

# Energy transfer processes along a supramolecular chain of $\pi$ -conjugated molecules

BY S. A. SCHMID<sup>1</sup>, R. ABDEL<sup>2</sup>, A. P. H. J. SCHENNING<sup>2</sup>, E. W. MEIJER<sup>2</sup>  
AND L. M. HERZ<sup>1,\*</sup>

<sup>1</sup>*Clarendon Laboratory, Department of Physics, University of Oxford,  
Oxford OX1 3PU, UK*

<sup>2</sup>*Laboratory of Macromolecular and Organic Chemistry, Eindhoven  
University of Technology, PO Box 513, 5600 Eindhoven, The Netherlands*

We have investigated the energy transfer dynamics in a supramolecular linear polymer chain comprising oligofluorene (OF) energy donor units linked by quadruple hydrogen-bonding groups, and oligophenylene (OPV) chain ends that act as energy acceptors. Using femtosecond spectroscopy, we followed the dynamics of energy transfer from the main chain of OF units to the OPV chain ends and simulated these data taking a Monte Carlo approach that included different extents of electronic wave function delocalization for the energy donor and acceptor. Best correlations between experimental and theoretical results were obtained for the assumption of electronic coupling occurring between a localized donor dipole moment and a delocalized acceptor moment. These findings emphasize that geometric relaxation following initial excitation of the donor needs to be taken into account, as it leads to a localization of the donor's excited state wave function prior to energy transfer. In addition, our simulations show that the energy transfer from the main chain to the ends is dominated by an interplay between slow and spatially limited exciton migration along the OF segments comprising the main chain and the comparatively faster hetero-transfer to the end-cap acceptors from directly adjoining OF segments. These results clearly support the description of host–guest energy transfer in linear polymer chains as a two-step mechanism with exciton diffusion in the host being a prerequisite to energy transfer to the guest.

**Keywords:** exciton delocalization; energy transfer; conjugated molecules;  
supramolecular polymers

## 1. Introduction

Absorption of light by a molecule generates excitations that may subsequently be transferred to another chromophore in the vicinity. Such ‘excitation energy transfer’ crucially influences the light-harvesting power of both biological light-harvesting systems [1] and man-made devices [2] based on conjugated molecules. The rate for an individual transfer step of an excitation (exciton) from a donor to

\*Author for correspondence ([l.herz@physics.ox.ac.uk](mailto:l.herz@physics.ox.ac.uk)).

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an acceptor site depends on the strength of the intermolecular electronic coupling and its relation to nuclear lattice relaxation and energetic disorder present in the system [3]. For the case of strong intermolecular coupling, the excitation can be assumed to be coherently delocalized across more than one chromophore, as proposed for some biological [4] and synthetic [5] light-harvesting materials. In the weak coupling regime, on the other hand, excitation transfer proceeds through incoherent ‘hopping’ processes between individual chromophores [6,7]. Such hopping migration has been observed in a range of synthetic molecular solids, as these typically display large energetic disorder and strong electron–phonon coupling that impede the coherent evolution of an excitation across several molecules. However, the extent to which excitation delocalization along *each individual* molecule of the molecular solid influences the energy transfer between the molecules is still a matter of debate. In particular, the standard model developed by Förster [8] to describe energy transfer in the weak coupling regime is based on interactions between point-dipoles (PDs) located on the energy donating and accepting molecules. While this simple model works well for large donor–acceptor separation, it has been reported to fail for transfer distances comparable to the exciton delocalization length [9]. For systems with a high chromophore density, such as molecular solids, more sophisticated models that account for the extended nature of the interacting states are therefore needed. Recently, the line-dipole (LD) model [10,11] and the distributed monopole model [12] have been proposed to describe extended conjugated molecules. However, it is currently unclear to what degree excitonic self-localization has to be incorporated into such models. Such effects feature strongly in organic materials as a result of significant lattice relaxation following soon after excitation, which leads to differences in the delocalization of the absorbing and the emitting excitonic state [12–14]. A clear assessment of the validity of these models has so far been prohibited by the disorder commonly present in organic materials. In particular, inhomogeneities arising from defects [15,16] and conjugation breaks in extended molecules need to be characterized to an unfeasibly high degree if accurate conclusions are to be drawn from a comparison between experimental and modelled observables.

In this study, we have assessed the importance of excitonic delocalization on the energy transfer dynamics along a conjugated molecular chain. In order to overcome issues associated with disorder, we have chosen a well-defined system of  $\pi$ -conjugated oligomers assembled through supramolecular interactions [17,18] into linear chains of chromophores with known length distribution. As a result, we are able to make a direct comparison between measured and simulated energy transfer dynamics, which has been elusive in the past for studies of disordered conjugated polymer materials [12]. Supramolecular systems mimic nature by exploiting non-covalent interactions to result in clearly defined structures in solution that allow investigations in relatively ordered molecular assemblies [19,20]. We compared time-resolved photoluminescence (PL) data with Monte Carlo simulations of the exciton diffusion along the chains, compiled for electronic coupling strengths based on different degrees of excitonic delocalization. Through these combined experimental and model results, we show that both the classical Förster PD and the extended LD models fail to describe the energy transfer dynamics accurately, with the former underestimating and the later overestimating the actual energy transfer rates. We show that an

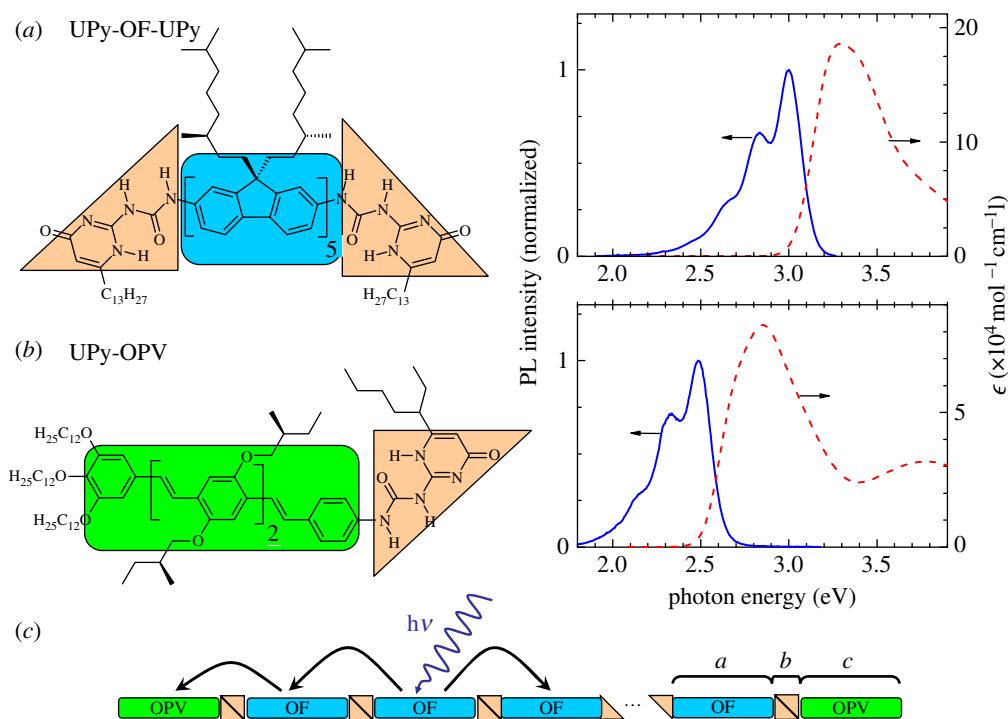


Figure 1. Chemical structures, absorption (dashed line) and steady-state PL spectra (solid line) for (a) bis-UPy-terminated oligofluorene (UPy-OF-UPy) and (b) UPy-terminated oligo(*p*-phenylenevinylene) (UPy-OPV) in  $\text{CHCl}_3$ , with  $\epsilon$  being the molar extinction coefficient. (c) A schematic of the self-assembly process into linear supramolecular polymers together with a definition of the structural parameters *a*, *b* and *c* (see text). The diagram shows how selective excitation of UPy-OF-UPy is followed by excitation transfer along the chain and to the UPy-OPV end groups. (Online version in colour.)

alternative model incorporating strong exciton self-localization after excitation yields an accurate description of the experimental data. In addition, we examined the extent to which exciton migration along a chain of oligofluorene (OF) chromophores contributes to the overall transfer of energy to the chain ends. We find that energy transfer to the chain ends is dominated by the interplay between slow and spatially limited exciton migration along the OF segments comprising the main chain and the comparatively faster energy transfer to end-cap oligo(*p*-phenylenevinylene) (OPV) acceptors from directly adjoining OF segments. These results clearly show that energy transfer from a polymeric host to an energy-accepting guest follows a two-step mechanism.

## 2. Material and methods

Figure 1 shows a schematic of the molecular building blocks that self-assemble in solution into the chains used as model system for this study. The main chain is made of OF pentamers that have 2-ureido-4 [1H]-pyrimidinone (UPy) groups attached to both ends. With two hydrogen

donating and accepting sites per unit, these UPy groups result in the formation of self-complementary quadruple hydrogen bonds with large dimerization constant [18]. Oligo(*p*-phenylenevinylene) (OPV) tetramer derivative was added to these solutions and, as it has a UPy group attached only to one end, acted as chain stopper. These molecules have been shown to form linear supramolecular polymers in mixed solutions, with UPy-OF-UPy molecules assembling into polymer-like chains terminated by UPy-OPV on both ends [21]. Mixed solutions of concentration  $\sim 4 \times 10^{-4} \text{ mol l}^{-1}$  were prepared in chloroform, for which the lifetime of the UPy-UPy hydrogen bond is approximately 0.1 s [22]. The composition of the supramolecular chains therefore remains static during the time scale of exciton migration along the chains. The average chain length is determined by the ratio of the number  $N_{\text{UPy-OPV}}$  of OPV molecules to the number  $N_{\text{UPy-OF-UPy}}$  of OF molecules in solution, i.e.  $x = N_{\text{UPy-OPV}}/N_{\text{UPy-OF-UPy}}$ . By varying  $x$ , changes in the average length of the chains are induced, which will in turn influence the energy transfer dynamics from the main chain to the chain ends. Details of the synthesis procedure for the compounds have been given by Dudek *et al.* [21] and Abbel *et al.* [23].

Time-resolved PL measurements were carried out using an up-conversion set-up that has already been described in detail by Chang *et al.* [14] and Parkinson *et al.* [24]. The liquid samples were kept in quartz cuvettes and excited at a photon energy of 3.30 eV and fluence of  $3 \text{ nJ cm}^{-2}$  with frequency-doubled pulses of 100 fs duration originating from a mode-locked Ti:sapphire oscillator. By using a half-wave plate and a Glan-Thompson polarizing prism to adjust the excitation polarization, the PL intensity components polarized parallel and perpendicular to the excitation polarization could be separately measured. The temporal resolution of the system was determined to be approximately 800 fs for solution samples in this geometry. Both time-resolved and steady-state PL measurements were based on a cooled charge-coupled device detection system. Absorption spectra were taken with a commercial spectrophotometer. All measurements were conducted at room temperature and corrected for spectral response of the apparatus.

### 3. Results and discussion

The absorption and steady-state PL spectra of UPy-OF-UPy and UPy-OPV in solution (figure 1) demonstrate that strong spectral overlap exists between the emission from UPy-OF-UPy and the absorption of UPy-OPV, as required for efficient energy transfer [8]. The absorption and emission spectra of UPy-OF-UPy also overlap considerably, thus allowing energy transfer to occur between OF chromophores. Therefore, excitation of the OF chromophores is expected to be followed by energy transfer between UPy-OF-UPy units of the same chain (homo-transfer) and by energy transfer to the UPy-OPV chain ends (hetero-transfer). Because the spectral overlap between UPy-OPV emission and UPy-OF-UPy absorption is negligible, the chain ends effectively act as energy traps for the excitation.

To investigate the energy transfer dynamics along the supramolecular chains, we preferentially excited UPy-OF-UPy molecules and then measured the temporal evolution of the PL intensity  $I(t)$  subsequently emitted from

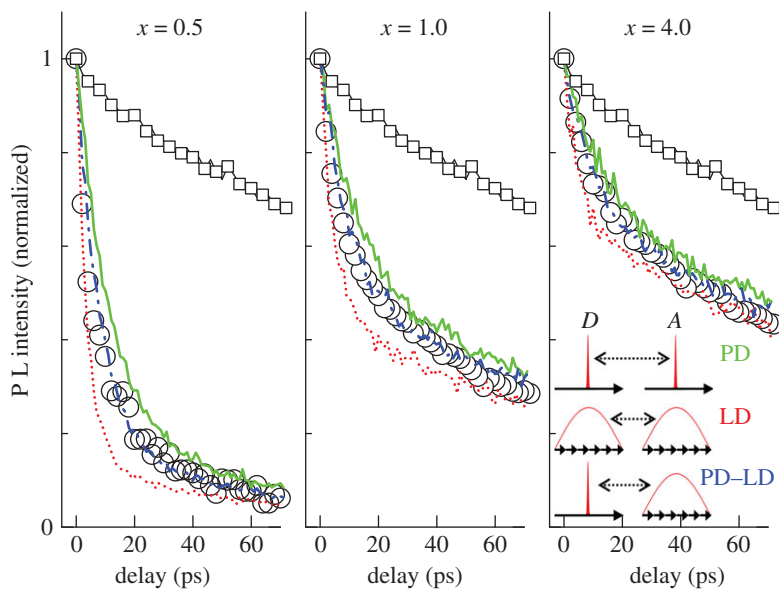


Figure 2. Black open circles: measured time-resolved PL emitted at 2.75 eV from UPy-OF-UPy in UPy-OF-UPy:UPy-OPV blend solutions for three different mixing ratios  $x$  shown together with simulated PL decay curves obtained from different models described in the text (PD, solid line; LD, dotted line; PD-LD, dashed-dotted line). The measured PL decay of UPy-OF-UPy in the absence of UPy-OPV (i.e.  $x = 0$ ) is shown by the black open squares. Inset on the bottom right: schematic of the excitonic wave functions for donor ( $D$ ) and acceptor ( $A$ ) in the point-dipole limit (PD), the standard line-dipole model (LD) and the modified LD model with the excited state on the donor being localized (PD-LD). The localized wave function is approximated by a  $\delta$ -function at the centre of the molecule. (Online version in colour.)

UPy-OF-UPy. Figure 2 shows  $I(t)$  for pure UPy-OF-UPy solutions ( $x = 0$ ) and for blend solutions of UPy-OF-UPy:UPy-OPV at various mixing ratios  $x$ . For pure UPy-OF-UPy, a mono-exponential decay is observed, but increasing addition of UPy-OPV increasingly leads to faster PL decays and deviations from mono-exponential behaviour. These measurements demonstrate that energy is transferred from the UPy-OF-UPy chains to the UPy-OPV end caps [25]: with increasing  $x$ , the average chain length is reduced and energy transfer to the end caps becomes more and more efficient, thus quenching the OF emission faster.

To test the validity of the PD and the LD models, we developed simulations based on these, with the aim of replicating the measured PL decay of the UPy-OF-UPy emission. For these simulations, the two major considerations are the structural parameters describing the composition and structure of the chains and the terms under which the rates for transfer between the chain component chromophores are calculated. The latter will need to incorporate the extent to which electronic wave function delocalization occurs along the OF and OPV chromophores.

To generate parameters describing the structure of the supramolecular chains, we conducted molecular modelling based on the semi-empirical Austin model 1 [26] using a commercial structure calculation software (GAUSSIAN v. 03).

The quadruple hydrogen bonds formed between two adjacent UPy groups were set to a fixed bond length of 3 Å, as previously determined by single-crystal X-ray diffraction measurements on diaminotriazine and diaminopyrimidine derivatives that exhibit equivalent self-complementary arrays of hydrogen bonds [17]. This process yielded values for the lengths of the conjugated segments on the UPy-OF-UPy and UPy-OPV oligomer (figure 1) of  $a = 40$  Å and  $c = 23$  Å, respectively, and the length of the UPy-UPy hydrogen-bonded bridge of  $b = 11$  Å, within an error of 1 Å. In addition, the calculations show that assemblies of both oligomer species form a straight line, with no significant chain bending and parallel orientation of the units, in agreement with our previous measurement of time-independent PL anisotropy [27]. In addition, the length distribution of supramolecular chains in solution needs to be considered, which is the result of random docking processes between the identical UPy hydrogen-bonding groups attached to the oligomers. As we have shown recently [27], the appropriate weight distribution function is given by the Flory distribution obtained for the lengths of covalently bonded polymer chains made by poly-condensation processes [28]. Thus, we obtain an accurate overall model of the geometric arrangement of the chromophores comprising the chains.

In order to simulate the movement of excitations along the chain and to the chain ends, we developed a Monte Carlo algorithm, which has already been described in detail elsewhere [27,29]. In brief, the migration of an excitation along an individual supramolecular chain, selected taking account of the length distribution function, started at a randomly chosen UPy-OF-UPy unit excited at time zero. At each Monte Carlo cycle, a random number generator was used to select from probability-weighted transfer options or a decay process, until the excitation has decayed on a UPy-OF-UPy unit or undertaken hetero-transfer to a UPy-OPV chain end. To determine the probabilities for all transfer options, the transfer rates were calculated within the weak-coupling limit using Fermi's golden rule as  $k_{\text{DA}} = 2\pi/\hbar I_{\text{DA}} V_{\text{DA}}^2$  [11]. The spectral overlap factor  $I_{\text{DA}}$  was calculated from the overlap of the emission spectrum of the donor (UPy-OF-UPy) and the absorption spectrum of the acceptor (UPy-OF-UPy or UPy-OPV for homo- or hetero-transfer, respectively). The matrix element  $V_{\text{DA}}$  for the electronic coupling between the donor and the acceptor incorporates information on the delocalization of the donor and acceptor wave functions, and three different approaches were used and compared with the data. The first was based on the LD approximation for which the transition dipole moments of the donor and the acceptor are subdivided into a set of  $n$  dipoles that are weighted according to an excitonic wave function  $\psi(n)$  given by a half-cycle sine wave spread along the conjugated segment [10]. For  $n = 15$ , stable values were obtained for the calculated transition rates that thus represent the fully delocalized donor and acceptor wave functions according to a quantum mechanical 'particle in a box' system [29]. For the second approach, simulations were based on the PD model by taking the results from the LD model for the case of  $n = 1$ , which assumes that both donor and acceptor wave functions are delta-functions positioned at the centre of the molecule as in the original model by Förster [8]. Finally, on the basis of a modification of the LD model, we developed a new approach that takes account of exciton self-localization following excitation. Here, the donor's excited state is assumed to be fully localized at the oligomer centre, i.e. the transition dipole moment is taken as a PD, while

the acceptor's ground state remains delocalized as in the LD model. These three different test cases are illustrated schematically at the bottom right of figure 2.

Figure 2 displays the decay curves for the donor emission obtained from Monte Carlo simulations based on the three different wave function delocalization scenarios together with the experimental data for three mixing ratios  $x$ . The general trend towards faster PL decay with increasing  $x$  is qualitatively reproduced by both models. However, the PD model clearly underestimates the electronic coupling between donors and acceptors in the present supramolecular system, in agreement with previous studies on energy transfer over small interchromophoric distances [11,12,30,31]. This should be expected, as in reality, the extent of the excitonic wave function along the segment places a certain amount of oscillator strength near the joining edges of two interacting chromophores in the present head-to-tail geometry. Since within the PD approximation the transfer rate depends on the inverse distance between the chromophores to the power of six [8], excitonic delocalization leads to an increase of the oscillator strength beyond that predicted by the PD model. However, our results demonstrate that the LD model appears equally unsuitable for replicating the experimental data as it overestimates the donor-acceptor coupling strength. We propose that this failure results from the incorporated assumption of equally delocalized ground and excited states. Strong electron-phonon coupling in conjugated materials has been predicted to cause an ultrafast self-localization of the excitonic state upon vibrational relaxation [13]. For example, the relaxed excited state for an oligo-indenofluorene was calculated to be delocalized across only approximately 2 of its repeat units [12]. Neglect of self-localization is thus expected to have strong influence on the calculated electronic coupling strength and represents a serious flaw of the LD model. In contrast, the new mixed PD-LD model we have developed [27,29] yields simulated PL decay curves that show excellent agreement with the experimental data. These combined results demonstrate that excitonic self-localization must be accounted for in order to describe energy transfer in dense molecular solids with accuracy.

Another issue of importance is how such energy transfer between semi-delocalized states affects the overall motion of excitations from UPy-OF-UPy donor chromophores to the UPy-OPV end caps of the supramolecular polymer. In conjugated polymeric guest-host systems, energy transfer from the host to the guest has been proposed to occur by a two-step mechanism [32]. As a primary step, an exciton created in the donor polymeric material first undertakes random migration within the donor until it has reached a site located sufficiently close to an acceptor. As a secondary step, the actual energy transfer from the host to the guest may then take place. In conjugated polymers, exciton migration typically involves diffusion both along the chains (intra-chain) and from one chain to another (inter-chain), with the relative predominance of each process depending on the aggregation state of the material. For example, while in the solid state exciton migration is mainly governed by inter-chain transfer steps between closely packed co-facial chains, intra-chain processes dominate in solutions [32]. For the supramolecular system presented here, inter-chain energy transfer is negligible because of the low concentration of chromophores in solution. Therefore, exciton migration can only involve motion between UPy-OF-UPy units that are part of the same supramolecular chain. In the following, the intra-chain exciton migration

in UPy-OF-UPy supramolecular polymers is discussed. With the help of Monte Carlo simulations, a qualitative and quantitative understanding of the exciton diffusion process can be achieved, and microscopic information can be extracted that is not directly available otherwise.

To examine the intra-chain diffusion process, we simulated the exciton migration along a single supramolecular chain composed of 30 UPy-OF-UPy units. For each cycle, an exciton was generated on a UPy-OF-UPy unit in the centre of the chain (denoted as site 0) and the location of the site on which it subsequently decayed was recorded. Choosing a chain of such a long length ensured that depopulation of the UPy-OF-UPy units due to hetero-transfer to the end-cap UPy-OPV was highly unlikely to occur (*vide infra*). Repeating this procedure for a large number  $N$  of excitons ( $N = 10^5$ ) allowed us to determine the probability of decay of an exciton as a function of displacement to the site of initial excitation, as shown in figure 3*a*. These statistics demonstrate that over its lifetime, an exciton only migrates between a few segments close to the initially excited chromophore. More than 50 per cent of all excitons remain on their initial site, and there is merely an approximately 3 per cent chance of migration over 3 or more segments. From the probability distribution in figure 3*a*, the statistical root-mean-square (r.m.s.) displacement  $\sqrt{\langle \Delta x^2 \rangle}$  of excitons at the end of their lifetime can be extracted. We find that an exciton on average only migrates over one UPy-OF-UPy segment next to the initially excited chromophore. Taking into account the length scales of the OF chromophore and the spacer, we thus determine a mean diffusion length of  $\sqrt{\langle \Delta x^2 \rangle} = 5$  nm, which is about one order of magnitude shorter than typical diffusion lengths reported in thin films of organic molecules [33]. For example, in polycrystalline pentacene, the exciton diffusion length was found to be approximately 65 nm [34] and Poulsen *et al.* [30] recently reported diffusion lengths of approximately 50 nm for distyrylbenzene being embedded in a host matrix of perhydrotriphenylene. The much shorter diffusion length observed here can be rationalized by the fact that exciton migration along the supramolecular chains is purely one-dimensional, in contrast to the three-dimensional exciton diffusion in thin films. Thus, there are significantly fewer energy accepting sites available in the local environment of an excited chromophore on an isolated chain, compared with the solid state. However, the exciton migration length found here is also significantly shorter than that found for intra-chain migration on isolated chains of conjugated polymers in solution, such as polythiophene [10] or polyphenylenevinylene with methoxy side chains [35] for which the excitons were reported to travel over six to seven spectroscopic units along the polymer chain prior to being trapped. This finding holds despite the fact that energetic disorder in the supramolecular system under investigation here is small and has been neglected in the Monte Carlo simulation. Energetic disorder is limited by the fact that well-defined oligomers form the building blocks of the chains, which have previously been shown to be linear [27] making conformational disorder negligible. In addition, the non-polar nature of the chromophores allows disorder arising from solvent–solute interactions to be at a minimal level. The observed inefficient intra-chain transport along the supramolecular chains is ascribed to the comparatively large separation of adjacent chromophores by the linking UPy groups, which reduces the electronic coupling between adjacent chromophoric units on a chain [29]. Through the r.m.s.



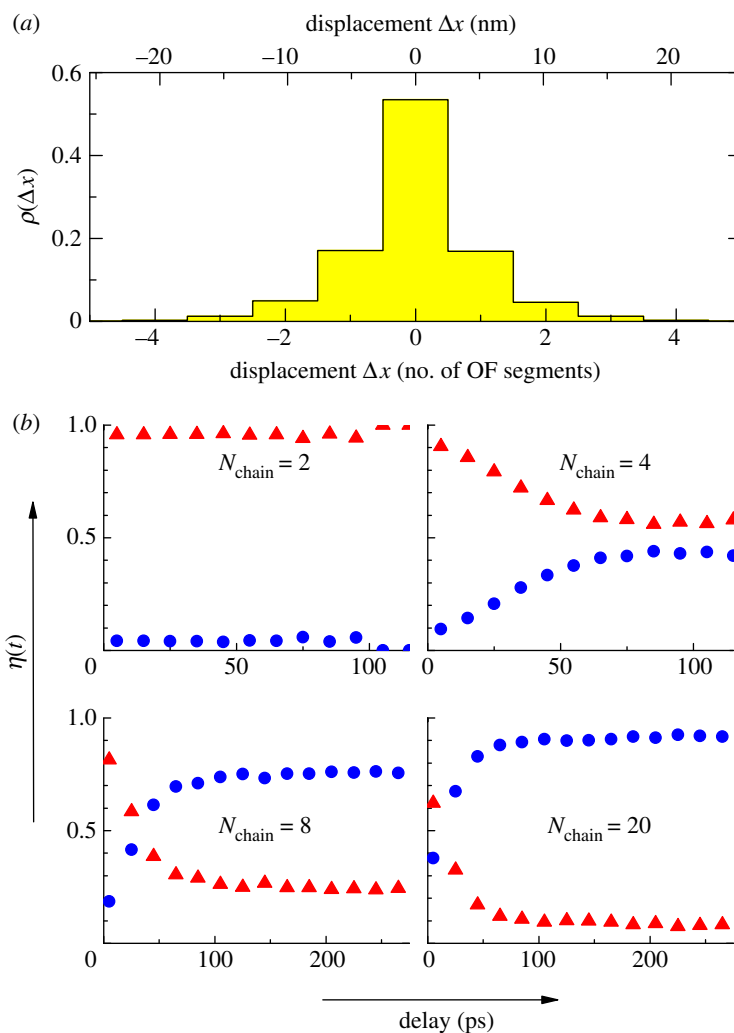


Figure 3. (a) Probability  $\rho$  of exciton decay as a function of the distance  $\Delta x$  to the site of initial excitation (site 0) on a supramolecular chain, as obtained from Monte Carlo simulations averaging over  $10^5$  individual exciton trajectories on a chain of length  $N_{\text{chain}} = 30$ . On the top axis,  $\Delta x$  is converted into the centre-to-centre distance between the excited and depopulated chromophore. For the simulation of the trajectories, the LD-PD model was used. (b) Time-dependent relative efficiencies  $\eta(t)$  (see text) of the two competing decay processes (ET = hetero-energy transfer, D = natural decay) accounting for exciton depopulation on a supramolecular chain, simulated for various chains composed of  $N_{\text{chain}}$  UPy-OF-UPy units. Triangles,  $\eta_{\text{ET}}$ ; circles,  $\eta_{\text{D}}$ . (Online version in colour.)

displacement  $\Delta x$ , the exciton diffusion coefficient  $D$  can be quantified, which, in the case of one-dimensional diffusion [31], follows

$$2Dt = \langle \Delta x(t)^2 \rangle.$$

With the r.m.s. displacement obtained earlier and an exciton lifetime of  $\tau = 305$  ps extracted from mono-exponential fits to the UPy-OF-UPy PL decay in

the absence of UPy-OPV, we determine an average over the exciton lifetime of  $D \sim 5 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ . This value is significantly lower than those recently reported for exciton diffusion in quasi-one-dimensional supramolecular helical stacks of OPV derivatives [31,36], which is mainly a result of the different packing geometry of the chromophores in both supramolecular architectures. The efficient exciton migration in helical OPV structures has been shown to result from close, co-facial packing of chromophores, leading to semi-coherent exciton motion [36]. In contrast, the head-to-tail arrangement of the UPy-OF-UPy units in the supramolecular chains investigated here leads to fully incoherent hopping migration between distinct chromophores located further away from one another.

Given the short exciton diffusion length along the UPy-OF-UPy main chain, it is interesting to investigate to what extent such homo-transfer actually contributes to the overall energy transfer of excitons from the main chain to the UPy-OPV end caps. In general, there are two mechanisms contributing to the overall decay of the exciton population  $\rho_{\text{OF}}(t)$  present on *the ensemble* of UPy-OF-UPy segments, which are natural decay (D) and energy hetero-transfer (ET) to UPy-OPV end caps. To disentangle the two contributions within the simulations, we define a time-dependent relative efficiency  $\eta(t)$  for each decay pathway,

$$\eta_{\text{ET}}(t) = \frac{\Delta\rho_{\text{OF}}^{\text{ET}}(t)}{\Delta\rho_{\text{OF}}(t)} \quad \text{for hetero-transfer}$$

and

$$\eta_{\text{D}}(t) = \frac{\Delta\rho_{\text{OF}}^{\text{D}}(t)}{\Delta\rho_{\text{OF}}(t)} \quad \text{for radiative decay}$$

with  $\Delta\rho_{\text{OF}}^{\text{ET}}(t)$  and  $\Delta\rho_{\text{OF}}^{\text{D}}(t)$  being the contributions of the corresponding decay process to the overall decrease in exciton population on the host at time  $t$ . Figure 3b shows the relative efficiencies  $\eta(t)$  of both competing processes as extracted from the simulations for different total chain lengths. These statistics show that the time-dependent competition between the natural decay of the exciton energy transfer and its transfer to the end groups is dominated by the interplay between slow and spatially limited exciton migration along the UPy-OF-UPy backbone and the comparatively faster hetero-transfer to the end-cap acceptors from neighbouring UPy-OF-UPy segments. A fast initial decay of  $\Delta\rho_{\text{OF}}(t)$  (not shown) suggests that within the first 50 ps after excitation depopulation of the UPy-OF-UPy chromophores directly linked to the UPy-OPV end caps occurs, so that these sites remain only poorly populated at later times. At longer times after excitation ( $\geq 50$  ps), the temporal evolution is determined by the repopulation of those UPy-OF-UPy segments closely located to the acceptor end caps through exciton migration from the chain centre towards the chain ends. Therefore, exciton migration along the backbone can be considered as the limiting step in the two-step energy transfer to energy-accepting end groups in this system. These findings are reflected in the extracted efficiencies for hetero-transfer  $\eta_{\text{ET}}(t)$  shown in figure 3b. For short chains of  $N_{\text{chain}} = 2$ , both UPy-OF-UPy chromophores are in the direct neighbourhood of an energy-accepting site and  $\eta_{\text{ET}}(t) \geq 95\%$  with natural decay playing a minor role at all times. As the chain length is increased, natural

decay becomes more and more important and  $\eta_D$  rises. For the intermediate chain length  $N_{\text{chain}} = 4$ , both processes are strongly competitive, with hetero-transfer and natural decay exhibiting efficiencies of approximately 55 and 45 per cent, respectively, in the long time limit. The fact that hetero-transfer is not more dominant here, even though the chain is still relatively short, points to the short exciton diffusion length here of approximately 1 UPy-OF-UPy unit, as discussed already. For the longest chains ( $N_{\text{chain}} = 8$  and 20, respectively), exciton decay represents by far the major cause of population decay on UPy-OF-UPy, except at early times after excitation. Excitations located on chromophores located further away from the UPy-OPV end caps need to be brought into close contact to those in order to enable hetero-transfer. However, owing to the small exciton diffusion length along the supramolecular chains, the majority of excitons are too distant to reach the chain ends via intra-chain migration, so that the likelihood for them to undergo hetero-transfer becomes negligible. Altogether, these findings are in agreement with those obtained from Hennebicq *et al.*, who performed similar calculations on a covalently bonded guest–host system based on polyindeno[1,2,3-*bc*]fluorene chains end-capped with perylene derivatives [12]. For both the covalently bonded system and for the supramolecular system considered here, intra-chain exciton migration represents the time-limiting step in the dynamics of energy transfer from the host to the guest. Furthermore, the results here clearly support the description of host–guest energy transfer as a two-step mechanism, as observed previously for covalently bonded polymers [25,32].

In order to illustrate further the influence of homo-transfer on the overall energy transfer dynamics to the chain ends, we have simulated the PL intensity decay dynamics for the supramolecular polymer solutions at high and low mixing ratios for two complementary scenarios: one in which exciton migration was allowed ('on') and one in which it was inhibited ('off'). Figure 4a shows that for both mixing ratios, the simulated PL generally decays faster if exciton migration is allowed, compared with the opposite case. These statistics indicate that, in particular at later time, exciton migration along the supramolecular chains results in an enhanced efficiency for energy transfer from the host to the guest, which is in agreement with recent findings on a three-dimensional guest–host [30]. However, it should be noted that because exciton diffusion is restricted to one dimension here, the relative difference in the decay dynamics between the 'on' and 'off' case is much smaller than that reported for three-dimensional systems [25]. Figure 4b shows the ratio between the intensities obtained for the 'on' and the 'off' cases in order to illustrate the degree by which exciton migration enhances the efficiency of guest–host energy transfer. While for low mixing ratio ( $x = 0.3$ ) and thus long chains the relative difference in the PL intensity decay remains fairly small ( $\leq 10\%$ ) over the entire lifetime of the exciton, this increases to approximately 50 per cent at late times after excitation for high ( $x = 4$ ) mixing ratios or short chains. This behaviour again demonstrates that on very long supramolecular chains, excitons initially placed at the centre are unlikely to reach the chain ends because of the short exciton diffusion length. Therefore, the effect of exciton migration on the overall transfer efficiency, and hence on the PL decay dynamics is small. In contrast, on short chains, exciton migration towards the chain ends leads to an efficient repopulation of chromophores close to the acceptor end group, and thus to a considerable enhancement of the PL decay.

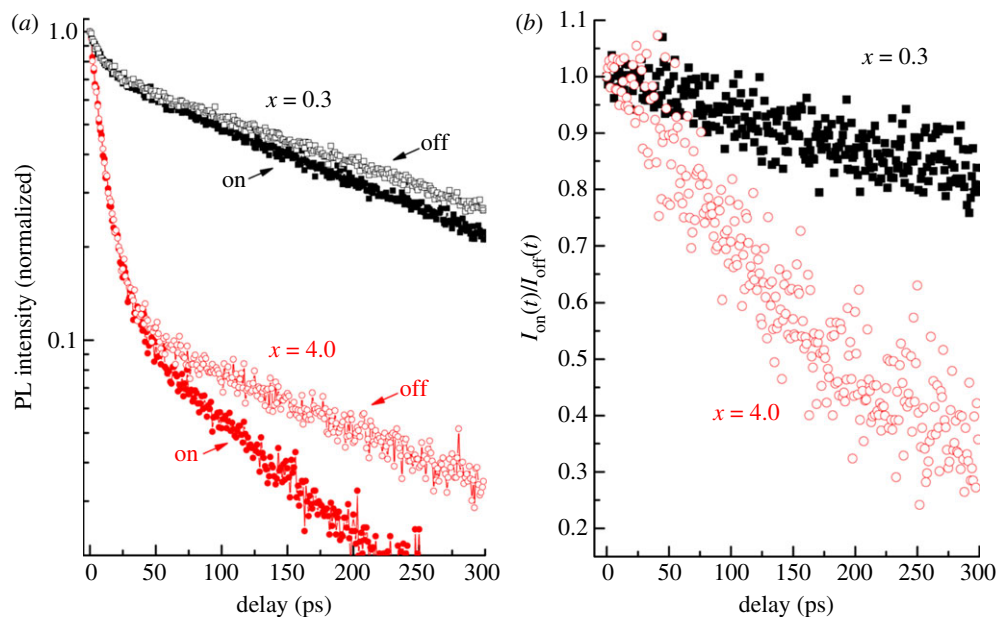


Figure 4. (a) PL intensity decay curves for solutions at two different mixing ratios ( $x = 0.3$  and  $x = 4.0$ ), simulated with intra-chain exciton migration or hetero-transfer being allowed ('on') and it being inhibited ('off'). (b) Temporal evolution of the ratio between the PL intensities obtained for the 'on' and 'off' situation, i.e.  $I_{\text{on}}(t)/I_{\text{off}}(t)$ , for both mixing ratios. (Online version in colour.)

#### 4. Conclusion

We have investigated the energy transfer dynamics in linear chains of conjugated molecules assembled through supramolecular interactions. Excitation energy transfer between the chain building donor and the chain stopping acceptor chromophores was shown to result in a dynamic quenching of the donor's emission. A Monte Carlo algorithm was created to simulate the observed excitation transfer dynamics from the main chain to the end groups, incorporating only experimentally derived parameters.

We examined three different scenarios for electronic wave function delocalization states of the energy-donating and -accepting chromophores. The first assumes that both donor and acceptor transition moments can be described by PDs located at the centres of the respective molecules, as originally described by Förster [8]. The second approach assumes that both donor and acceptor wave functions are completely delocalized across the  $\pi$ -conjugated segments according to a 'particle-in-a-box' scenario, as introduced by the so-called LD model [10]. The third case incorporates a localized emitting state and a delocalized accepting state in a mixed (PD-LD) model. Comparison of the simulated curves with the experimental data demonstrates that the PD-LD model gives the most accurate description of the energy transfer. These findings suggest that for incoherent energy migration in the weak electronic coupling regime, excitation of a donor molecule is followed by geometric lattice relaxation that localizes its excitonic

wave function prior to energy transfer. Energy transfer thus occurs between a localized donor transition moment and a delocalized ground state acceptor moment.

In addition, we examined the extent to which exciton migration along the chain of OF chromophores contributes to the overall transfer of energy to the chain ends. With the help of Monte Carlo simulations, we find that exciton diffusion along the supramolecular polymer chain is inefficient: an exciton on average only moves along one segment, or approximately 5 nm, with respect to the initially excited chromophore. As a result, energy transfer to the chain end is dominated by the interplay between slow and spatially limited exciton migration along the OF segments comprising the main chain and the comparatively faster hetero-transfer to the end-cap acceptors from directly adjoining OF segments. These results clearly support the description of host–guest energy transfer as a two-step mechanism, as observed previously for covalently bonded polymers [32].

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