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Energy transfer in π-conjugated polymers: Interchain *vs.* intrachain processes in polyindenofluorene

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Abstract

The energy transfer processes taking place in conjugated polymers are investigated by means of correlated quantum-chemical calculations applied to polyindenofluorene. The calculations go beyond the usual point-dipole model approximation and account for geometric relaxation phenomena in the excited state prior to energy migration. The results indicate a higher efficiency of the interchain transfer process, which is mainly due to larger electronic coupling matrix elements.

Keywords: semi-empirical models; optical absorption and emission spectroscopy; conjugated polymers.

1. Introduction

Energy transfer is a key process in the working mechanism of a number of devices based on conjugated materials. [1-5] In addition, a striking demonstration of ultrafast energy transfer in conjugated polymers has been the recent discovery of highly sensitive biological and chemical sensors based on reversible fluorescence quenching in a polyanionic poly(*p*-phenylenevinylene), PPV.[6] One of the main issues here concerns the relative efficiencies of *interchain* versus *intrachain* energy transfer processes, a problem that has been elegantly tackled by Schwartz and co-workers.[7]

In this contribution, we assess theoretically intrachain and interchain transfer processes in conjugated polymers, taking polyindenofluorene (PIF), Figure 1, as an example. The theoretical approach is based on an improved Förster model, wherein the electronic matrix elements for energy transfer are calculated from a multicentric atomic representation of the transition moments, *i.e.*, under the form of atomic transition densities.[8] We successively consider the case of *intramolecular* energy transfer, where exciton transport takes place via hopping along the PIF chains, and *intermolecular* energy transfer simulated by considering two chains in close contact. In both cases, the roles of geometric relaxation and local interactions between the atomic transition densities are emphasized.

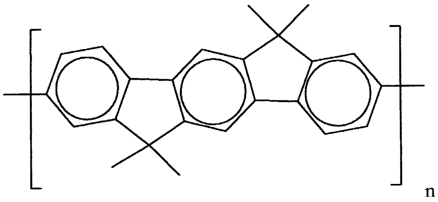

Figure 1. Structure of methyl-substituted polyindenofluorene.

2. Theoretical methodology

The ground-state [excited-state] geometries of a methyl-substituted PIF model chain were optimized at the AM1 [AM1/Configuration Interaction-C1] level assuming planar conformations. For the simulation of intermolecular energy transfer, the interchain structural parameters were first optimized at the molecular mechanics level and the intrachain geometries were then refined using the AM1 approach. The optimized geometries are then used as input for excited-state calculations performed by means of the INDO/SCI (Intermediate Neglect of Differential Overlap/Single Configuration Interaction) formalism. As an output of these calculations, we obtain the excitation energies and transition dipole matrix elements from the ground state to the lowest excited states, as well as the corresponding atomic transition densities.

In Förster theory, the electronic coupling V_{da} that promotes energy transfer from one molecule to another is usually calculated on the basis of a point-dipole model. Such an approach averages away the shapes of the donor and acceptor units and is valid when the size of the molecules is small with respect to intermolecular separations. This is, however, hardly the case in polymeric materials, where the calculation of the long-range (dominant) Coulombic interactions should take into account the local character of the molecules in interaction. The distributed monopole method,[8] wherein the total electronic coupling is estimated as the sum over atomic transition charges, takes into account the spatial shape of the donor and acceptor via the transition densities. It has been used here to calculate V_{da}:

$$V_{da} = \frac{1}{4\pi\varepsilon_0}\sum_m\sum_n \frac{q_d(m)q_a(n)}{r_{mn}} \quad [1]$$

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In Eq. 1, the summations run over all sites m [n] on the donor [acceptor], r_{mn} denotes the distance between m and n, and $q_d(m)$ [$q_a(n)$] is the INDO/SCI atomic transition density on site m [n] calculated for the lowest optical g → e excitation on the donor [acceptor].

Our aim here is to provide a *qualitative* description of intrachain versus interchain energy transfer in conjugated materials. Our analysis is based on a simple model that assumes that, for the donor, energy is localized over one conformational subunit of the polymer chain. For the acceptor in an intrachain energy migration process, we also assume that electronic interactions between neighboring acceptor conformational subunits are small enough that the acceptor density of states is not perturbed by electronic coupling between subunits. This can be a rather severe approximation for a quantitative treatment of intrachain energy migration; however, in the linear chain model where there is no critical dependence on spectral overlap (*e.g.*, the donor and acceptor densities of states are broad), this approximation will allow us to provide an upper bound on the fastest intrachain energy transfer hopping rate[9].

With the transfer rate, k_{da}, expressed in ps^{-1} and the electronic coupling, V_{da}, in cm^{-1}, we use Eq. 2 for the donor-to-acceptor hopping rate:[10]

$$k_{da} = 1.18 \left| V_{da} \right|^2 J_{da} \quad [2]$$

J_{da}, the overlap factor, is calculated on the basis of the simulated (normalized) donor emission and acceptor absorption spectra, obtained assuming a single-mode displaced harmonic oscillator model.[11] Here, a single vibrational mode at 0.18 eV is considered and the relaxation energies are calculated from INDO/SCI vertical excitation energies, as obtained on the basis of the AM1 ground-state and excited-state optimized geometries. The absorption and emission spectra are then convoluted by means of Lorentzian functions whose full width at half maximum is fixed at 0.07 eV, thereby accounting for the spectral inhomogeneity of the conformational subunit absorptions that are obscured within the broad polymer absorption band. For this reason, because we use transition densities to calculate the electronic couplings, our analysis differs significantly from the usual application of Förster theory to energy transfer involving conjugated polymers.

3. Results and discussion

The actual conjugation length, *i.e.*, the length between two kinks along the conjugated path (most likely limited by conformational disorder), has been estimated to lie in the range of 5-7 repeat units from extrapolation of the absorption and emission spectra of well-defined oligo(indenofluorenes) to those of the homopolymer.[12] Since the conjugation length is much shorter than the real length of the chains, it is likely that excitation of one polyindenofluorene segment induces exciton hopping along the main chain. Thus, we have first explored this scenario.

For that purpose, we applied Eq. 2 to the computation of the electronic couplings, spectral overlaps, and energy transfer rates for intramolecular energy transfer among PIF conjugated segments (hereafter denoted $(PIF)_n$, where n is the number of repeat units). The results are reported in Table 1 for a number of donor/acceptor couples, differing by the size of the indenofluorene segments participating in the energy transfer process. We find that the electronic couplings for intrachain energy migration (and the corresponding transfer rates) drop quickly with the size of the donor and acceptor groups. This arises from the increased inter-site separations in Eq. 1, together with a concomitant decrease in transition density at the edges of the subunits. We stress that these results are obtained on the basis of the relaxed donor excited-state geometry; when considering the unrelaxed ground-state geometries, a somewhat smaller chain-length dependence is found. This behavior stems from the localization of the atomic transition densities around the center of the conjugated chains upon lattice relaxation in the excited state, see Figure 2, an evolution that is fully consistent with experimental data on oligofluorenes.[13]

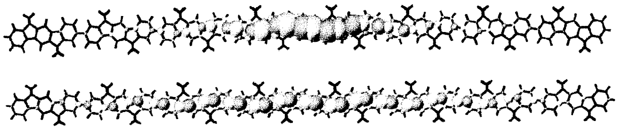

Figure 2. Transition density plot for the lowest excitation in the 8-unit PIF segment, as obtained on the basis of the ground-state (bottom) and excited-state (top) geometries.

From Table 1, the typical electronic couplings for exciton hopping between two adjacent segments with sizes ranging from 4 to 6 repeat units (*i.e.*, close to the actual conjugation length) are on the order 20-100 cm^{-1}. This translates into transfer rates on the order of a few hundreds of ns^{-1} for a single hop event. We stress that, since only hopping to the nearest neighbor has been considered here, this provides an upper limit to the actual rate of homopolymer energy motion process; a more quantitative description is given elsewhere.[14] Note also that we have neglected the role of the collective excitation of coupled acceptors, which is a reasonable approximation when the donors and acceptors are coupled linearly.[9] At this stage, it is instructive to compare these results to the values obtained within a simple point-dipole model. Although such a model correctly reproduces the qualitative evolution of V_{da} with donor-acceptor separation, it strongly underestimates (by roughly one order of magnitude) the electronic couplings and transfer rates in comparison to the description provided on the basis of the atomic transition densities.[15] This large discrepancy arises from the fact that the point-dipole model cannot adequately account for local interactions between nearby donor and acceptor chain ends. Such considerations are especially important for linear molecules.[8]

Next, we turn to the discussion of interchain energy transfer that we expect to be significant in polymer films. We have considered the case of two interacting poly(indenofluorene) chains to model intermolecular chain-chain energy transport. The chains were packed in a cofacial arrangement with a center-to-center distance of 5 Å (depending on the nature of the side groups and conformation of the chains, molecular mechanics calculations yield average intermolecular distances ranging from 4 to 5 Å).[16] The electronic couplings and transfer rates calculated for the PIF-PIF cofacial complexes are always found to be larger than the corresponding on-chain couplings (owing to the reduced center-to-center distance), see Table 1. Thus, it clearly appears that close contacts between molecules should provide an efficient pathway for energy migration in conjugated materials as a result of increased donor-acceptor electronic couplings. Note also that, in contrast to the case of intrachain exciton migration, V_{da} is largely overestimated when considering only the dipolar contribution to the interchain interaction energy.[14]

To summarize, we have explored the mechanisms for energy transfer in polyindenofluorene. We have modeled the elementary steps involved in both intrachain and interchain energy migrations. The rather slow rate for the intrachain mechanism is due essentially to modest electronic couplings. In contrast, direct contact between conjugated segments of two macromolecules leads to both large electronic matrix elements and good spectral overlap for intermolecular energy transfer. Overall, the qualitative picture emerging from the theoretical modeling confirms the observed increase in energy transfer rate when going from a solution (of the rigid-rod macromolecules) to the solid state [14] due to an efficient interchain hopping process. These results indicate that, in the case of solutions of conjugated macromolecules that can coil, such as the biosensors developed by McBranch and co-workers,[6] the fast energy transfer rate has to be related to hops between stacked conjugated segments of the same chain rather than hops along the chain.

Table 1. Electronic matrix elements (V_{da}), spectral overlaps (J_{da}), and rates (k_{da}) for exciton hopping along $(PIF)_n$ conjugated chains and interchain PIF to PIF energy migration; n is the oligomer length. R is the center-to-center donor-acceptor separation.

Donor	Acceptor	R (Å)	V_{da} (cm^{-1})	J_{da} (eV^{-1})	k_{da} (ps^{-1})
Intrachain					
$(PIF)_2$	$(PIF)_2$	25.0	413	1.14	29
$(PIF)_2$	$(PIF)_4$	36.1	225	1.44	11
$(PIF)_2$	$(PIF)_6$	50.0	149	1.39	4.5
$(PIF)_2$	$(PIF)_8$	63.5	111	1.33	2.4
$(PIF)_4$	$(PIF)_4$	50.1	96	1.36	1.8
$(PIF)_4$	$(PIF)_6$	64.0	67	1.48	0.97
$(PIF)_4$	$(PIF)_8$	76.5	52	1.53	0.61
$(PIF)_6$	$(PIF)_6$	76.5	37	1.52	0.30
$(PIF)_6$	$(PIF)_8$	90.0	29	1.61	0.20
$(PIF)_8$	$(PIF)_8$	103.2	18	1.65	7.8×10^{-2}
Interchain					
$(PIF)_2$	$(PIF)_2$	5	903	1.14	139
$(PIF)_2$	$(PIF)_4$	5	412	1.44	37
$(PIF)_2$	$(PIF)_6$	5	201	1.39	15
$(PIF)_2$	$(PIF)_8$	5	111	1.33	2.4
$(PIF)_4$	$(PIF)_4$	5	394	1.36	30
$(PIF)_4$	$(PIF)_6$	5	222	1.48	11
$(PIF)_4$	$(PIF)_8$	5	135	1.53	4.1
$(PIF)_6$	$(PIF)_6$	5	232	1.52	12
$(PIF)_6$	$(PIF)_8$	5	147	1.61	5.1
$(PIF)_8$	$(PIF)_8$	5	149	1.65	5.3

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