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Impact of nuclear lattice relaxation on the excitation energy transfer along a chain of π-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 π-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[1] and organic materials and devices[2] based on π-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.[3] 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,[3] such approaches later proved inappropriate for dense systems with transfer distances comparable to the exciton delocalization length.[4] 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.[5–7] 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.[7–9] To date, experimental investigations trying to establish the significance of such effects for EET have been hampered by significant disorder common in molecular solids.[10,11]

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 π-conjugated molecules assembled through supramolecular interactions[12–14] 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.[13] 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-OF-UPy molecules assembling into polymerlike chains and UPy-OPV terminating the chain on both ends.[15] Mixed solutions of concentration $\sim 4 \times 10^{-4}$ mol l^{-1} were prepared in chloroform, for which the lifetime of the UPy-UPy hydrogen bond is ~ 0.1 s.[16] 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-

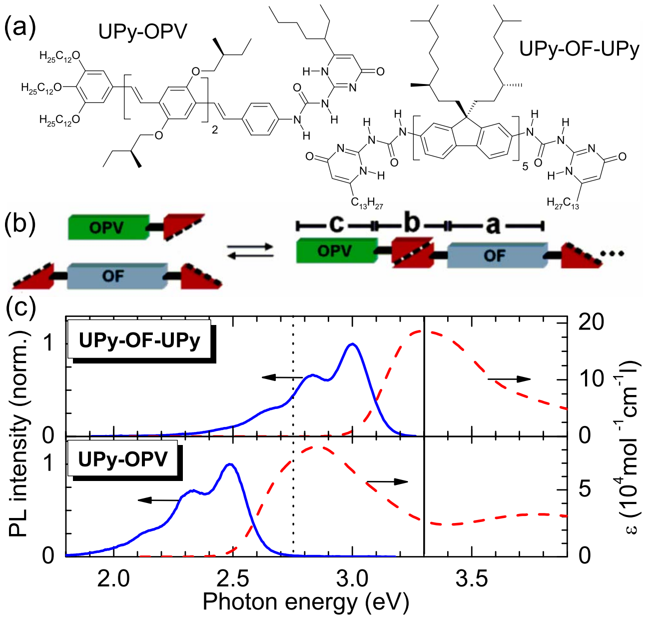

FIG. 1. (Color online) (a) Chemical structure of UPy-terminated oligo(*p*-phenylenevinylene) (UPy-OPV) and bis-UPy-terminated oligofluorene (UPy-OF-UPy). (b) Schematic representation of the self-assembly process into linear supramolecular polymers together with a definiton of the structural parameters *a*, *b*, and *c* (see text). (c) Absorption (red, dashed line) and steady-state PL spectra (blue, solid line) for UPy-OF-UPy and UPy-OPV in CHCl$_3$, with ϵ being the molar extinction coefficient. The wavelengths of excitation (solid) and signal detection (dotted) are indicated as vertical lines.

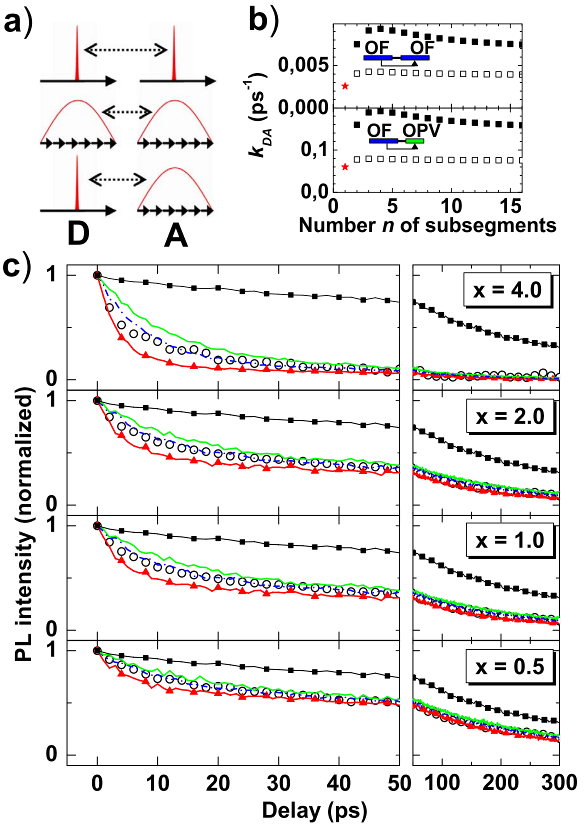

FIG. 2. (Color online) (a) Schematic of the excitonic wave functions for donor (d) and acceptor (a) in the PD limit (top), the standard LD model (center), and the modified line-dipole model with the excited state on the donor being localized (PD-LD) (bottom). The localized wave function is approximated by a δ function at the center of the molecule. (b) Energy-transfer rates for the homodimer (top) and the heterodimer (bottom) as a function of the number of subdipoles, calculated with the LD (full squares) and the PD-LD model (open squares). For $n=1$, both models are equivalent with the PD model (red stars). (c) Comparison between the experimental time-resolved PL emitted at 2.75 eV from UPy-OF-UPy in UPy-OF-UPy:UPy-OPV blend solutions of various mixing ratios (open circles) and the simulated PL decay curves obtained from different models (PD: green dotted line, LD: red dashed-dotted line, and PD-LD: blue solid line). The PL decay of UPy-OF-UPy in the absence of UPy-OPV is indicated with black full squares.

ready been described in detail elsewhere.[9] The liquid samples were kept in quartz cuvettes and excited at a photon energy of 3.30 eV and fluence of 3 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 ($I_\parallel$) and perpendicular ($I_\perp$) to the excitation polarization could be separately measured and the PL emission anisotropy determined as $r=(I_\parallel-I_\perp)(I_\parallel+2I_\perp)^{-1}$. The temporal resolution of the system was determined to be ~800 fs. 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.

III. RESULTS AND DISCUSSION

Figure 1(c) 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 caps:[18] as x is increased, the average chain length is reduced and energy transfer to and trapping at the end caps becomes more and more efficient.

To assess the influence of excitonic delocalization on EET, we developed simulations based on these with the aim of replicating the measured PL decay of the UPy-OF-UPy emission. In order to generate parameters describing the structure of the supramolecular chains, we carried out molecular modeling based on the semiempirical Austin Model 1,[19] using a commercial structure calculation software (Gaussian 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 diaminopyrimidines derivatives that exhibit equivalent self-complementary arrays of hydrogen bonds.[12] This process yielded values for the lengths of the conjugated segments on the UPy-OF-UPy and UPy-OPV molecules (see Fig. 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 molecular species form a straight line, with no significant chain bending and parallel orientation of the units. This finding is in agreement with our experimental measurements of the PL emission anisotropy[20] for UPy-OF-UPy solutions. We find an anisotropy of ~ 0.4 that does not change over the first 300 ps after excitation (not shown) in accordance with exciton motion along molecules oriented parallel to one another.[6] This observation also allows us again to rule out the possibility of three-dimensional cluster formation, or aggregation, as transfer between molecules within the cluster would lead to rapid PL depolarization. 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 conjugated molecules. For the simulations, we used the appropriate length distribution function established by Ercolani for the weight fraction of supramolecular chains in a blend of chain building and chain stopping monomers.[21,22] This function is equivalent to the Flory distribution obtained for the lengths of covalently bonded polymers chains made by polycondensation processes.[23]

To replicate the experimentally observed donor emission decay in the presence of the acceptor chain ends we implemented a MC algorithm to simulate the movement of excitations along the chain and to the chain ends. For these simulations, 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 MC 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 heterotransfer to a UPy-OPV chain ends.[22]

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 in its ground state may then be calculated using using Fermi's Golden Rule as[24]

$$k_{DA} = \frac{2\pi}{\hbar}|V_{DA}|^2 J^*_{DA}, \tag{1}$$

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[3,25]

$$k_{DA} = \frac{1}{\tau_D}\left(\frac{R_0}{R_{DA}}\right)^6 \tag{2}$$

with

$$R_0 = \left[\frac{9000 \ln 10}{128\pi^5}\frac{\kappa^2\Phi_D}{\tilde{n}^4 N}J_{DA}\right]^{1/6} \tag{3}$$

being the Förster radius.[3,25] Here, τ_D is the lifetime of the donor excitation in the absence of acceptors, $\tilde{n}$ the refractive index of the solvent, N is Avogadro's number, and Φ_D the PL quantum yield of the donor. κ 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 $\kappa^2=4$.[20] 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 ν emitted per unit wave number from the donor in absence of acceptors,

$$J_{DA} = \int f_D(\nu)\epsilon_A(\nu)\frac{d\nu}{\nu^4}. \tag{4}$$

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.[4,26] 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_i, each of which is weighted according to the exciton wave function $\psi(i)$.[5] Within this approximation, the excited state of the donor and the ground state of the acceptor are generally assumed to be equally delocalized.[6,10] By approximating the shape of the molecule as a finite, one-dimensional periodic chain, $\psi(i)$ can be derived as

$$\psi(i) = \frac{\sin[\pi i/(n+1)]}{\sum_a^n \sin[\pi a/(n+1)]}, \tag{5}$$

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

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

where R_{DAij} denotes the center-to-center distance between the ith subdipole on the donor and the jth one on the acceptor.

We calculated energy-transfer rates k_{DA} based on both the PD and the LD models to obtain the necessary input parameters for the subsequent Monte Carlo simulations of the energy transfer. The rates for nearest-neighbor transfer are shown in Fig. 2(b) for both homotransfer and heterotransfer as a function of the number n of subsegments the conjugated segment was divided into. Using these transfer rates as input into the simulations, we are thus able to compare the effect of full excitonic delocalization ($n=15$) across the donor and acceptor molecules, as described by the LD model, with that of total localization at the center of the molecule ($n=1$) as assumed for the PD model. Figure 2(c) displays the decay curves for the donor emission obtained from simulations based on the PD and the LD models together with the experimental data. Note that all input parameters for these simulations 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 chormophores in the present head-to-tail geometry. Since within the point-dipole approximation, the transfer rate depends on the inverse distance 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 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.[8] For example, the relaxed excited state for an oligoindenoflorene was calculated to be delocalized across only ~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 serious flaw of the LD model.

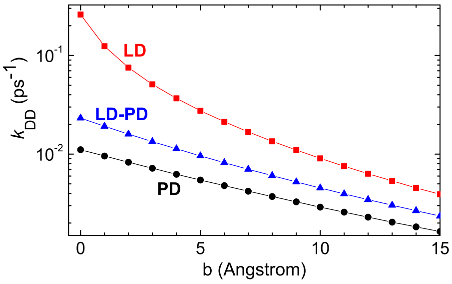

FIG. 3. (Color online) Dependence of nearest-neighbor homotransfer rates on the length b of the interchromophore spacer, as calculated from the three models described in the text.

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 taken as a point dipole while the acceptor's ground state remains delocalized as in the LD model. Equation (6) then simplifies to

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

Here, R'_{DAj} is the distance from the center of the donor to the center of the jth 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 simulations based on the PD-LD approach were subsequently carried 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 energy 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 ($b=11$ Å) was used, however, typical conjugation breaks in conjugated polymers 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, calculated 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 (~Å) spacers because it places small fractions of the donor's and the acceptor'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 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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