Impact of nuclear lattice relaxation on the excitation energy transfer along a chain of $\pi$-conjugated molecules


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We have investigated the extent to which delocalization of the ground-state and excited-state wave functions of a $\pi$-conjugated molecule affects the excitation energy transfer (EET) between such molecules. Using femtosecond photoluminescence spectroscopy, we experimentally monitored the EET along well-defined supramolecular chains of extended conjugated molecules. Comparison with Monte Carlo simulations reveals that only a model incorporating a localized emitter and delocalized absorber wave function accurately reproduces these data. Our findings demonstrate that self-localization of the initially excited state, following fast relaxation of the nuclear lattice, has a significant impact on the EET dynamics in molecular assemblies.

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I. INTRODUCTION

Excitation energy transfer (EET) is an important mechanism governing biological light-harvesting systems and organic materials and devices based on $\pi$-conjugated molecules. This process is commenced by the absorption of a photon by a donor molecule, leading to the generation of an initially excited state (an exciton) that may subsequently be transferred to a new (acceptor) site through dipole-dipole interactions. However, a fundamental issue to be resolved is the extent to which the delocalization of the excitonic wave function along the conjugated molecule affects the energy transfer between sites. While early theory applied to dilute molecular systems assumed interactions to occur between pointlike transition moments, such approaches later proved inappropriate for dense systems with transfer distances comparable to the exciton delocalization length. More recent models have therefore treated both the energy-donating and energy-accepting sites as featuring delocalized photon-emitting and photon-absorbing states, in analogy with a quantum-mechanical “particle-in-a-box” approach. However, it is currently unclear to what degree excitonic self-localization affects the energy transfer between molecules. Such effects feature strongly in organic materials as a result of significant nuclear lattice relaxation following soon (<100 fs) after excitation, which leads to differences in the delocalization of the absorbing and the emitting electronic states. To date, experimental investigations trying to establish the significance of such effects for EET have been hampered by significant disorder common in molecular solids.

In the present study, we demonstrate that EET in a chain of conjugated molecules is significantly affected by excitonic self-localization into the relaxed nuclear lattice potential well. We have combined an experimental study on the excitation energy transfer along well-defined supramolecular chains of extended conjugated molecules with Monte Carlo (MC) simulations and find that only a model based on localized emitter and delocalized absorber wave functions gives an accurate representation of the experimental data. In dense molecular materials, such as organic semiconductors and biological light-harvesting systems, self-localization of the energy-donating exciton must therefore be included for an accurate understanding of EET processes.

II. MATERIALS AND EXPERIMENTS

In order to overcome issues associated with disorder, we have chosen a well-defined system of extended $\pi$-conjugated molecules assembled through supramolecular interactions into linear chains with known length distribution. Figure 1 depicts the building blocks that self-assemble in solution into the molecular chains used as model system for this study. The main chain is made of oligofluorene (OF) pentamers which have 2-ureido-4[1H]-pyrimidinone (UPy) groups attached to both ends. With two hydrogen donating and accepting sites per unit, these UPy groups represent self-complementary docking points for quadruple hydrogen bonding with large dimerization constant. In addition, an oligo(p-phenylenevinylene) (OPV) with a UPy group attached only to one end was used as chain stopper. These molecules have been shown to form linear supramolecular polymers in mixed solutions even down to very low concentration, with UPy-OPV molecules assembling into polymerlike chains and UPy-OPV terminating the chain on both ends. Mixed solutions of concentration $\sim 4 \times 10^{-5}$ mol l$^{-1}$ were prepared in chloroform, for which the lifetime of the UPy-UPy hydrogen bond is $\sim 0.1$ s. The composition of the supramolecular chains thus remains static during the time scale of exciton migration along the chains. In addition, the spectral shape of the absorption and emission does not change when lowering the solution concentration significantly, indicating the absence of chain stacking into aggregates. By varying the ratio $x = N_{\text{UPy-OPV}} / N_{\text{UPy-OF-UPy}}$ of the number $N$ of each type of molecule in the solution, changes in energy-transfer dynamics with chain length can be observed. Details of the synthesis procedure for the compounds are given in Refs. 15 and 17.

Time-resolved photoluminescence (PL) measurements were conducted using an up-conversion setup that has al-
Figure 1 shows the absorption and steady-state PL spectra of UPy-OF-UPy and UPy-OPV in solution. Strong spectral overlap exists between the emission from UPy-OF-UPy and the absorption of UPy-OPV, as required for efficient energy transfer.\(^3\) In addition, the absorption and emission spectra of UPy-OF-UPy overlap considerably. Therefore, excitation of the oligofluorene chromophores is expected to be followed by energy transfer both between UPy-OF-UPy units of the same chain (homotransfer) and by energy transfer to the UPy-OPV chain ends (heterotransfer). Since negligible spectral overlap exists between UPy-OPV emission and UPy-OF-UPy absorption, the chain ends effectively act as energy traps for the excitation.

To investigate the energy-transfer dynamics along the supramolecular chains, we measured the temporal evolution of the PL intensity \(I(t)\) emitted from UPy-OF-UPy following preferred excitation of these molecules. Figure 2(c) shows \(I(t)\) for pure UPy-OF-UPy solutions and for blend solutions of UPy-OF-UPy:UPy-OPV at various mixing ratios \(x\). While for \(x=0\) (pure UPy-OF-UPy) a monoexponential decay is observed, increasing addition of UPy-OPV increasingly leads to faster PL decays and deviations from monoexponential behavior. These trends are clear indicators of energy transfer from the UPy-OF-UPy chains to the UPy-OPV end.
To determine the probabilities for all transfer options, the transfer rates were determined within the weak-coupling limit, for which the excited UPy-OF-UPy chromophore is expected to have geometrically relaxed to its equilibrium lattice configuration prior to energy transfer. The rate for energy transfer from an excited donor to an acceptor is its ground state may then be calculated using using Fermi’s Golden Rule as

\[ k_{DA} = \frac{2\pi}{\hbar} |V_{DA}|^2 J_{DA}^*, \]

where \( J_{DA} \) denotes the spectral overlap between donor emission and acceptor absorption spectra normalized on an energy scale and \( V_{DA} \) is the matrix element for the electronic coupling between the donor and the acceptor.

The first successful attempt to calculate energy-transfer rates for conjugated molecular systems was completed by Förster, who assumed that the donor and acceptor transition dipoles were pointlike, i.e., totally localized at the center of the molecule. This classical point-dipole (PD) approximation yields a transfer rate of

\[ k_{DA} = \frac{1}{\tau_D} \left( \frac{R_0}{R_{DA}} \right)^6 \]

with

\[ R_0 = \left( \frac{9000 \ln 10 \kappa^2 \Phi_D}{128\pi^3 \kappa N_{DA}} \right)^{1/6} \]

being the Förster radius. Here, \( \tau_D \) is the lifetime of the donor excitation in the absence of acceptors, \( \kappa \) the refractive index of the solvent, \( N \) Avogadro’s number, and \( \Phi_D \) the PL quantum yield of the donor. \( \kappa \) is the orientation parameter and describes the dependence of the transfer rate on the relative orientation of the two transition dipole moments and their displacement vector. For the supramolecular chains considered here, donor and acceptor molecules adopt a parallel in-line geometry for which \( \kappa^2 = 4 \). The spectral overlap factor \( J_{DA} \) is calculated as the overlap between the molar decadic extinction coefficient of the acceptor \( \epsilon_a(\nu) \) and the fraction of photons \( f_D(\nu) \) with wave number \( \nu \) emitted per unit wave number from the donor in absence of acceptors,

\[ J_{DA} = \int f_D(\nu) \epsilon_a(\nu) d\nu \sqrt{\nu^2}. \]

For the simulations presented in this study, \( J_{DA} \) was directly calculated from the experimentally determined spectra.

For intermolecular separations that are comparable to the chromophore lengths, such PD models are unlikely to be an appropriate choice, as they average away the local character of the chromophore. Line-dipole (LD) models have therefore recently been presented, which allow the delocalization of the exciton on the chromophores to be taken into account. Here the transition dipole moment \( M \) is divided into a set of subdipoles \( M_\mu \), each of which is weighted according to the exciton wave function \( \phi(\mu) \). Within this approximation, the excited state of the donor and the ground state of the acceptor are generally assumed to be equally delocalized. By approximating the shape of the molecule as a finite, one-dimensional periodic chain, \( \phi(\mu) \) can be derived as...
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coupling in conjugated materials has been predicted to 


were determined from experimental observables, i.e., no attempts of fitting the curves to the data by varying 

their values were made. The general trend toward faster 

PL decay with increasing \( x \) is qualitatively reproduced by 

both models. However, the PD model yields slower decay 

dynamics while the LD model predicts faster decaying 

PL intensities than experimentally observed. These observations 

hold even if the structural parameters are varied within 

their error limits. 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.\(^6,7,27,28\) 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 point-dipole approxima-
tion, the transfer rate depends on the inverse distance be-

between the chromophores to the power of six,\(^3\) excitonic 

delocalization leads to an increase in 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 fail-

ure results from the incorporated assumption of equally de-

localized 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.\(^8\) For example, the relaxed excited state 

for an oligoindenoflorene was calculated to be delocalized 

across only \( \sim 2 \) of its repeat units.\(^7\) Neglect of self-

localization is thus expected to have strong influence on the 

calculated electronic coupling strength and represents a seri-

ous flaw of the LD model. 


We have therefore chosen a new approach that modifies 

the LD model to take account of exciton self-localization 

following excitation. As illustrated at the bottom of Fig. 2(a), 

the donor’s excited state is assumed to be fully localized at 

the molecule’s center, i.e., the transition dipole moment is 

then taken as a point dipole while the acceptor’s ground state 

remains delocalized as in the LD model. Equation (6) then 
simplifies to 

\[
 k_{DA} = \frac{1}{\tau_D} \left( R_0 \right)^6 \sum_{i,j} \frac{\psi(i)\psi(j)}{R_{DA}^3} \left( \sum_{i,j} \frac{\psi(i)\psi(j)}{R_{DA}^3} \right)^2 . \tag{7} 
\]

Here, \( R_{DA}^3 \) is the distance from the center of the donor to the 

center of the \( j \)th subdipole on the acceptor. 


We find that this mixed PD-LD model yields values for 

the transfer rates that are in between those obtained from the 

PD and the LD models [see Fig. 2(b)]. Monte Carlo simula-
tions based on the PD-LD approach were subsequently car-

ried out to produce the theoretical PL decay curves shown in 

Fig. 2(c). These curves show excellent agreement with the 

experimental data, which demonstrates that excitonic self-

localization must be accounted for in order to describe en-

ergy transfer in dense molecular solids with accuracy. 


Finally, we address the influence of the spacer length \( b \) 

on the calculated energy-transfer rates. For the model system 

investigated here, a relatively large spacer \( (b=11 \, \text{Å}) \) was 

used, however, typical conjugation breaks in conjugated 

copolymers may extend over as little as a few angstroms.\(^10,11\) 

Figure 3 shows the dependence on spacer size of the energy-

transfer rate between neighboring UPy-OF-UPy units, calcu-

lated using the PD, LD, or PD-LD model. The discrepancies 

between the three approaches increase significantly as the 

spacer size is reduced. In particular, the LD model strongly 

overestimates the transfer rates for small \( (\sim \text{Å}) \) spacers be-

cause it places small fractions of the donor’s and the accep-
	or’s transition moments within very close proximity at the 

connecting ends. These findings suggest that for the cases of 

extended conjugated chains or denser molecular solids, the 

\[
\psi(i) = \frac{\sin[\pi i/(n + 1)]}{\sum_n \sin[\pi a/(n + 1)]} , \tag{5} 
\] where \( n \) is the number of subdipoles. The total electronic 
donor-acceptor coupling is then calculated as the sum of the interactions between each pair of subdipoles. In analogy to the procedure for the point-dipole model, the transfer rate is then determined to be 

\[
 k_{DA} = \frac{1}{\tau_D} \left( R_0 \right)^6 \sum_{i,j} \frac{\psi(i)\psi(j)}{R_{DA}^3} \left( \sum_{i,j} \frac{\psi(i)\psi(j)}{R_{DA}^3} \right)^2 . 
\]
influence of geometric relaxation on the energy-transfer rates will be even more pronounced than for the system investigated here.

IV. SUMMARY

In conclusion, we have demonstrated that EET in molecular systems occurs between donor and acceptor wave functions with different degrees of delocalization. Strong nuclear relaxation commonly occurring in conjugated molecules soon after excitation induces a self-localization of the donor exciton such that EET occurs between a localized donor and a delocalized acceptor state. While simplified models incorporating either no or full delocalization of both donor and acceptor wave functions are able to provide an accurate picture of EET processes in very dilute molecular systems, they clearly fail to apply to denser assemblies such as biological light-harvesting systems and molecular solids. These findings are important for the design of molecular materials aimed at light-harvesting applications, such as solar cells.

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