the Förster radius, defined as the value of intermolecular distance at which the hopping rate is equal to the decay rate. r_F is a spectroscopically accessible quantity, that depends on the fluorescence quantum yield, the acceptor's absorption and donor's emission spectrum and the refractive index. Strictly speaking, the above equation is exact in the limit where the donor and acceptor molecules can be considered as point dipoles. However, for polymers this approximation might break down when the intermolecular distance is small compared to the size of the chromophores[16], which is the typical case as interchain distances of the order of nm are comparable to the molecular dimensions. A generalised Förster model that goes beyond the point dipole approximation will take into account the spatial extent of the excited state wavefunction[17]. Using first order perturbation theory, the transfer rate, expressed in ps^{-1}, between a donor D and an acceptor A molecule reads:

$$k_{DA} = 1.18\left|V_{DA}\right|^2 J_{DA} \tag{2}$$

with V_{DA} the excitonic coupling, in cm^{-1}, and J_{DA} the spectral overlap between the simulated, at the INDO/SCI level, donor emission $F_D(\omega)$ and acceptor absorption spectra $A_A(\omega)$, given by:

$$J_{DA} = \int_0^\infty F_D(\omega) A_A(\omega) \mathrm{d}\omega \tag{3}$$

The simulated spectra have been obtained within the Franck-Condon approximation and a two mode displaced harmonic oscillator model. In what follows, we have calculated the excitonic coupling between all donor D molecules and each of

the fifty nearest neighbor acceptor A oligomers in an assembly of 507 PIF chains (having 11 chromophores each) using the distributed monopole approximation[17,18] that expresses V_{DA} as a Coulomb interaction term (ie neglecting orbital overlap mechanisms):

$$V_{DA} = \frac{1}{4\pi\varepsilon_0} \sum_{i\in D} \sum_{j\in A} \frac{\rho_D(\vec{r}_{D_i})\rho_A(\vec{r}_{A_j})}{\left|\vec{r}_{D_i} - \vec{r}_{A_j}\right|}, \tag{4}$$

where the sum runs over the donor $\vec{r}_{D_i}$ and acceptor $\vec{r}_{A_j}$ atomic positions, ρ are the atomic transition charge densities for the S_0 to S_1 excitation and ε_0 the vacuum permittivity. The transition charges have been computed through single configuration interaction (SCI) calculations, using the intermediate neglect of differential overlap INDO Hamiltonian[19].

2.2 Monte Carlo

To compute the transport properties we use a kinetic Monte Carlo simulation[20] that treats the diffusion of the exciton as a stochastic process of discrete random walk steps with each step being independent of previous events and having a rate calculated via equation (2). The Monte Carlo procedure is as follows: Initially, an exciton is placed at a random molecular site in the assembly, or at a site of given length in the case of site selective excitations. The exciton will have various options for the next Monte Carlo step: either to hop to a neighbor site or to emit radiatively. A waiting time for each available jump can be calculated from an exponential distribution[21] as:

$$\tau_{ij} = -\frac{1}{k_{ij}} \ln(X) \ , \tag{5}$$

where k_{ij} is the transfer rate from an initial site i to a target site j and X is a random variable drawn from a box distribution between 0 and 1. Besides the possible events of hopping to nearest neighbors we also define a rate for radiative emission, ie recombintation of the hole and electron that constitute the exciton, as $\tau_i^{em} = -\tau \ln(X)$. This decay rate is in competence to the hopping events. All events are placed in an array and the event that requires the smallest waiting time is selected and executed. If the chosen event is hopping then a new set of waiting times is generated. In the case where the event with the smallest waiting time is decay then the Monte Carlo trial stops and a new exciton is created in the system until completion of all the number of trials, that are typically of the order of 10^4, large enough to provide us with statistics of importance and construct averages.

3. TRAP LIMITED DIFFUSION

In the case of site selective excitations the average chromophore energy at a given time can be calculated from the time dependent population of the excited chromophores. This quantity is presented on the left panel of Figure 2 as solid lines for excitations initially placed on chromophores of length 3,4,5,6,7 and 8, plotted in decreasing starting energy. For comparison we also display room temperature experimental results on the spectral diffusion of the 0-1 photoluminescence peak for energy selective excitations in a drop-cast PIF sample[11]. We observe that excitons created at the shortest segments will lose their energy moving downhill while excitons created at longest segments will gain energy moving uphill in the energy manifold. Eventually, thermal equilibrium will be reached. Although the simulation and experimental results show a similar behavior, there are clear differences on the timescale for energy relaxation. Experiment suggests an exciton relaxation time of about 300 ps while theory predicts a much faster t_{rel}, of approximately 20 ps.

Now we switch on to include trapping events in the transport simulation. Random sites are assigned as attractive traps for the excitation with a trapping rate much higher (100 times faster) than the hopping rate. Such values are realistic as they correspond for example to the transfer rate to a lower energy acceptor site, for example a perylene molecule[17]. The trapping events will influence the energy relaxation of the excitation at large times, as shown in Figure 2. By allowing a small percentage of the sites, ~0.5%, to act as traps we can obtain a reasonable timescale for exciton relaxation. This

demonstrates that in a 3 dimensional polymer system a small percentage of trapping sites can very effectively capture the excitations. It is not only the relaxation rate that is is affected from the presence of traps but also the distance over which the excitons travel, ie the diffusion length. This quantity can be estimated from the Monte Carlo simulations as the average travelled distance of all completed trials. As it is depicted on

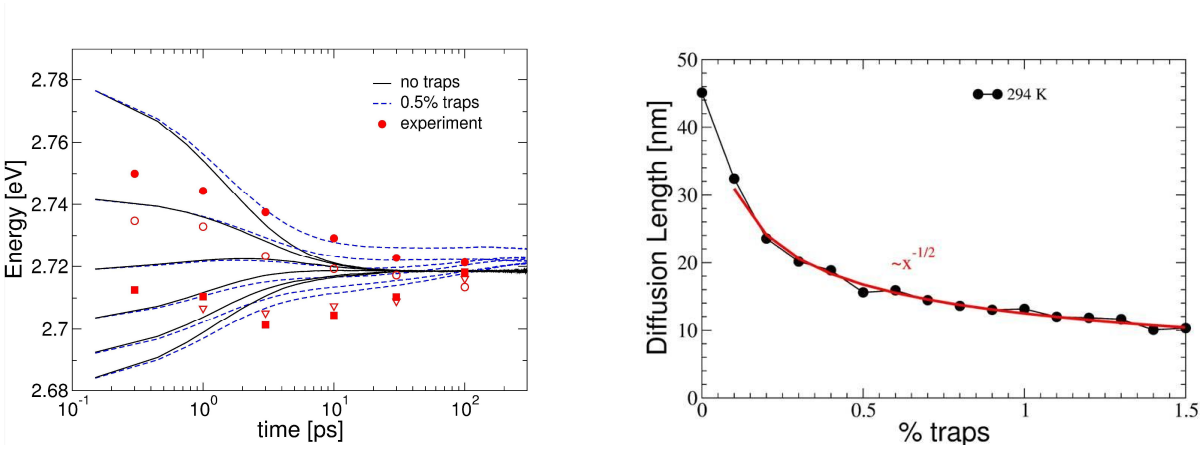

Figure 2. Left panel: Exciton energy relaxation in PIF as a function of time for site selective excitations in a trap free film (black solid lines) and in the presence of traps (blue dashed lines). In order of decreasing starting energy the lines correspond to excitations initially placed in trimers, tetramers, pentamers, hexamers, heptamers and octamers. Red symbols are experimental results from Ref. 11 for excitation energies of 3.062 eV (filled circles), 2.952 eV (open circles), 2.884 eV (filled squares) and 2.851 eV (triangles down). Right panel: Reduction of L_D with increasing trap concentration.

the right panel of Figure 2 a small percentage of trapping sites greatly reduces the diffusion length from ~45 nm to values typically measured in polymers ~10 nm. For small concentration of trap sites the reduction of the diffusion length with the trap percentage x, is in agreement with the expected inverse square root dependence[22]: $L_D = r\sqrt{N_{hop}}$ and therefore $L_D = 1.23\frac{r}{\sqrt{x}}$.

4. ENERGETIC DISORDER

We now turn our attention to the influence of energetic disorder, expected to be present in polymeric solids[14], on exciton diffusion. As a preamble to the analytical calculations we perform a MC study of exciton migration on a morphology at which the molecular sites have been replaced by single atomic centers on a cubic lattice with a lattice constant of a=1 nm and the transfer rates between nearest neighbor sites are given by:

$$k_{ij} = \frac{1}{\tau}\left[\frac{r_F}{r}\right]^6 \times \begin{cases} \exp\left(-\frac{E_j - E_i}{k_B T}\right), & E_j > E_i \\ 1, & E_j \le E_i \end{cases} \tag{6}$$

where E_i and E_j are the site energy values of the initial and target site respectively, k_B is the Boltzmann constant and T the temperature. It is clear from the above equation that it is easy to move downwards in energy but more difficult to perform an upward in energy jump, since the latter is phonon assisted and requires excessive thermal energy. The above equation has been parametirised via quantum-chemical calculations: (i) an effective orientation averaged value for the Förster radius of 3.1 nm has been extracted. This is in good agreement with the value measured experimentally ~3.3 nm in films of PIF[11]. (ii) an exciton lifetime of 500 ps has been computed by averaging the lifetimes of the

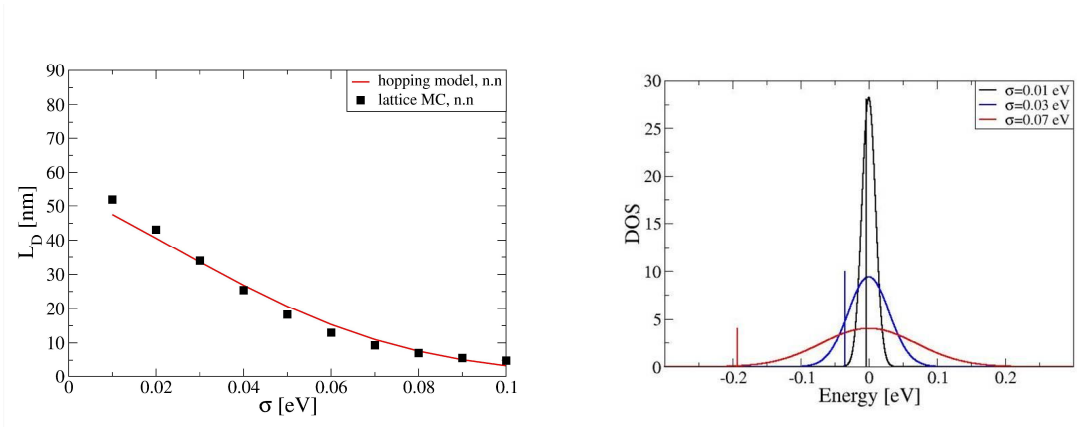

Figure 3. Left panel: L_D as a function of σ for the analytical model(red line) and the lattice MC simulations(squares). Right panel: Shift of the thermal level(vertical lines) with increasing σ for a Gaussian DOS.

different length chromophores: $\tau = \frac{3\varepsilon_0 \hbar c^3}{8\pi^2 \mu^2 \nu^3}$ with the dipole moment of the transition μ and absorption frequency ν obtained from the INDO/SCI calculations. Static, uncorrelated energetic disorder has been introduced to the site energy values and distributed according to a Gaussian with a standard deviation σ that we will allow to vary.

Our central result, summarised in Figure 3, is that energetic disorder in conjugated polymers can cause a dramatic decrease leading to diffusion length values below 10 nm. To test this scenario, we employ analytical tools to derive an expression for L_D in a medium of randomly positioned hopping sites with diagonal(on-site) energetic disorder. This model has as a starting point the Förster equation (6) that can be rewritten as a function of a hopping parameter u: $\Gamma = \frac{1}{\tau}\exp[-u]$ with $u(E,E',r) = 6\ln\left(\frac{r}{r_F}\right) + \frac{\theta(E'-E)}{k_B T}$, where θ the Heaviside function. An average number of target sites with hopping parameter smaller than u can be calculated via integration over space and energy[25] and eventually one can derive an expression for the diffusion coefficient on the assumption of thermal equilibrium(Boltzmann statistics):

$$D = \frac{1}{\tau}\frac{\int_{-\infty}^{+\infty} g(E)\exp(-E/k_B T)\exp[-<u(E)>]<r^2(E)>dE}{\left[\int_{-\infty}^{+\infty} g(E)\exp(-E/k_B T)dE\right]} \cong$$

$$\cong \frac{r_F^{\,6}}{\tau}\left(\frac{4\pi N_t}{3}\right)^{4/3} \frac{\int_{-\infty}^{+\infty} g(E)\exp\left(-\frac{E}{k_B T}\right)dE}{\left[\int_{-\infty}^{+\infty} g(E)\exp(-E/k_B T)dE\right]}\left\{\int_{-\infty}^{E} g(E')dE' + \exp\left(\frac{E}{2k_B T}\right)\int_{E}^{+\infty} g(E')\exp\left(-\frac{E'}{2k_B T}\right)dE'\right\}^{4/3}. \qquad (7)$$

Where $<r^2>$ is the mean square hopping distance and g(E) the excitonic density of states (DOS). It is straightforward to compute the diffusion length:

$$L_D = \sqrt{D\tau} = r_F \left[\frac{\int_{-\infty}^{\infty} g(E)\exp(-E/kT)\exp(-\frac{2}{3} < u(E) >)dE}{\int_{-\infty}^{\infty} g(E)\exp(-E/kT)dE} \right]^{1/2} \quad (8)$$

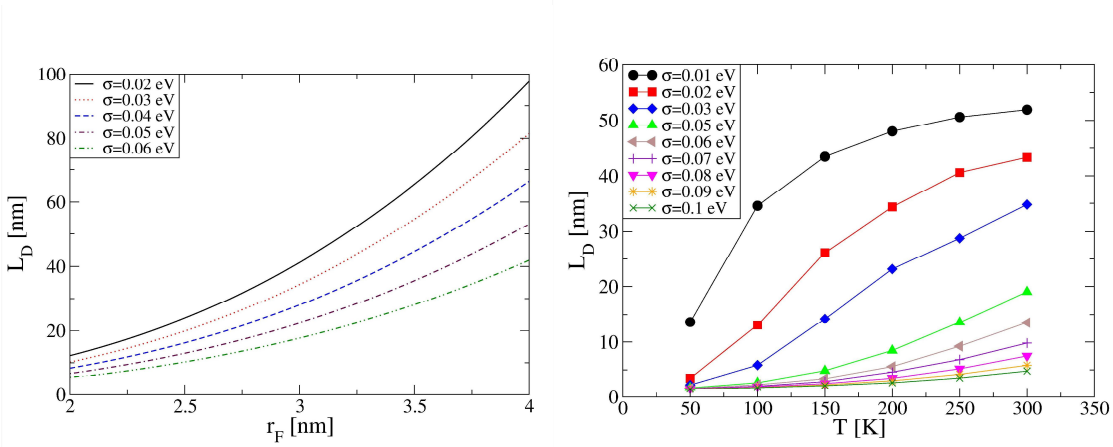

Figure 4. Left panel: Analytical results of L_D as a function of the Förster radius for different values of disorder σ. Right panel: The temperature dependence of L_D for various σ as computed from the MC simulations.

In Figure 3 we display the results obtained from equation 8 for a Gaussian DOS and for a Förster radius of 3.1 nm, a lifetime of 500 ps and a chromophore density of 10^{21} cm^{-3} in order to be consistent with the parameters used in the MC model. As illustrated, L_D is very sensitive to the standard deviation of the Gaussian distribution and greatly reduces with increasing disorder as also predicted from the MC simulations. To understand this behavior, we have to consider that at room temperature, excitons created at any place of the Gaussian distribution will quickly relax to the thermal level, located $-\sigma^2/k_BT$ from the center of the distribution[23]. However, with increasing disorder the thermal level shifts towards the low energy tail of the excitonic density of states, as illustrated in Figure 3, where there is a small number of energetically accessible sites to hop. Henceforth, increasing disorder reduces the paths for exciton transport. There are two other important issues that follow from the analytical calculations: Firstly the diffusion coefficient scales with the chromophore density and the Förster radius according to the expected law $D \sim N_t^{4/3} \frac{r_F^6}{\tau}$ [15,24], see equation 7, and therefore $L_D \sim N_t^{2/3} r_F^3$. This behavior is illustrated in Figure 4 which shows the increase of L_D with the Förster radius, at different levels of disorder. Another interesting result is that as disorder increases, the increase of L_D with r_F becomes less pronounced and in the high disorder limit, chemically different polymers, or a given polymer exhibiting different intermolecular interactions (e.g due to different packing) will exhibit very similar L_D.

The temperature dependence of the diffusion length has been also studied in the framework of MC simulations. For low temperatures, the available energy from the bath is not sufficient in order to overcome energy barriers on the course of the exciton path. The average exciton transfer rate and total number of hops become smaller, resulting to lower L_D values, see Figure 4. Eventually above a certain temperature(that depends on the value of σ) the diffusion becomes thermally activated. These results are in line with recent experimental evidence of thermally activated diffusion in MDMO-PPV[9]. It is therefore the synergetic effect of disorder strength and temperature that controls the exciton diffusion

process. Both MC simulations and the analytical model have shown that L_D exhibits an Arrhenius like behavior only at high T with an activation energy increasing with σ[25].

5. CONCLUSIONS

We have described theoretical tools for modelling the diffusion of singlet excitons in disordered conjugated polymers. These tools include quantum-chemical calculations of exciton transfer rates and Monte Carlo simulations to study the dynamics of the exciton diffusion. The model has been applied in a PIF polymer to examine the influence of single trap sites and energetic disorder on the magnitude of the diffusion length. Additionally an equilibrium analytical model has been applied to justify the dependence of L_D on the disorder strength. These results demonstrate that the simple continuous analytical model, with minimum input parameters the Förster radius and exciton lifetime, provided either by experiment or by quantum-chemical calculations, could be used to estimate the value of the exciton diffusion length and it's variation with disorder strength. We conclude that the small values of the measured diffusion lengths in conjugated polymers are a result of the disorder inherent in these materials. We have shown how traps and energetic disorder can pin down the diffusion length measured in conjugated polymers to values below 10 nm. Although different in nature, both scenarios yield to a reduction of L_D. In reality, both mechanisms are expected to be present in a material. However, if such materials could be engineered to be free of traps and exhibit small values of energetic disorder then the exciton diffusion length values can be improved by at least one order of magnitude.

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