

Energy Transport along Conjugated Polymer Chains: Through-Space or Through-Bond?*

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On the basis of a quantum-chemical description of the lowest singlet electronic excited states of bi-chromophoric model systems, we have disentangled the through-bond (TB) from the through-space (TS) contributions to the electronic interactions mediating energy hopping in rigid-rod conjugated polymers. While TB interactions lead to significant mixing between local and charge-transfer excitations in the ground-state (acceptor) configuration, this effect is reduced in the excited-state (donor) configuration as a result of the self-confinement induced by geometric relaxation phenomena. Thus, an improved Förster-type hopping model retaining only long-range TS contributions between donors and acceptors but accounting for excited-state delocalization among acceptors (possibly driven by TB interactions) appears as a minimal model to treat excitation transport along polymer chains.

1. Introduction

Fast and sensitive quenching of the photoluminescence (PL) of conjugated polymers in presence of analytes has been largely exploited to design (bio)chemical sensors.^[1] The amplified sensory response reported for polymers in comparison to molecules of similar chemical structures apparently arises from collective effects among the monomer units, though the detailed mechanism at the origin of such synergic effects is still unclear. In the limiting case of strong electronic couplings between the repeating units along the polymer chains, the latter behave as single quantum objects with fully delocalized electronic excited states. In contrast, for weakly interacting units, the electronic excitations self-localize due to coupling to intra-molecular vibrations and diffuse incoherently via a sequence of hopping events. Spatial confinement of the electronic excitations in conjugated polymers is also induced by the presence of both energetic and positional disorder. A number of experimental^[2,3] and theoretical^[4,5] investigations support this multi-chromophoric picture for conjugated polymers. Upon light absorption, the photoinduced electronic excitations thus funnel through the complex energy landscape resulting from the distribution in conjugated lengths and site energies to reach a small number of low-energy (red) sites.^[6] These might correspond to chromophores that are brought into

close contact as a result of either coiling of flexible conjugated polymer chains or inter-molecular interactions in rigid-rod structures.

Recent spectroscopic investigations have shown that the efficiency of energy transport along poly(*p*-phenylene ethynylene)s (PPE) chains in solutions is significantly improved when the polymer is dissolved in a nematic liquid crystalline (LC) solvent.^[7] It was argued that the increased conjugation in the straightened and planarized polymer chains in the LC phase promotes large through-bond electronic couplings along the polymer chains and the subsequent formation of a continuous π -pathway mediating energy transport. The key role of through-bond interactions was also inferred to explain the enhancement in intra-chain energy transfer efficiency measured in rigid-rod polymers with extended excited-state lifetimes.^[8]

At first glance, the very concept of chromophore in conjugated polymers seems to apply mostly to flexible polymer chains (e.g., phenylenevinylene-based polymers like MEH-PPV) where the confinement of the electronic excitations is driven by conformational disorder. Yet, single molecule spectroscopy studies have unambiguously demonstrated that rigid-rod ladder-type polyparaphenylenes do also support multiple chromophoric emission.^[9] This finding is apparently at odds with the enhanced excitation diffusion reported upon increasing the conjugation length in PPE chains.^[7] To reconcile these two different views, one has to keep in mind that chromophores in conjugated polymers are in fact dynamical objects, namely both the average conjugation length and the exciton size evolve in time.^[10,11] Instantaneous photo-induced excitation might therefore trigger electronic excitations delocalized over extended conjugated segments (possibly owing to through-bond interactions and delocalization of the π -system), which subsequently confine over smaller subunits as a result of either conformational fluctuations in the ground state (in 'floppy' chains) or geometric relaxation in the excited state (in both floppy and rigid-rod chains). In that respect, one might

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[**] This work was supported by the European Commission through the STREP project MODECOM (NMP-CT-2006-016434). The authors gratefully acknowledge the Belgian National Fund for Scientific Research (FNRS-FRFC) for its financial support. E. H. and D. B. are FNRS Postdoctoral Research Fellow and Research Associate, respectively. B. V. A. acknowledges a grant from FRIA ('Fonds pour la Formation à la Recherche dans l'Industrie et dans l'Agriculture').

have to think of excitation diffusion in conjugated polymers in terms of delocalized ‘effective acceptors’ (in their ground-state configuration, i.e., prior to thermalization on the excited-state potential energy surface) and localized ‘donors’ (in their excited-state configuration).^[10] In other words, when raising the question of the amount of excited-state delocalization in conjugated polymers, it is important to remind that the answer critically depends on the time scale over which this delocalization is actually probed.

Here, we assess the relative importance of through-space (TS) versus through-bond (TB) contributions to the electronic coupling between the lowest electronic singlet excited states of model phenylenebutadiynylene-based bi-chromophoric systems. By applying semi-empirical quantum-chemical calculations, it is shown that while both TB and TS interactions are sizeable in the ground-state geometry and can yield extended π -delocalization in defect-free polymer chains, confinement of the electronic excitations driven by geometric relaxation on the donor strongly reduces direct overlap between the donor and acceptor wavefunctions, so that TS couplings dominate after thermalization on the donor. Implications of these results for excitation diffusion in conjugated polymers are discussed.

The bi-chromophoric systems under study are composed of two planar conjugated segments (OPE_n , with $2 \leq n \leq 7$) of identical lengths separated by a conformational kink, Figure 1. For all coupling strengths, the singlet electronic excited-state wavefunctions of these bi-chromophoric systems can be expanded in a basis including the localized excitations over the two chromophores ($|1^*2\rangle$ and $|12^*\rangle$) and the charge-transfer configurations among them ($|1^+2^-\rangle$ and $|1^-2^+\rangle$). As described by Scholes et al.^[12] and Thompson et al.,^[13] these electronic configurations mix together in the bi-chromophore via either purely covalent ($\langle 1^*2|H|12^*\rangle$), ionic ($\langle 1^+2^-|H|1^-2^+\rangle$) or mixed-type (e.g., $\langle 1^*2|H|1^+2^-\rangle$) interactions (with H the inter-chromophore Hamiltonian). These couplings can be partitioned into a long-range Coulomb contribution that is operative provided spin selection

rules are obeyed and short-range contributions that invoke direct overlap between the wavefunctions of the two chromophores. The latter encompass two-electron exchange terms and one-electron transfer integrals that both decay exponentially with distance. Note that: (i) excitation hopping is mediated by Coulomb dipole–dipole terms in the Förster model while only exchange terms are retained in the Dexter model; and (ii) at short separations (such as the characteristic bond lengths between the repeating units of a polymer), the one-electron terms are expected to overwhelm the two-electron exchange interactions.^[14] In the ZDO (zero differential overlap) approximation considered here, the covalent couplings between the localized configurations reduce to the two-electron Coulomb contributions (exchange interactions are neglected) while the covalent-ionic couplings responsible for the mixing between localized and charge-transfer excitations involve one-electron transfer integrals. These Coulomb and transfer integrals yield the

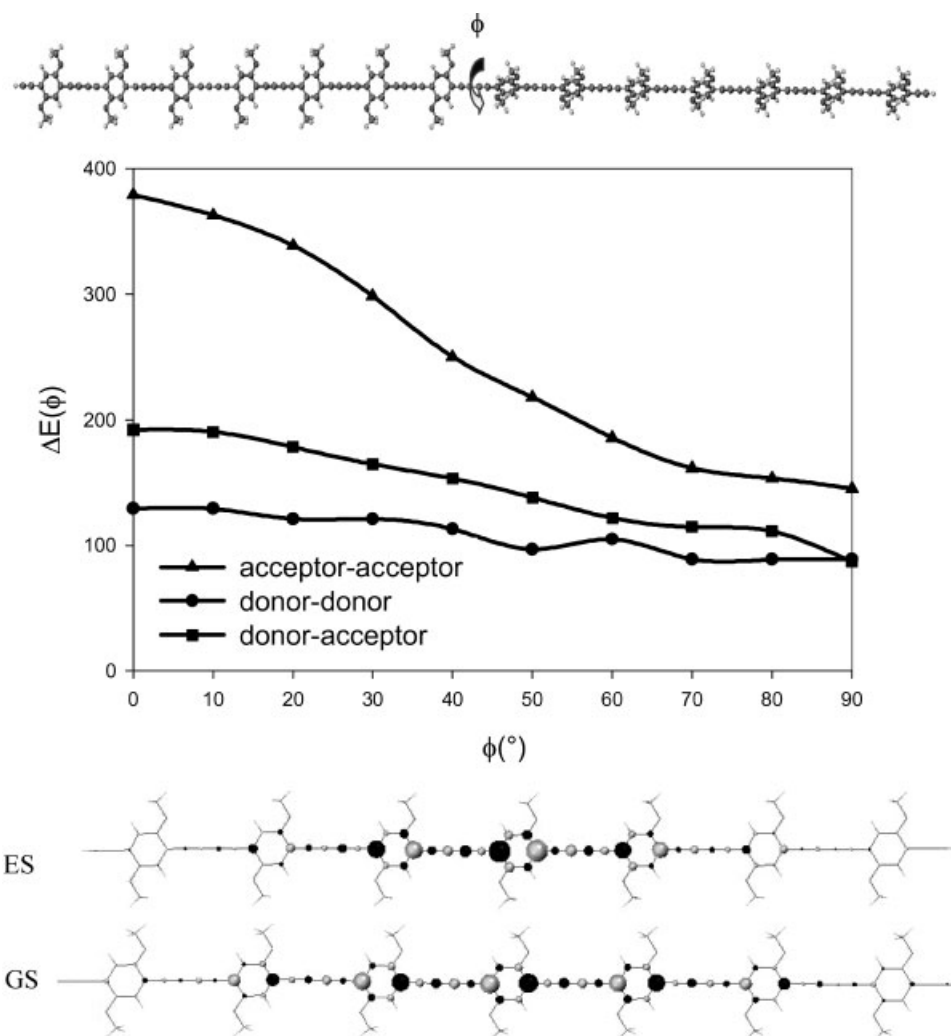


Figure 1. Evolution of the excited-state splitting, ΔE , with ϕ as computed at the INDO/SCI level for different configurations of the bi-chromophoric system displayed on top. The transition densities computed for the isolated 7-unit chromophore in its ground-state (GS) and excited-state (ES) geometry are shown at the bottom.

through-space and through-bond contributions to the excited-state splitting, which are the central quantities in this work.

2. Results and Discussion

We first consider the case where the two chromophores lie in their ground-state geometry. This corresponds to a vertical transition process of the bi-chromophore as would be probed by linear absorption spectroscopy. Figure 1 portrays the evolution of the splitting between the lowest two excited states, ΔE , with the dihedral angle, ϕ , between the planes of the conjugated segments ($n=7$), as obtained on the basis of the INDO/SCI calculations. From perturbation theory, the electronic coupling indeed amounts to half this splitting in the case of two equivalent chromophores interacting in a symmetric configuration. Because of the rotational symmetry around the main molecular axis (the transition dipoles on the two chromophores are co-aligned along the rod direction), a completely flat dependence of ΔE on ϕ is expected (and actually obtained, results not shown) if only TS interactions would be operative. The full calculations, however, show a much more pronounced increase in the splitting as the dihedral angle is reduced. This arises from TB interactions between the two conformational subunits and simply reflects π -delocalization. A similar evolution is obtained for chromophore sizes ranging from $n=2$ to $n=7$, Figure 2a. It is interesting to note that the overall excited-state splitting decreases with increasing oligomer size, an evolution that reflects the dilution of the excited-state wavefunction over the subunits and the concomitant lower contributions over the edges of the interacting chromophores. As a result, both the long-range Coulomb interactions and the transfer integrals contributing, respectively, to the TS and TB couplings lessen with the number of repeating units. This is better appreciated in Figure 2b that shows the evolution of ΔE with n for torsion angles of 90° (purely through-space mechanism) and 0° (combination of through-bond and through-space). From this plot, it can also be anticipated that the electronic splitting should decrease to vanishingly small values in systems with extended conjugation lengths (from linear extrapolation of ΔE with $1/n$, the splitting is comparable to kT at room temperature for $n \sim 10$ units and goes to zero for $n \sim 15$ at any value of ϕ). Hence, any source of energetic disorder (such as fluctuations in the dielectric environment or the presence of structural or chemical kinks) should disrupt the conjugation and chop the polymer chains into chromophores that at best would not extend further than 20 repeating units in the ground-state configuration.

Before moving on, it is interesting to analyze these results in the light of the models that have been developed to depict excitation migration in conjugated systems.^[14] The widely used Förster theory is based on a perturbative treatment of the electronic coupling between donors and acceptors and assumes that: (i) relaxation on the donors proceeds on a time scale that is considerably faster than that of hopping from donors to

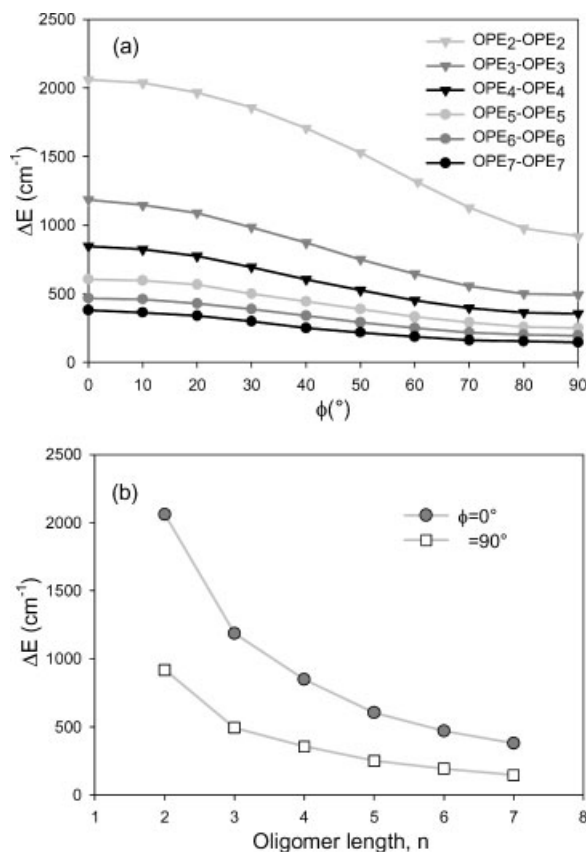


Figure 2. a) Evolution of the excited-state splitting, ΔE , with ϕ as computed at the INDO/SCI level for the acceptor–acceptor configuration of bi-chromophoric systems of increasing size. b) Evolution of ΔE with the size of the interacting chromophores OPE_{*n*}, for $\phi=0^\circ$ and 90° .

acceptors; and (ii) the coupling to intra- and inter-molecular vibrational modes (bath) is larger than the electronic coupling between donors and acceptors. This is the weak coupling limit where the electronic excitation diffuses through an incoherent sequence of hopping steps each proceeding from the thermalized donor. In the opposite strong coupling regime, the donor and acceptor electronic states mix strongly to produce new, delocalized, states and the energy migration process is coherent. The geometric relaxation energies computed on the basis of the AM1/SCI geometries decrease from $\sim 1500 \text{ cm}^{-1}$ for $n=2$ to $\sim 700 \text{ cm}^{-1}$ for $n=7$. From Figure 2b, the electronic coupling (half the energy splitting) between the chromophores in their ground-state geometry ranges from $\sim 450 \text{ cm}^{-1}$ (at $\phi=90^\circ$) to $\sim 1000 \text{ cm}^{-1}$ (at $\phi=0^\circ$) for $n=2$, and from $\sim 70 \text{ cm}^{-1}$ (at $\phi=90^\circ$) to $\sim 190 \text{ cm}^{-1}$ (at $\phi=0^\circ$) for $n=7$. Thus, except for very short conjugation lengths ($n \sim 2-4$), the relative magnitude of the intramolecular relaxation energy versus the electronic coupling places PPE (as well as other rigid-rod conjugated polymers)^[4] in the weak coupling limit. To further test this, we compare in Figure 3 the geometric distortions taking place upon going from the ground state to the lowest singlet excited state of the $n=7$

bi-chromophore, as computed at the AM1/SCI level in the diabatic (equilibrium geometries of the isolated segments, i.e., neglecting the coupling between the chromophores) and adiabatic (equilibrium geometries of the entire bi-chromophoric systems) limits. The lattice deformations are found to be mostly confined on a single chromophore, see Figure 3. This is fully consistent with the conclusion above that extended conjugated segments along PPE chains are weakly coupled.

To investigate the effect of geometric relaxation phenomena on the electronic interactions between the chromophores, we now move to the extreme case where the *two* OPE₇ chromophores adopt their singlet excited-state equilibrium geometry (as obtained at the AM1/SCI level for the individual conjugated segments). This donor–donor configuration has been built by assembling the two isolated chromophores in their respective geometries (i.e., in the diabatic limit) and would correspond to the formation of two electronic excitations on neighboring segments. In contrast to the ground-state case, the INDO/SCI results provide a splitting ΔE that is quasi-independent of ϕ when both OPE segments are in their excited-state geometry, Figure 1. The transition density plots (see Figure 1) provide a simple rationale behind this result: the self-localization induced by geometric relaxation in the excited state minimizes direct spatial overlap between the tails of the excited-state wavefunctions, hence the vanishing TB contributions. Note that a similar yet weaker effect is observed for the

TS contributions: At $\phi = 90^\circ$ (purely TS), the electronic coupling is reduced by about 30% when going from the acceptor–acceptor to the donor–donor configuration; the drop in coupling (by $\sim 70\%$) is far more larger at $\phi = 0^\circ$ where TB interactions dominate in the ground-state configuration but become negligible when both chromophores take their equilibrium excited-state nuclear configuration. Similar geometric relaxation effects resulting from partial cancellation between TB and TS interactions have been reported in meta-linked phenylene-based oligomers.^[13]

We are now prepared to discuss the nature of the electronic coupling mediating excitation motion in PPE. As described above, in the weak coupling limit relevant here, energy diffusion occurs via a sequence of hopping steps taking place after geometric relaxation on the donor. The hopping rate can then be expressed via a Fermi Golden Rule expression as the product of the spectral overlap factor between donor emission and acceptor absorption (accounting for the eventual energy mismatch between the chromophores) and the squared electronic coupling.^[4] This coupling is usually calculated on the basis of the geometry of the reactants (the donor in its excited-state geometry and the acceptor in its ground-state geometry) rather than at the transition state between reactants and products (where the electronic excitation spreads symmetrically over the donor and the acceptor), thus invoking the Franck–Condon approximation. However, in view of the high sensitivity of the electronic interactions with geometric structure demonstrated

above, this approximation is questionable and we have therefore decided to compute the couplings at the transition-state geometry. This approach provides the additional advantage that for such a symmetric configuration the electronic coupling can still be extracted as half the splitting between the lowest two excited states, ΔE , without the need for a tedious correction due to the energy mismatch associated with geometric relaxation in the asymmetric donor–acceptor configuration.^[15] To build these structures, the geometrical parameters of the two conjugated segments in the bi-chromophoric systems were interpolated at midway between their values in the ground-state and excited-state geometries. A similar approach has been successfully applied to study the optical absorption of delocalized polarons in conjugated polymers.^[16] This is hereafter referred to as the donor–acceptor configuration.

The results obtained for bi-chromophores with two $n = 7$ conjugated segments in the donor–acceptor geometry are intermediate to those obtained for the donor–donor and accep-

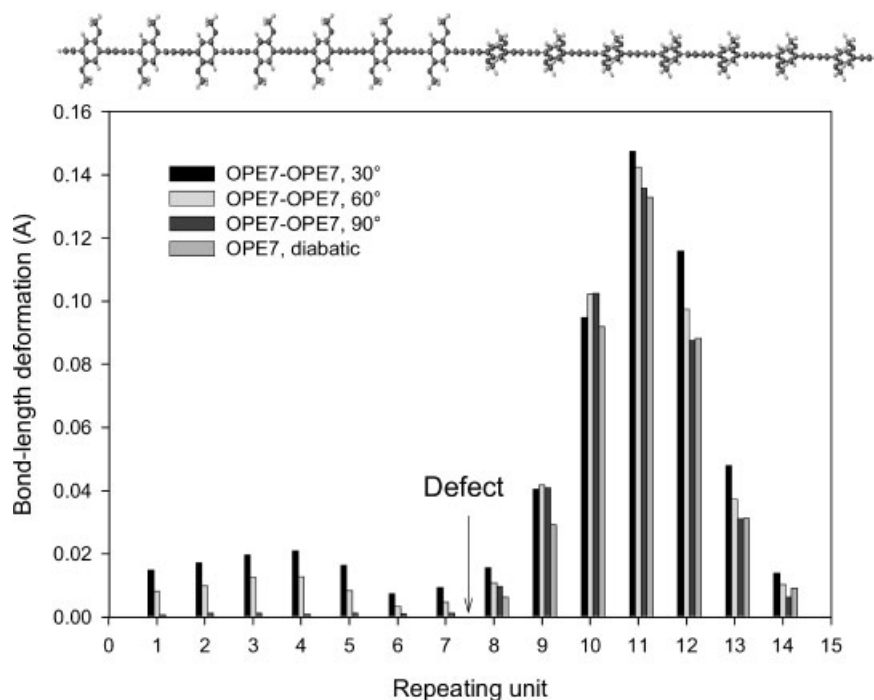


Figure 3. Geometric deformations (sum of the amplitudes of the bond-length changes per repeating unit) upon going from the ground state to the lowest singlet excited state of the OPE₇-OPE₇ bi-chromophore for different values of the torsion angle ϕ (adiabatic limit). For comparison, the corresponding structural rearrangements computed for the isolated OPE₇ oligomer (diabatic limit) are also shown.

tor-acceptor configurations, yet much closer to the former, Figure 1. The excited-state energy splitting shows a weaker dependence on torsion angle in comparison to the acceptor-acceptor case because of the self-localization induced by geometric relaxation phenomena (though this effect is less pronounced than in the donor-donor configuration as the geometric distortions on each segment are weaker in the transition-state geometry). For instance, when $\phi = 0^\circ$ (TB+TS), ΔE is decreased by $\sim 50\%$ in going from the configuration with both chromophores in the ground-state geometry to the donor-acceptor configuration, while this decrease is by $\sim 30\%$ when $\phi = 90^\circ$ (TS only). A similar yet size-dependent drop in the through-bond contribution to the overall electronic coupling is observed for the other bi-chromophoric systems investigated, see Figure 4. While a very flat dependence of ΔE with respect to ϕ is found in long oligomers ($n > 4$), this is not the case in the smaller systems featuring a stronger increase of the excited-state energy splitting with decreasing torsion (similar to the evolution obtained in the acceptor-acceptor configuration). This is not surprising as geometric relaxation does not significantly alter the amount of excited-state delocalization in these short segments, which is primarily limited by finite size effects. Hence, the conjugated segments in these small ($n < 4$) bi-chromophores are predominantly coupled through TB interactions, even in the relaxed excited-state geometry. These should thus be considered as single entities when modeling the excitation transport along PPE chains, as was anticipated from the discussion of electronic couplings versus geometric relaxation energies above (the weak coupling regime does not apply to short conjugated segments). It is interesting to note that the switching from the short-segment to the long-segment behavior occurs at $n \sim 4$, which is roughly the natural size of a polaron-exciton in PPE (i.e., the length over which the geometric deformations extend).

Finally, to get a deeper insight into the origin for the, respectively, large and small TB contributions to the electronic coupling in the acceptor-acceptor and donor-donor configurations,

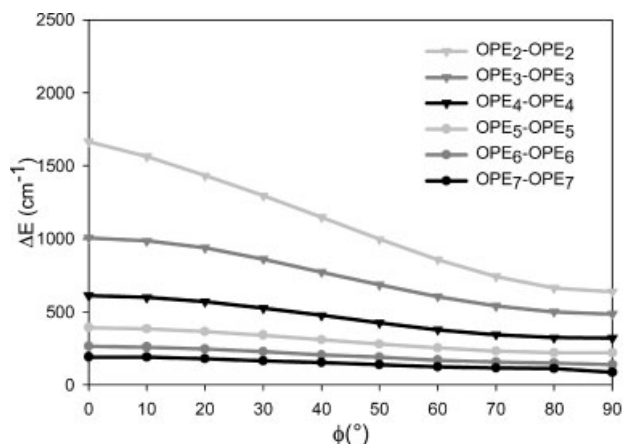


Figure 4. Evolution of the excited-state splitting, ΔE , with ϕ as computed at the INDO/SCI level for the donor-acceptor configuration of bi-chromophoric systems of increasing size.

urations, we have set up a simple four-state model for the $n = 7$ bi-chromophore that includes localized excitations on the two chromophores and charge-transfer (CT) excitations among them. The electronic configurations $|1^*2\rangle$ and $|12^*\rangle$ are coupled to one another via a long-range TS Coulomb interaction V and mix with CT through an angle-dependent TB interaction of the form $t \times \cos(\phi)$. The energy separation obtained by diagonalizing this simple effective Hamiltonian is reported in Figure 5a. A good match is found between the results of the four-state model and the INDO/SCI calculations, highlighting the central role played by the geometry-dependent mixing between localized and CT configurations: (i) In the acceptor-acceptor configuration, the lowest excited state (mainly a symmetric superposition of $|1^*2\rangle$ and $|12^*\rangle$) is stabilized through mixing to CT (while the position of the second excited state, an anti-symmetric combination of the same configurations, is not affected owing to cancellation

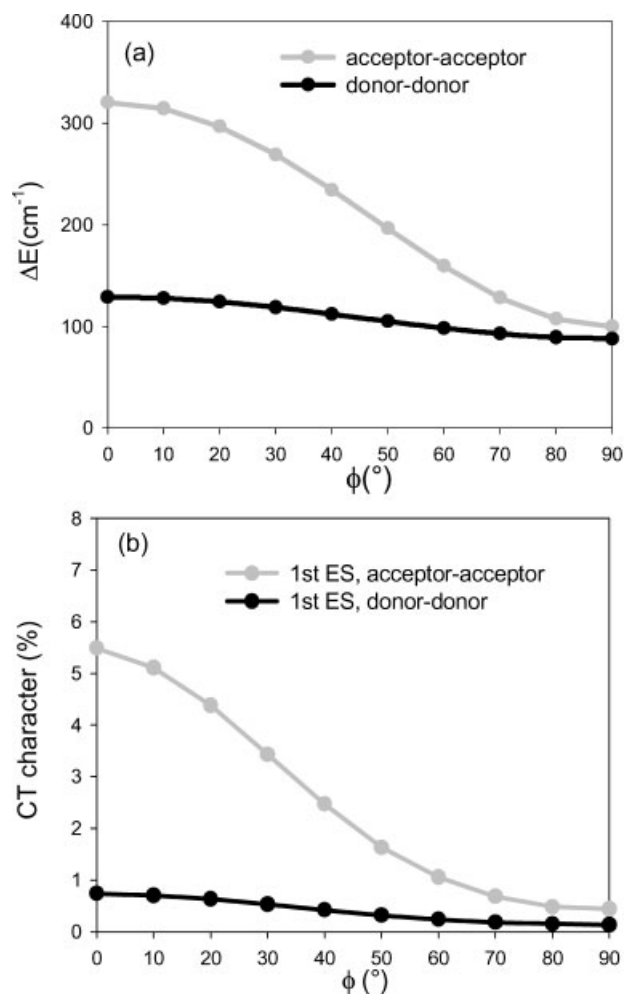


Figure 5. a) Evolution of ΔE with ϕ computed from the four-state model for the bi-chromophore displayed in Figure 1; b) CT contributions computed at the INDO/SCI level in the lowest first and second excited state. The CT character is lower than 1% in the second excited state of the donor-donor and acceptor-acceptor configuration and is not shown.

effects), hence the increased ΔE with decreasing ϕ . (ii) In the donor–donor configuration, a similar configuration mixing occurs but to a much smaller extent because of the reduced TB matrix element (see above) and the larger, by E_{rel} , energy spacing, hence the almost constant ΔE value. The predictions from this simple model are fully consistent with an electron-hole analysis of the INDO/SCI excited-state wavefunctions, Figure 5b: (i) In the acceptor–acceptor configuration, the first excited state features a significant CT character in contrast to the second excited state; and (ii) the CT contributions are markedly reduced for both states in the donor–donor configuration.

3. Conclusions

To conclude, we have disentangled the through-bond and through-space contributions to the electronic interactions mediating singlet energy transfer in model systems for rigid-rod conjugated polymers. We found that in long enough conjugated segments ($n > 4$) the coupling is dominated by TS interactions once geometric relaxation has settled on the donor (shorter segments interact predominantly through bond and should be considered as single quantum entities). In other words, the traditional Förster type model appears as a rather robust starting point to investigate energy transport in conjugated polymers. Yet, this model might need to be extended to take into account the possible delocalized character of the ‘acceptors’. This effect partly arises from TB couplings and π -conjugation in the ground-state configuration of polymers and might be at the origin of their enhanced sensory response. A generalized Förster-like formalism where donors and acceptors are not treated on the same footing has been recently proposed^[10,14] and successfully applied to phenylenevinylene-based conjugated polymers^[17] and supramolecular conjugated wires.^[18]

4. Theoretical Methodology

The optical properties for OPE oligomers were computed with semiempirical methods. INDO/SCI^[19] calculations have been performed on the basis of the AM1 [AM1/SCI]^[20] optimized ground-state [excited-state] geometries that yield the eigenstates of the whole system taking into account both TS and TB contributions. The INDO method used has been shown to provide reliable estimates of the optical bandgaps of a wide range of conjugated systems, see, e.g., Ref. ^[21]. The active space used in the INDO/SCI calculations includes $40 \times n$ molecular orbitals for the bi-chromophores with two n -unit OPE segments, which is large enough to ensure full convergence of the excited-state properties. To disentangle between long-range and direct overlap contributions to the electronic couplings, the same calculations have been repeated for torsion angles ϕ between the two innermost units (structural kink) ranging from 0° to 90° ; because the two π -systems are completely decoupled for

$\phi = 90^\circ$, the results obtained in this limiting case provide direct information on the magnitude of the TS interactions (TB = 0 at $\phi = 90^\circ$). For such orthogonal orientation of the two conjugated segments, the excited states of the bi-chromophoric system can be adequately described within a Frenkel exciton formalism neglecting charge-transfer configurations (thus retaining only the $|1^*2\rangle$ and $|12^*\rangle$ configurations above) and expanding the electronic interactions on the basis of atomic transition densities computed for the interacting chromophores.^[22] Although these results are not discussed here, we have checked that the electronic couplings computed on the basis of such an exciton approach agree with the values obtained using the INDO/SCI approach when the torsion angle is 90° or when setting to zero in the INDO Hamiltonian the one-electron transfer integrals along the C–C bond connecting the two conjugated segments (thus effectively turning off the TB interactions in both cases).

To gain more insight into the INDO/SCI results, we have solved a simple 4-state model, including two excitations localized on chromophores 1 and 2, $|1^*2\rangle$ and $|12^*\rangle$, and two charge-transfer excitations among them, $|1^+2^-\rangle$ and $|1^-2^+\rangle$. The two (degenerate) localized excitations are separated from the (degenerate) charge-transfer configurations by an energy spacing $\delta\varepsilon$ in the acceptor–acceptor configuration; the corresponding energy difference is $\delta\varepsilon + E_{\text{rel}}$ in the donor–donor configuration, where E_{rel} is the energy gain induced by geometric relaxation in the excited state of one chromophore. The localized and charge-transfer configurations mix through short-range transfer integrals, $t \times \cos(\phi)$ with ϕ the dihedral angle between the chromophores; interaction between the two localized excitations is mediated by a long-range electronic coupling, V ; the coupling among the charge transfer excitations is neglected. V , $\delta\varepsilon$, E_{rel} and t have been adjusted against the quantum-chemical results (Table 1): V is taken as half the excited-state splitting for $\phi = 90^\circ$; E_{rel} is computed at the INDO/SCI level on the basis of the AM1/CI geometries; t has been fitted to reproduce the excited-state energy splitting at $\phi = 0^\circ$.

In the acceptor–acceptor configuration and neglecting the coupling between localized and CT excitations, the excited-state wavefunctions write as:

$$\frac{1}{\sqrt{2}}(|1^*2\rangle \pm |12^*\rangle) \text{ and } \frac{1}{\sqrt{2}}(|1^+2^-\rangle \pm |1^-2^+\rangle) \quad (1)$$

Using the Hamiltonian described above, the matrix elements mixing these configurations are different from zero only for the two symmetric combinations. Hence, in the acceptor–acceptor configuration, only the lowest localized excited state (symmetric superposition of $|1^*2\rangle$ and $|12^*\rangle$) acquires some CT character when the interactions between CT

Table 1. Parameters used in the 4-level model. All values are in cm^{-1} .

Configuration	V	t	E_{rel}	$\delta\varepsilon$
Acceptor-acceptor	−50	−350	0	2800
Donor-donor	−44	−200	1340	2800

and localized excitations are switched on. The same holds for donor–donor interactions. However, the energy spacing between the localized and CT configurations is now raised by E_{rel} and the coupling, t , between these configurations is reduced owing to geometric relaxation induced excited-state localization. Thus, the admixture of CT to the lowest two excited states is much less pronounced.

Received: May 23, 2007

Revised: July 24, 2007

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