Spectroscopic Units in Conjugated Polymers: A Quantum Chemically Founded Concept?

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In conjugated polymers the concept of spectroscopic units belonging to different spatial segments of the chain, which are responsible for the spectroscopic properties of the polymer, has been used to explain the spectral heterogeneity and the excitation migration by (Förster type) hopping transfer. In the present work we study the possible mechanism of segmentation of polythiophene into spectroscopic units by using quantum-chemical methods (ZINDO). We found that static geometric defects such as kinks or torsions do not result in a significant localization of the excited states to a certain segment. Hence, we propose that a dynamic localization of excitation due to the interaction between the nuclear and electronic degrees of freedom is responsible for the formation of the spectroscopic units.
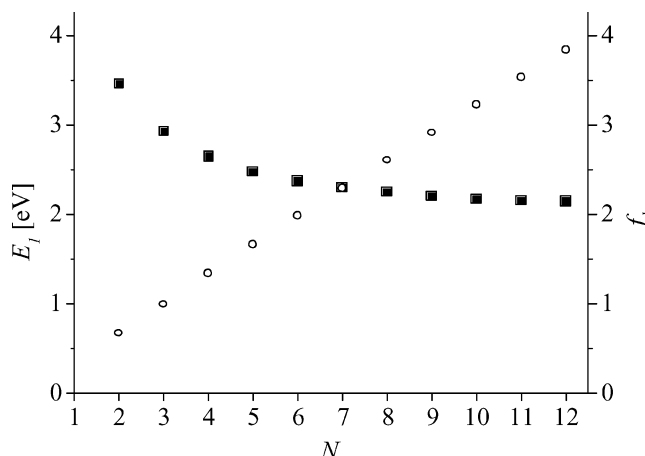
1. Introduction

The electronic structure of photoexcited states of conjugated polymers is one of the fundamental issues in studies at these promising materials. The conjugated polymers might be seen as one-dimensional semiconductors and correspondingly be described in terms of electronic band structures.[1−4] However, in a bulk polymer structural and chemical defects, like hydrogenated double bonds, kinks, and torsions, are expected to break the translation symmetry and limit the delocalization of the electronic wave functions.[5−8] A similar effect is well-known for molecular aggregates.[9,10] Hence, the conjugated polymer is usually described as a chain partitioned into so-called spectroscopic units the excited states are delocalized over. In this model the spectroscopic properties and the excitation energy transfer of the polymer are described as those of an ensemble of spectroscopic units.[11,12]

For oligothiophenes it has been experimentally shown that absorption energy and oscillator strength for the first singlet excited state (S_1) depend on the number of conjugated thiophenyl rings N.[13] Our own results obtained by the semiempirical quantum-chemical method ZINDO[14,15] for several straight transoid oligothiophenes are shown in Figure 1. These results fit remarkably well to the energy dependence predicted by exciton theory[16] as

$$E_1(N) = 4.8 \text{ eV} - 2.7 \text{ eV} \times \cos\left[\frac{\pi}{N+1}\right] \qquad (1)$$

One may be tempted to conclude that the S_1 energy of the polythiophene is represented by the asymptotic value 2.1 eV for $N \rightarrow \infty$. The measured absorption spectra of polythiophenes, however, show a significant inhomogeneous broadening toward higher energies. This suggests a segmentation of the polymer chain into spectroscopic units, which are assumed to have the same properties as oligothiophenes of the corresponding length. According to the random distribution of their lengths, the transition energies of the spectroscopic units vary. Thus the

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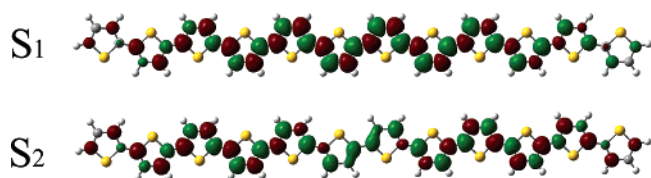

Figure 1. Transition energies E_1 (filled squares) and oscillator strengths f_1 (open circles) of the S_1 excitation for oligothiophenes in dependence of the number (N) of thiophenyl rings.

inhomogeneous broadening of the absorption spectrum of polythiophenes would be explained. Analogously, excitation energy transfer from the shorter spectroscopic units, with consequently higher S_1 energy, to the longer ones, with lower S_1 energy, can explain the strongly red-shifted, and in comparison to the absorption narrower, luminescence spectra.[17−20] Furthermore, models based on spectroscopic units have been successfully applied to simulate the measured transient anisotropy decay in polythiophenes.[21,22]

In the current article we analyze the possible origins of the segmentation into spectral units for polythiophene, which is used for organic light emitting devices. We apply the ZINDO method to study the excited states of several dodecithiophenes, each deformed by a single specific defect, i.e., either a hydrogenated double bond, a kink, or a torsion. The results are discussed in the context of a possible segmentation of polythiophenes into spectroscopic units—in particular to what extent these resemble the optical properties of transoid oligothiophenes of various length.

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Figure 2. Transition densities for the first (S_1) and second (S_2) singlet-excited state of a straight all-transoid dodecithiophene.

Figure 3. Transition densities for the first (S_1) and second (S_2) singlet-excited state of the transoid 2''''',3'''''-dihydrododecithiophene.

2. Theory

Various possibilities exist to evaluate the spatial extension of excited electronic states of a conjugated system. An obvious, but elaborate approach would be to inspect visually all molecular orbitals contributing to the corresponding excitation. Recently, Tretiak et al.[23] used the transition density matrix in a site representation to analyze the electron−hole coherence as well as excitation delocalization in PPV oligomers. Also quite common is the so-called distributed monopole method.[24−26] In this work we have chosen to use the transition density $\rho_i(\mathbf{r})$ of the singlet excited state $|S_i\rangle$ in cube representation[27] (e.g., in Figure 2 for a linear transoid dodecithiophene). This quantity determines the transition dipole

$$\mu_i = \int \mathbf{r}\rho_i(\mathbf{r})\, \mathrm{d}^3 r \qquad (2)$$

giving the strength and the orientation for the interaction with the electromagnetic field. Analogously, higher transition multipoles can be derived from $\rho_i(\mathbf{r})$.

In the present work the singlet excited states $|S_i\rangle$ have been calculated by the semiempirical quantum-chemical method ZINDO,[14,15] as it is implemented in the software package Gaussian 98.[28] This method is optimized to provide reliable transition energies and dipoles for molecules and molecular aggregates—in particular for systems that are far too large for multireference ab initio methods. The latter are practically limited to quaterthiophene.[29] The ZINDO calculation consists of a Hartree−Fock calculation on a parametrized STO basis and a subsequent diagonalization of the single-configuration interaction (single-CI) Hamiltonian. All integrals except for the overlaps are parametrized. This parametrization implicitly takes into account a part of the electron correlation, which is not included in ab initio single-CI calculations. The eigenstates of the single-CI Hamiltonian for singlet excitation yield as

$$|S_i\rangle = \sum_{\mu,\nu}\zeta_{i\mu\nu}\frac{1}{\sqrt{2}}(c_{\mu\uparrow}^{+}c_{\nu\uparrow} + c_{\mu\downarrow}^{+}c_{\nu\downarrow})|S_0\rangle \qquad (3)$$

where $\zeta_{i\mu\nu}$ represents the eigenvector of the single-CI Hamiltonian. The configurations are constructed by the operators $c_{\mu s}^{+}$ and $c_{\nu s}$ for the creation and annihilation of an electron with spin s in the molecular orbitals $\phi_\mu(\mathbf{r})$ and $\phi_\nu(\mathbf{r})$, respectively. $|S_0\rangle$ is the Hartree−Fock ground state. The transition density for the transition from the ground state $|S_0\rangle$ to the singlet excited state $|S_i\rangle$ is then given by

$$\rho_i(\mathbf{r}) = \sum_{\mu,\nu}\zeta_{i\mu\nu}\phi_\mu^{*}(\mathbf{r})\,\phi_\nu(\mathbf{r}) \qquad (4)$$

The molecular orbitals $\phi_\mu(\mathbf{r})$ and the CI eigenvectors $\zeta_{i\mu\nu}$ have been calculated by the ZINDO method, as mentioned above. In Figure 2 the results for a straight chain of 12 thiophenyl rings (transoid dodecithiophene) are shown. Due to the symmetry of the transition density, the S_1 state has a nonvanishing transition
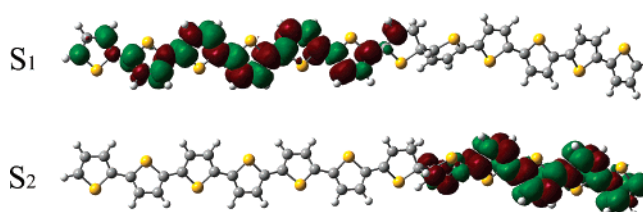
dipole moment oriented along the molecular axis, whereas the transition dipole of the S_2 state is zero.

3. Results

We have studied how the excited states S_1 and S_2 of the dodecithiophene are affected by the following chemical and steric defects: (i) interjectional single bonds by hydrogenation of a double bond, (ii) horizontal as well as azimuthal kinks, and (iii) torsions.

3.1. Interjectional Single Bonds. For poly(*p*-phenylenevinylene) (PPV) interjectional single bonds replacing the vinyl bonds can effectively break the π-conjugation.[22] To search for a similar effect in polythiophenes, we modeled a transoid dodecithiophene where the (2,3)-bond of the sixth thiophenyl ring has been saturated by hydrogenation (2''''',3'''''-dihydro-dodecithiophene; see Figure 3). The geometry of the whole system has been optimized by using DFT (B3LYP for basis set 6-31G) as implemented in Gaussian 98.[28] The subsequent ZINDO calculation of this system reveals a clear segmentation of the transition density at the single bond for the two lowest singlet excitations (see in Figure 3). The transition energies of 2.50 eV for the S_1 excitation and 2.73 eV for the S_2 excitation, however, are more comparable to oligomers of 4−5 and 3−4 thiophenyl rings than to those of 6 and 5 thiophenyl rings, respectively, whereas the resulting oscillator strengths of 2.5 and 1.08 are comparable to those for oligomers with 7−8 and 3−4 rings, respectively. Thus, the calculated transition frequencies and oscillator strength of the two lowest excited states do not fit perfectly to the values that would correspond to the length of the respective segments. The sum of the two oscillator strengths corresponds to an oligomer of 11 thiophenyl rings, which is shorter than the undisturbed transoid dodecithiophene (12 thiophenyl rings). This effect can be explained by the imperfectness of the hydrogenated thiophenyl ring. However, the loss of oscillator strength originates mainly from the shorter segment, which contains five undisturbed thiophenyl rings but has the oscillator strength corresponding to only 3−4 rings. Qualitatively similar results are obtained for hydrogenation of the double bonds between the seventh and eighth thiophenyl ring (not shown). In PPV the defect by saturation of a vinyl bond does not significantly affect the structure of the neighboring phenyl rings. Therefore, with respect to the segmentation by interjectional single bonds, the spectroscopic-unit model is appropriate for PPV. In this context it has to be noted that for PPV the average amount of interjectional single bonds can be controlled by synthesis method.[22] To the best of our knowledge, for polythiophenes neither a controlled nor an accidental injection of single bonds into the π-conjugated system has been reported.

3.2. Horizontal and Azimuthal Kinks. To test the effect of kinklike defects, we have modeled a bent dodecithiophene in such a way that the two straight end chains are formed by five and three thiophenyl rings, respectively. The defect has been built up by the remaining four thiophenyl rings in the middle,
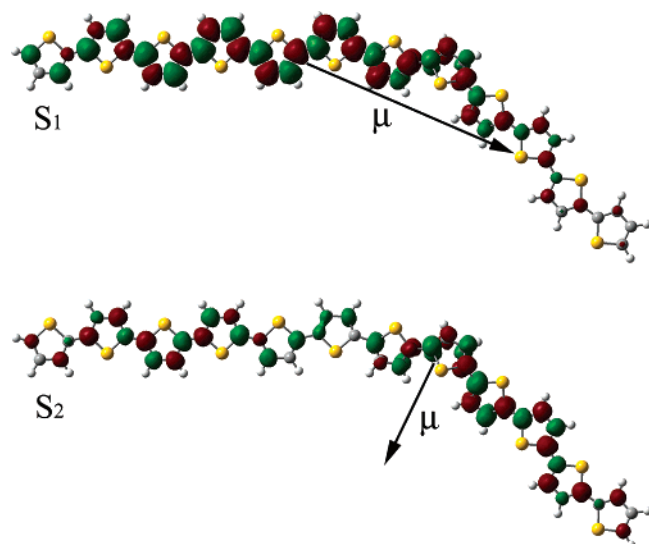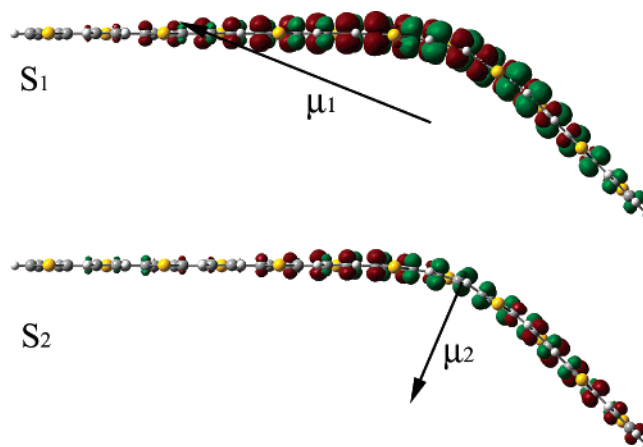
Figure 4. Transition densities and dipoles (μ) for the first (S_1) and second (S_2) singlet-excited state of a horizontally kinked transoid dodecithiophene.

Figure 5. Transition densities and dipoles (μ) for the first (S_1) and second (S_2) singlet-excited state of an azimuthally kinked transoid dodecithiophene.

which has been partially relaxed by an incomplete geometry optimization using molecular mechanics (UFF method as implemented in Gaussian 98[28]). The optimization avoids unrealistic structures, where stressing forces would not only break the π-conjugation, but also the σ-bonds. Usually the oligothiophene molecule would try to escape the stress on the σ-bonds by torsion of the bonds between the thiophenyl rings. Because torsions shall be studied separately, for the horizontal kink we allowed this degree of freedom (constricted to transoid character) for the four thiophenyl rings forming the kink. The others remain in the same plane. In the case of azimuthal kinks (see below) we froze the torsional degree of freedom in the geometry optimization for the whole molecule. In Figure 4 we present the transition density for the two lowest singlet excitations (S_1 and S_2) for the horizontally kinked dodecithiophene. Even though the transition densities for the S_1 excitation are more concentrated on the longer branch of the kinked molecule, there is no clear segmentation. The transition density on the other branch is still significant. This has an important effect on the orientation of the transition dipole: It is out of line with the longer branch. For the S_2 excitation at first view one would assume a similar picture where only the transition density is now concentrated on the shorter branch.

However, a closer investigation reveals that the symmetry of the transition density for the S_2 excitation is completely different from that obtained for the S_1 excitation. They result in transition dipoles (μ_1 and μ_2) nearly perpendicular to each other. For spectroscopic units the transition dipoles should have been parallel to the respective branches left and right of the kink. Also the strengths of the transition dipoles do not correspond to the length of the two branches. For the S_2 excitation we obtained only 20% of the oscillator strength of the S_1 excitation. Due to the fact that the oscillator strength of an oligothiophene depends linearly on its length, we would have expected to get a ratio of 5:7 (or 4:6 for excluding the two thiophenyl rings forming the kink). However, the transition energies of 2.37 eV for the S_1 excitation and of 2.61 eV for the S_1 excitation fit quite well to oligomers of six and four thiophenyl rings, respectively.

The next defect to be studied, the azimuthal kink, is obtained by bending the dodecithiophene out of the molecular plane. Here the transition density (Figure 5) does not show any sign of

segmentation. On the contrary, the transition densities are concentrated around the azimuthal kink. In the same way as for the horizontal kink the different symmetries of the transition densities result in transition dipoles μ_1 and μ_2, which are nearly perpendicular to each other. Also the ratio between the oscillator strengths of the S_2 and the S_1 excitation of approximately 1:5 is not what one would expect for a clear segmentation into two branches of 4–5 and 6–7 rings, respectively. The S_2 energy of 2.5 eV does roughly fit to oligomers of 4–6 thiophenyl rings. However, the S_1 energy of 1.9 eV is even lower than that of the S_1 excitation of the straight dodecithiophene (2.14 eV). We attribute this to an increased ground-state energy due to the stress on the binding π-bond at the azimuthal kink. In the S_1 state the π-bonds at the kink have a more antibinding character and thus they are less stressed. Consequently, the transition energy from S_0 to S_1 is lowered. The S_2 state has a node at the kink. Thus the π-bonds remain of a similar binding character as in the ground state and the transition energy from S_0 to S_2 is not lowered.

Concluding, we can state that neither horizontal nor azimuthal kinks give rise to a spatial segmentation of the transition density of a polythiophene chain.

3.3. Torsions and Cisoid Defects. Our model for the torsional defect in a polythiophene chain is a straight dodecithiophene with six transoid thiophenyl rings at the one end and four transoid thiophenyl rings at the other end. These subchains are planar in themselves but perpendicular to each other. They are bridged by two thiophenyl rings each of them turned by 150° in respect to the neighbors. A subsequent geometry optimization has not been applied, because such torsions between two thiophenyl rings are not significantly hindered for dihedral angles between 130° and 210°. Actually the 2,2′-bithiophene has a structure where the dihedral angle between the two thiophenyl rings is about 150°, though the barrier at 180°, i.e., for the planar geometry, is very low.[30–32]

It has been suggested that torsions of 90° around the axis of the chain breaks the π-conjugation completely. Contrary to this, we found that for the given geometry the transition densities have not even a node at the torsional defect (Figure 6). With respect to the distribution along the molecular axis, the transition densities are very similar to those obtained for the planar molecule. Consequently, the oscillator strength for the S_1 excitation ($f_1 = 4$) is approximately the same as for the planar transoid dodecithiophene, and the optical transition to the S_2 state, which in the planar case is forbidden by symmetry, has

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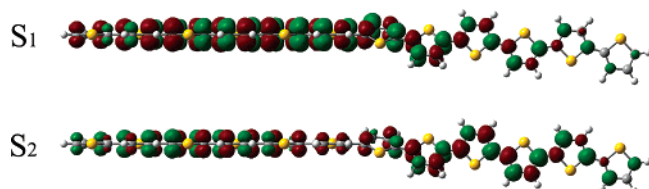
Figure 6. Transition densities for the first (S_1) and second (S_2) singlet-excited state of a partially twisted transoid dodecithiophene.

Figure 7. Transition densities and dipoles (μ) for the first (S_1) and second (S_2) singlet-excited state of a cis−transoid dodecithiophene.

Figure 8. Difference of the electron density $\Delta\rho_{22}$ between the S_2 state and the ground state for the horizontally kinked transoid dodeci-thiophene (red, excess electron; green, hole). The resulting nuclear forces $\mathbf{F}_n(\mathbf{R}_n)$ are indicated by arrows (arbitrary units).

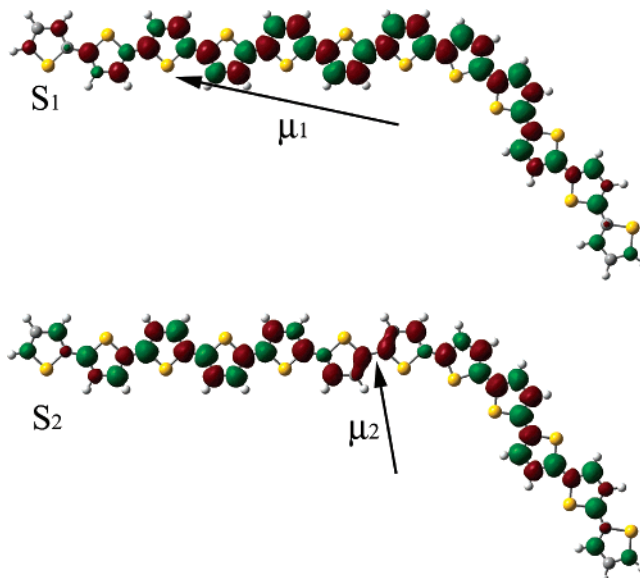only small oscillator strength ($f_2 = 0.26$). That there exists an axial transition dipole μ_2 results from the shift of the transition density node, which in the planar case is in the center, toward the torsional defect. The transition energies are 2.38 eV for the S_1 state and 2.60 eV for the S_2 state. These correspond to oligothiophenes consisting of six and four thiophenyl rings.

A special kind of defect is related to the cis−transoid stereomerism for the bonds between two thiophenyl rings. In the present work we study a dodecithiophene where two cisoid bonds form a bow between two straight chains with six and three transoid bonds. The cisoid bond can formally be seen as a torsion about 180°, but the resulting geometry is also similar to a horizontal kink. However, the cisoid bonds are less stressed than the bent transoid bonds, which form the horizontal kink described above. In principle, there is no big difference between a cisoid and a transoid π-conjugation. Both transition densities, for the kinked cis−transoid as well as for the straight all-transoid dodecithiophene, do not show any segmentation (cf. Figures 2 and 4). In both cases the characteristic node for the S_2 state is located between the sixth and seventh thiophenyl ring. The nonzero transition dipole moment μ_2 of the cis−transoid stereomer (corresponding to oscillator strength $f_1 = 0.57$) results from the bent geometry. For the same reason the oscillator strength of the S_1 excitation ($f_1 = 3.26$) is somewhat smaller than for the straight all-transoid dodecithiophene. Like for the horizontal kink, the two transition dipoles μ_1 and μ_2 are almost perpendicular to each other. The energies of 2.15 eV for the S_1 state and 2.42 eV for the S_2 state are nearly the same as those found for the straight all-transoid dodecithiophene (2.14 and 2.41 eV, respectively). Concluding, we can state, that the change from transoid to cisoid orientation of the thiophenyl rings hardly affects the transition densities with respect to their distribution on the atoms following the trajectory of the polymer chain. In particular, there occurs no segmentation (Figure 7).

4. Discussion

The concept of spectroscopic units has been used for describing various stationary and ultrafast spectroscopy experiments (see above). Usually, one relates the length of a spectroscopic unit to the length of conjugation, which is assumed to be broken by various chemical and structural defects. In the current work we have used the transition density as a measure for the spatial extent of the excited electronic state, which should be related to the spectroscopic unit. According to our results, however, geometric defects, i.e., kinks or torsions, do not segment the transition density of the excited states.

From the experimental point of view, there is little reason to mistrust the concept of spectroscopic units, but we need to find a reliable microscopic model for their origin. In this context it is useful to relate the problem to the well-established theory of excitons in linear molecular aggregates.[1,33,34] In the exciton model the eigenstates of the electronic Hamiltonian are delocalized, i.e., the exciton states span over the whole aggregate, as long as the disorder of the site energies is low.[10,35] However,
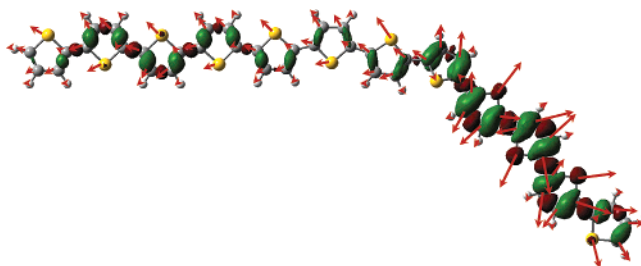
when nuclear dynamics are included into the model, this delocalization may be destroyed by formation of an exciton−polaron. It is the ratio between the excitonic interaction and electron−phonon coupling, which determines whether the state will stay delocalized or it will localize.[36−38] The same process will also take place in conjugated polymers forming so-called neutral polarons.[39−42]

In our quantum-chemical calculations the nuclear motion has not be taken into account. Hence, the calculated states S_j do not represent the relaxed excited states. Nevertheless, we can qualitatively describe how the localization process acts. We calculate the difference of electron density between the excited state S_i and the ground state S_0 from ZINDO as

$$\Delta\rho_{ii}(\mathbf{r}) = \sum_{\mu,\nu,\kappa} (\xi_{i\mu\kappa}\xi_{i\nu\kappa} - \xi_{i\kappa\mu}\xi_{i\kappa\nu})\phi_\mu(\mathbf{r})\,\phi_\nu(\mathbf{r}) \qquad (5)$$

Due to this change of the charge distribution in the molecule after excitation, the nuclei will be driven out of the ground-state potential minimum by forces

$$\mathbf{F}_n(\mathbf{R}_n) = \frac{e^2}{4\pi\epsilon_0}Z_n\int\frac{\mathbf{r}-\mathbf{R}_n}{|\mathbf{r}-\mathbf{R_n}|^3}\Delta\rho_{ii}(\mathbf{r})\,\mathrm{d}^3r \qquad (6)$$

For example in Figure 8 both, the difference of electron density and resulting nuclear forces, are shown for the S_2 state of the horizontally kinked dodecithiophene (cf. Figure 4). One can see

that the resulting forces of the nuclei belonging to the right side of the kink are much stronger than those on the left side. Notably, they result mainly in a displacement of the potential minimum for the C—C stretching mode of the analogue oligothiophene ($\bar{\nu}_{C-C} \approx 1300$ cm^{-1}). This situation is very similar to what has been found for excitonically coupled heterodimers.[36] Hence, we expect that the feedback from the changed positions of the nuclei to the electronic system will result in a localization for the relaxed S_2 state (as represented by its transition and different electron density) on the shorter branch of the kinked dodecithiophene. Analogously, the relaxed S_1 state will be localized on the longer branch. Important for this dynamic localization is that it is seeded by an initial preference of the excited state to one of the straight branches, i.e., the transition as well as electron density are more concentrated to the right or left side of the kink, respectively. Consequently, horizontal kinks and torsional defects (cf. Figures 4 and 6) can partition the excitation into spatially separated spectral units by dynamic localization, whereas azimuthal kinks will most likely not separate spectroscopic units but may act as a trap at least for the S_1 excitation (see above, Figure 5). For all-transoid chains as well as such with cisoid defects, dynamic localization may happen as well. However, in this case the localized excitation is not constricted by local defects but as an exciton—polaron with increased effective mass it may either move along the chain or be self-trapped at an arbitrary position.[43] Our model provides only a qualitative description of the formation of spectroscopic units in polythiophenes. For a more quantitative results quantum-dynamic calculations, which include equations of nuclear motion explicitly, have to be performed. Attempts in this direction for PPV are in agreement with our qualitative model.[23,40,44,45]

There exist also experimental hints to dynamic localization of the excitation in polythiophenes by nuclear motion. Due to our model, the initially created delocalized excited state relaxes to a localized state on the time scale of the nuclear motion. For a kinked polymer this means a localization of the transition density to one branch (see above), and an alignment of the corresponding transition dipole vector along the axis of the respective branch. The necessary turn of the transition dipole should be observable as an ultrafast transient anisotropy decay. Indeed, a kinetic component of 37 ± 5 fs has been recently observed for the anisotropy decay in ultrafast pump—probe experiments for films of the polythiophene PTOPT.[46] It was argued that this part of the kinetics is too fast to originate from a Förster transfer between spectroscopic units, but fits well to the time scale of nuclear dynamics for the mentioned C—C stretching mode of 1300 cm^{-1} (oscillation period of 25 fs).[47,48]

5. Conclusion

By quantum chemical calculations for a model system we have shown that only interjectional single bonds leads to a static segmentation of a polythiophene chain into spectroscopic units. However, by dynamic localization of the excitation due to the nuclear motion, horizontal kinks and torsions in the chain can act as separators for spectral units for relaxed excited states. The localization dynamics are important for understanding fluorescence and excitation transfer by Förster hopping and can be related to the experimentally observed ultrafast transient anisotropy decay.

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