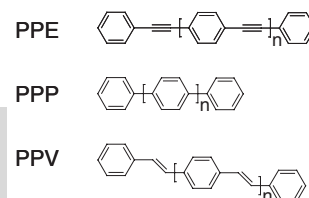# The Singlet–Triplet Exchange Energy in Conjugated Polymers**

By *Anna Köhler** and *David Beljonne*

PPE

PPP

PPV

Electron–electron interactions in organic semiconductors split the lowest singlet and triplet states by the exchange energy, ΔE_{ST}. Measurement of singlet and triplet emission spectra in a large number of conjugated polymers yield an almost constant ΔE_{ST} value close to 0.7 eV. This is in contrast to the situation in molecules, where the exchange energy is found to depend on molecular size and to vary over a wide range. Quantum-chemical calculations are performed to address the origin of the constant exchange energy in phenylene-based conjugated polymers. The electron–hole separation in the lowest singlet and triplet excited states is found to be independent of the π-conjugated backbone, and saturates for chains longer than a few repeating units, resulting in a constant exchange energy. In shorter conjugated oligomers, confinement of the excitations destabilizes the singlet with respect to the triplet through exchange interactions and leads to a larger and size-dependent singlet–triplet energy separation.

I. Introduction

Light-emitting diodes (LEDs) based on molecular or polymeric organic semiconductors have now reached efficiencies that make them commercially viable for display applications.[1] Further improvements in terms of light output require a detailed understanding of the photophysical properties of conjugated materials. Organic materials are usually characterized by weak spin–orbit coupling and therefore only the singlet state is emissive. However, in an operating LED, charges with spin 1/2 are injected from the electrodes into the polymer layer and recombine to form both singlet and triplet excitons.[2]

The lack of light emission from triplet states is detrimental to the ultimate efficiency in organic LEDs.[3,4] In addition, collisions between triplet excitons and charge carriers can limit the current flow through the devices and so reduce the device efficiency further.[5] Such annihilation processes are also thought to impede the development of electrically pumped polymer lasers. These problems can be overcome in a number of ways.[6] One approach is to transfer the triplet excited state from the organic polymer onto an organometallic dye from which triplet-state emission (phosphorescence) can occur, due to strong metal-induced spin–orbit coupling; the success of such an energy-harvesting scheme has been demonstrated in molecular or polymeric hosts doped with such triplet emitters.[4,7] Efficient triplet-energy transfer requires matching between the energies of the lowest triplet state in the polymer and the dye. Knowledge of the triplet energy in organic polymers is therefore essential for the systematic design of such guest–host system. A different approach is to increase the fraction of singlet states generated from the recombination of electrons and holes in an LED. Theoretical work has suggested that this fraction may be affected by the energy separation between the lowest singlet S_1 and triplet T_1 excited states, i.e., the exchange energy.[6,8–13] There is thus a need for a fundamental understanding for the dependence of the exchange energy on chemical structure. Besides these practical aspects, understanding the exchange energy is necessary to develop a full picture of the nature of the singlet and triplet excitations. For example, a large exchange energy implies a localization of the electron–hole pair and thus a high exciton binding energy, while a small exchange energy is associated with a delocalized state, and a small exciton binding energy.

There have been recent experimental developments that made it possible to determine the energy of the lowest triplet state, and hence also the exchange energy in a wide range of conjugated polymers. The triplet energy can be determined directly und unambiguously by phosphorescence measurements[14–16] or indirectly via energy-transfer measurements.[17]

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Monkman and co-workers advanced the latter approach.[17] They use pulsed radiolysis to create a high concentration of triplet excitons in a solvent, which subsequently transfer onto the polymer under investigation. Energy transfer from the triplet excited state in the polymer onto a dye will occur when the triplet energy in the dye is lower than in the polymer, thus providing an estimate for the triplet energy in the polymer. The spectral and time-dependent data obtained through phosphorescence measurements yield richer information yet can be difficult to obtain as phosphorescence is spin-forbidden and thus extremely weak in organic compounds. In contrast to molecules, diffusion to dissociation sites and other bimolecular processes further reduce the efficiency of phosphorescence in polymers. Consequently, phosphorescence is reported for only a few organic conjugated polymers. Bässler and co-workers pioneered a gated time-resolved detection method to separate the weak phosphorescence signal from the strong fluorescence background.[14,15,18] However, the phosphorescence efficiency can be greatly enhanced when heavy atoms, which enhance the spin–orbit coupling, are included in the polymer chain and emission is therefore partially allowed owing to the mixing of the singlet and triplet wavefunctions. It then becomes possible to study a large number of polymers and to investigate the dependence of the triplet-state energy on the chemical structure.[16] It is also possible to place the heavy atom not in the main chain but next to the chain, such as through solvents or chemical residuals.[19,20]

The picture emerging from these measurements is that the triplet state appears to be systematically located about 0.7 ± 0.1 eV below the singlet state in all polymers investigated. This uniformity of the exchange energy is startling and contrasts with the situation encountered in molecules, where the singlet–triplet splitting can take either large values (e.g., 1.3 eV for polyacenes,[21] 1.75 eV for terthiophene[22]) or small values (0.3 eV for porphyrin and C_{60}).[7,23] In this paper we attempt to elucidate the origin of the constant exchange energy in conjugated polymers. We first shortly review the experimental findings obtained from phosphorescence measurements on organic and Pt-containing polymers and molecules. These results are then analyzed in the light of correlated quantum-chemical calculations performed on model systems.

2. Experimental Determination of the Exchange Energy

The dependence on chemical structure of the exchange energy has recently been measured for conjugated polymers including platinum in the main chain (Fig. 1).[16] The conjugation along the backbone is preserved as a result of mixing between the frontier molecular orbitals of the conjugated ligands and the platinum sites.[24] The optical gap in these polymers is tuned over a wide range (from 3.1 eV to 1.7 eV), which mostly reflects the different nature of the repeat units, such as a change of the heteromatic ring (spacer **1**, **2**, and **5**), an increase in the number of heteromatic rings (**5**, **9**, and **10**), donor–acceptor combinations in the spacer R (**6**, **8**), or the use of strong electron-accepting units (**7**, **11**–**15**). Figure 2 shows the evolution of

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(a)   Polymers:

Monomers:

Spacer R:

(b)   PPE

PPP

PPV
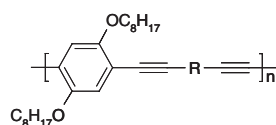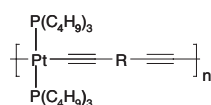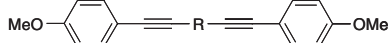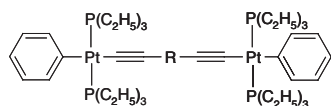
Figure 1. a) Chemical structures of the Pt-containing and organic phenylene ethynylenes investigated experimentally (R denotes the spacer unit). b) Chemical structures of the PPV, PPP, and PPE oligomers considered in the calculations.
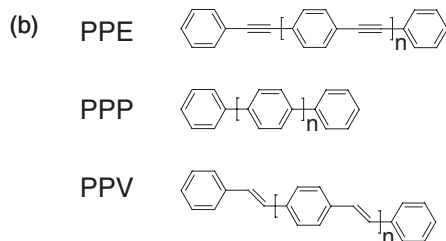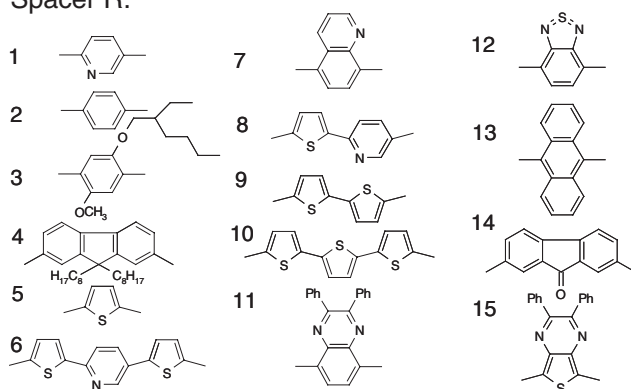
the excited-state energies and the S_1–T_1 gap in these materials as a function of the optical gap in the Pt-containing polymer; the emission energies in the monomers and polymers are collected in Table 1. By comparing monomer and polymer singlet excited-state energies, it is possible to disentangle the effects associated with the nature of the repeating units and interactions between them (delocalization). First, focusing on the S_1 monomer emission data, one can clearly see that compounds **11–15** display a much lower energy S_1 to S_0 optical transition than molecules **1–5**. Such a difference arises from the strong electron-withdrawing character of the R groups in the series **11–15**, which is expected to lead to a low-lying lowest unoccupied molecular orbital (LUMO) primarily localized on R (while the highest occupied molecular orbital (HOMO) should

be centered on the platinum site). Hence, the lowest optical transition, which has a strong metal-to-ligand charge-transfer character, occurs at lower energies in monomers **11–15** than in molecules **1–5** (while molecules **6–10** have an intermediate optical gap); see Figure 3.

Another intriguing observation from Figure 2 and Table 1 is the fact that a significant red shift in singlet emission energy occurs when going from monomer to polymer in compounds **1–5**, in contrast to molecules **11–15**. This indicates that there is significant communication between the monomer units in the former set of molecules, while there is hardly any for structures **11–15**. We attribute this to a large energy difference between the low-lying LUMO levels (and, to a lesser extent, the HOMO levels) of the individual ligand acceptor and Pt donor sites, as shown in Figure 3, which prevents efficient mixing of their wavefunctions and thus reduces delocalization between neighboring repeat units.

In contrast to the S_1 singlet state, the polymer and the corresponding monomer display very similar T_1 triplet energies through the whole series of chemical structures investigated. This reflects the strongly localized character of the triplet excited state, which in these Pt-containing compounds is expected to spread over no more than a single repeat unit.[24] It is worth stressing that

- in the polymer, the triplet-state energy follows the singlet-state energy and is about 0.7 eV below the S_1 state. This is striking since the nature of the spacers investigated varies greatly.
- the S_1–T_1 splitting for monomers **1–5** is larger than in the corresponding polymers while it is insensitive to chain length for spacers **11–15**. This effect arises from confinement of the singlet exciton on the monomers from the spacers **1–5**, which increases the singlet-state energy while the triplet-state energy remains almost unchanged.

These results, especially the constancy of the exchange energy in the polymers, are not unique to the Pt-containing model systems, but are more generally applicable. For purely organic analogues (see chemical structures in Fig. 1a with spacers **2–4**) or phenylene-based polymers such as poly-(p-phenylene) (PPP), poly[2,7-(9,9-bis(2-ethylhexyl)fluorene)] (PF2/6), poly (indenofluorene) (PIF), methyl-substituted ladder-type poly(p-phenylene) (MeLPPP),[14] and phenyl-substituted poly(p-phenylene vinylene) (PhPPV)[15] similar singlet–triplet energy splittings have indeed been found (Fig. 2b). These results are also consistent with the values estimated by Monkman et al. on the basis of energy-transfer measurements when taking the onset of absorption as the S_1 energies (except for compounds with a strong torsion angle, which will be discussed below).[17]
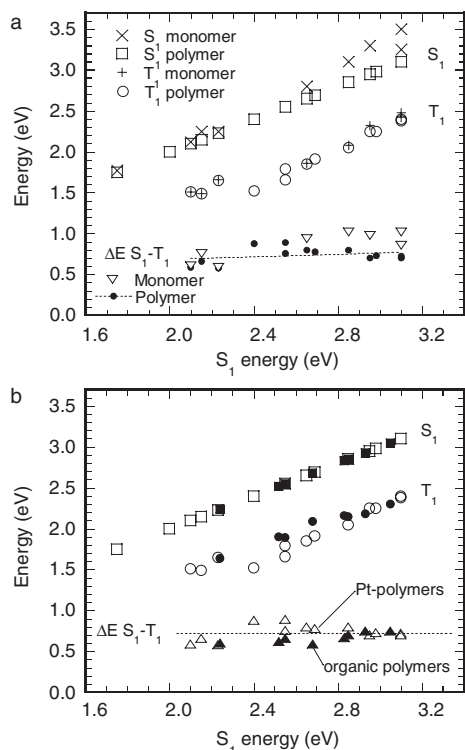
Figure 2. Transition energies from S_0 to the S_1 and T_1 excited states and S_1–T_1 energy gap as a function of S_1 energy for: a) the Pt-containing polymers and monomers given in Table 1; and b) the Pt-containing polymers (open symbols), the organic polymers given in Table 2 (closed symbols), and the phenylene-based polymers reported in references [14,15,25] (closed symbols).

Figure 3. Schematic one-electron energy diagram showing the relative positions of the HOMO and LUMO energy levels on the platinum donor site and on the conjugated ligand for a weakly electron-accepting R group (spacers **1–5**, solid line) and a strongly electron-accepting R group (spacers **11–15**, dotted line). The arrows represent metal-to-ligand charge transfer (MLCT)-like electronic excitations.

3. Theoretical Modeling of Singlet and Triplet Excitations

In order to gain insight into the influence of chemical structure and chain length on the S_1–T_1 energy gap, we have performed quantum-chemical calculations on the singlet and triplet excitations in oligomers of increasing size. We considered as model systems poly(*p*-phenylene vinylene) (PPV), PPP, and poly(*p*-phenylene ethynylene) (PPE), which have different singlet energies yet are based on a similar hydrocarbon backbone. The case of fully planar structures is first addressed to concen-
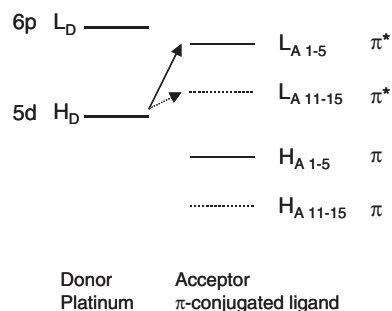
trate on the influence of chemical structure; the effects of torsion between repeat units are then explored focusing on PPP chains.

Figure 4a shows the evolution of the calculated vertical $S_0 \rightarrow S_1$ and $S_0 \rightarrow T_1$ excitation energies as a function of oligomer length for PPE, PPP, and PPV. There are two features to notice. Firstly, the energy of the S_1 states decreases faster with increasing oligomer length than the energy of the T_1 states, and consequently the S_1–T_1 energy gap reduces with oligomer length. The slower evolution with oligomer length of the T_1 state reflects its more localized character (in the sense of electron–hole separation, vide infra) due to the exchange term, which allows for a stronger confinement of the triplet exciton with respect to the singlet exciton.[32] Secondly and most importantly, the energies of S_1 and T_1 decrease almost identically when the chemical structure of the repeat unit is changed from PPE, through PPP, to PPV, and as a consequence the S_1–T_1 energy difference converges towards about the same value (~1 eV) in all polymers investigated. This finding is consistent with the experimental results of a S_1–T_1 energy gap that is largely material-independent for conjugated polymers, as shown in Figure 2.

The effect of altering the coupling between the repeat units has been studied, considering oligophenylenes as model systems; to this aim, the results obtained for a fully planar geometry and for a geometry where each of the phenyl rings is twisted by 40° with respect to its neighbor according to a helix config-

Table 1. Transition energies to the S_1 and T_1 excited states of Pt-containing polymers and monomers with the spacer units R as shown in Figure 1a. The energies are taken from the 0–0 peak of the emission [26–31].

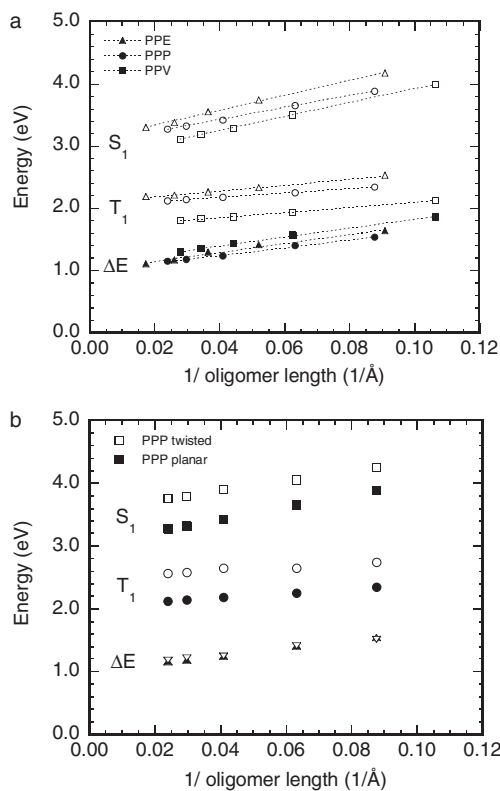| Spacer R =	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Polymer															
S_1 [eV]	3.10	3.10	2.95	2.98	2.85	2.69	2.65	2.55	2.55	2.40	2.23	2.15	2.10	2.00	1.75
T_1 [eV]	2.38	2.40	2.25	2.25	2.05	1.91	1.85	1.79	1.66	1.52	1.65	1.49	1.51	-	-
Monomer															
S_1 [eV]	3.25	3.50	3.30	-	3.10	-	2.80	-	-	-	2.25	2.25	2.12	-	1.77
T_1 [eV]	2.42	2.48	2.32	-	2.08	-	1.86	-	-	-	1.66	1.49	1.51	-	-

Figure 4. Transition energies from the singlet ground state to the lowest singlet (S_1) and triplet (T_1) excited states and S_1–T_1 energy gap as a function of oligomer length in: a) PPE, PPP, and PPV, and b) for PPP with a torsion angle of 40° (open symbols) or 0° (closed symbols) between neighboring phenyl rings. The dotted lines are a guide to the eye.

Table 2. Transition energies to the S_1 and T_1 excited states and their energy difference, ΔE_{ST}, of some organic polymers with the spacer units R as shown in Figure 1a and of the poly(p-phenylene)-based polymers reported in references [14,15,25]. The energies are taken from the 0–0 peak of the emission.

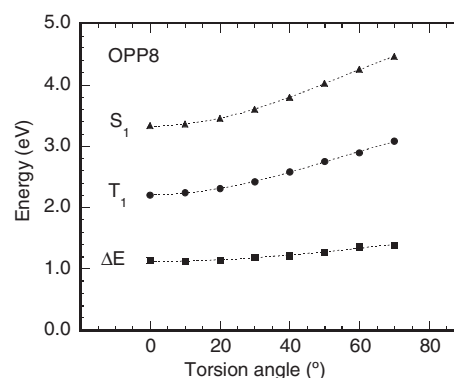| Polymer [14,15,43] or Spacer R	S_1 [eV]	T_1 [eV]	ΔE_{ST}
DDO-PPP	3.05	2.30	0.75
PF2/6	2.93	2.18	0.75
PIF	2.85	2.15	0.70
R = 4	2.83	2.16	0.67
MeLPPP	2.68	2.09	0.59
R = 2	2.55	1.89	0.66
R = 3	2.52	1.90	0.62
PhPPV	2.24	1.64	0.60

Figure 5. Transition energies to the S_1 and T_1 excited states and S_1–T_1 energy gap as a function of the torsion angle between neighboring phenyl rings for OPP8. The dotted lines are a guide to the eye.

uration are compared in Figure 4b. Again, we observe a stronger evolution with chain length of the S_1 excitation energies relative to the T_1 excitation energies, and, strikingly, S_1 and T_1 are destabilized in parallel when the coupling between neighboring units is reduced as a result of the large torsion angle. In fact, the exchange energy is exactly the same for the planar and the twisted oligomers. At first sight, this appears to be at odds with the measurements reported by Hertel et al. on a series of PPP-type polymers where stiffening bridges give varying degrees of planarity, and where the S_1–T_1 energy gap was found to decrease with the increasing planarity of the ground-state geometry (Table 2).[14]

We have therefore investigated in more detail the dependence of excited-state energies on the torsion angle between monomers in the eight-unit phenylene oligomer octylphenyl (OPP8), see Figure 5. We find that for increasing torsion angles, the energies of the S_1 and T_1 states both follow a cosine function, but with a larger amplitude and shorter period for the singlet than for the triplet excited state. Nevertheless, for angles up to 40°, that is to say the most common range of torsion angles, the S_1–T_1 energy difference, ΔE, increases only slightly by ~0.1 eV. A cosine dependence, as found here for the transition energies, was also reported from early electronic structure calculations[33] and is reminiscent of simple tight-binding models. In contrast to the long-range coulomb integrals, the ex-

change interactions, K, splitting S_1 from T_1 are short-range and are only significantly reduced when approaching orthogonal orientations of the repeat units, hence the increased S_1–T_1 energy difference for torsion angles close to 90°.

In the calculations for Figure 4b, we have deliberately used a fixed planar or twisted geometry for all phenylene oligomers. Yet from the series investigated by Hertel et al.,[14] only the fully planarized, stiff LPPP chains will have the same torsion angle for both S_1 and T_1. In the more flexible PPP polymer, the strongly confined triplet excited state is expected to force the geometry locally into a more quinoid and planar structure than in the more extended singlet excited state. AM1/CI (Austin Model 1/configuration interaction) geometry optimizations in the lowest singlet and triplet excited states of OPP8 indeed confirm this hypothesis. According to the calculations shown in Figure 5, the S_1–T_1 energy gap increases if T_1 adopts a smaller torsion angle between phenyl rings than S_1, and this is exactly what is found when considering the fully relaxed singlet and triplet excited-state geometries of OPP8: the S_1–T_1 energy separation is raised with respect to the planar conformations. These results also account for the trend observed experimentally in the PPP series when the backbone is made less rigid. This rotational degree of freedom may also be invoked to

explain the differences in ΔE_{ST} reported by Monkman et al. for polymers with the same backbone yet different sidechains, such as the thiophenes poly(3-octyl-4-methylthiophene) (PMOT) and poly(3-octylthiophene) (P3OT), the pyridinediyls poly(2,5-pyridinediyl) (PPY) and poly(3-hexyl-2,5-pyridinediyl) (HPPY), and the phenylene vinylenes poly[2-methoxy-5-(2-(ethylhexy-loxy)-*p*-phenylenevinylene] (MEH-PPV), poly(2′,5-octyloxy-phenylenevinylene) (DOOPPY), and poly(2,5-hexyloxyphenyl-enevinylene) (DHOPPV).[17] It further follows that the lowest possible S_1–T_1 splitting for a given polymer backbone will be obtained for the fully planarized structure.

The experimental results reported in the literature[14,16,17] and the calculations presented here clearly demonstrate that the exchange energy is sensitive to dissimilar torsion angles for S_1 and T_1 or to oligomer length. Yet the S_1–T_1 energy separation hardly depends on the detailed chemical structure of the polymers, as seen from Figures 2,4. It is important to remember that exchange is an interaction that scales with the electron–hole wavefunction overlap and hence decays exponentially with distance; as a consequence, it operates only at short range, i.e., a few angstroms. Therefore, the singlet–triplet splitting is only affected when the excitations are strongly confined (such as in small oligomers or at large torsion angles) but is constant with respect to variations in conjugation lengths beyond the range of exchange interactions.

The evolution with torsion angle or with oligomer size of the average electron–hole separation $\langle r_{eh} \rangle$ (as deduced from the singlet and triplet two-particle wavefunctions) fully confirms the picture described above. Figure 6 shows that:

- A significant reduction of the electron–hole distance occurs for large torsion angles ($> 40°$) and short oligomer length (< 25 Å—this corresponds to about 4 phenyl rings in PPE and PPV and 6 phenyl rings in PPP), consistent with the strong evolution of the singlet–triplet splitting in this range.
- The values for the electron–hole separation $\langle r_{eh} \rangle$ are almost the same for all planar phenylene-based materials investigated, hence the weak dependence of the exchange energy on chemical structure.
- $\langle r_{eh} \rangle$ is smaller in the triplet T_1 state than in the singlet S_1 state, consistent with the more localized character of the triplet excitation and the different chain-length dependence for the S_0–S_1 and S_0–T_1 excitation energies in Figure 4a. In fact, just as for the excitation energies in Figure 4a, $\langle r_{eh} \rangle$ is a linear function of the reciprocal of the oligomer length ($\langle r_{eh} \rangle = 3.17$ Å $- 8.77/$(oligomer length in angstroms) for S_1, and $\langle r_{eh} \rangle = 2.30$ Å $- 5.44/$(oligomer length in angstroms) for T_1). The absolute values we observe for the mean separation in the singlet state are in reasonable agreement with the calculated value of 4 Å reported by Rissler et al.,[34] and the experimental value of 7 Å reported by Harrison et al.[35]
- The absolute values for the different singlet excitation energies calculated and observed for the different polymers arise mainly from the different nature of the repeat units, and only to a lesser extent from the slightly different conjugation lengths across the series of materials investigated (as
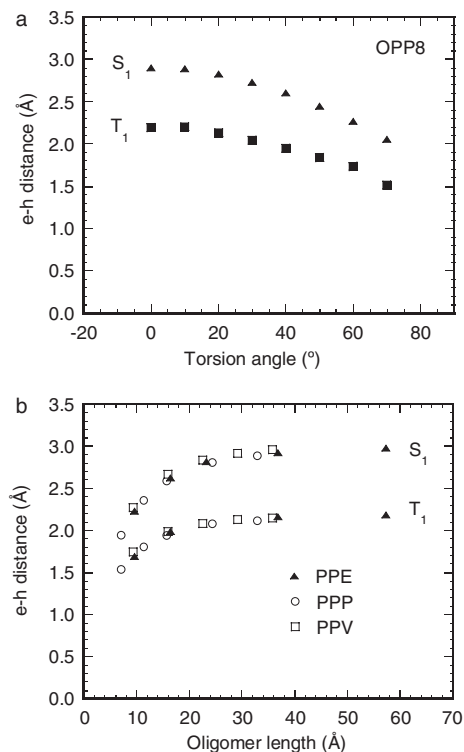

Figure 6. Average electron–hole distance calculated in the S_1 and T_1 excited states: a) as a function of the torsion angle between neighboring phenyl rings for OPP8; and b) as a function of chain length for planar PPE, PPP, and PPV oligomers.

indicated by the very small variations in $\langle r_{eh} \rangle$ in S_1). However, the stronger evolution of $\langle r_{eh} \rangle$ in S_1 than in T_1 with torsion angle or reciprocal oligomer length demonstrates that the more extended S_1 state is more susceptible to confinement than the more localized T_1 state, and consequently, the singlet energy is increased more by confinement than the triplet energy (as in compounds **1–5** in Fig. 2a, or Fig. 4a).

According to these results, the spatial overlap of the orbitals involved in the electronic transition needs to be decreased in order to further reduce the S_1–T_1 energy splitting. A small orbital overlap is also the cause of the small exchange energy in molecules with transitions from n to π* orbitals such as benzo-phenone.[19] It will remain interesting to see whether, in polymers with nitrogen or oxygen atoms in the main backbone (such as polymers based on carbazole, fluorenone, or phenyla-mines like TFB[36] and PFB[37]), the admixture of n-orbitals in the π-conjugated backbone will be strong enough to alter the orbital overlap and give a S_1–T_1 gap significantly smaller than 0.7 eV. Experimental data already available show that the inclusion of pyridine rings in the polymer backbone alone is not sufficient to achieve a smaller exchange energy (see polymers **1**, **6**, and **8** of Fig. 2 and Table 1; see also PPY in the literature[17]). A different approach to reduce the electron–hole wavefunction overlap could be to increase the mean distance between electron and hole by using well-spaced donor and ac-

ceptor sites on a polymer backbone. The polymers shown in Figure 2 include donor–acceptor compounds, yet the distance between the platinum donor and the acceptor R is largely constant.

4. Conclusions

Experimental results have shown the triplet T_1 state to be 0.7 ± 0.1 eV below the singlet S_1 state in a variety of rigid-rod conjugated polymers, while a larger energy gap is observed for analogous oligomers or very twisted polymers.

We attribute the S_1–T_1 splitting to the sensitivity of the exchange interactions on the overlap between electron and hole wavefunctions. We have considered the mean electron–hole separation as an approximate measure for the wavefunction overlap. This separation has a very comparable magnitude in the lowest triplet state of extended rigid-rod polymers, and we therefore believe this accounts for the constant S_1–T_1 energy separation. In contrast, in short oligomers (< 25 Å), confinement of electron and hole significantly enhances the short-range exchange interactions and destabilizes S_1 with respect to T_1. A similar, albeit weaker, confinement effect causes a dependence of the S_1–T_1 energy gap on different torsion angles in the relaxed geometries of the singlet and triplet excited states (with the triplet involving more pronounced and localized deviations from the ground-state values).

The smallest possible S_1–T_1 energy gap is therefore achieved for fully planar conformations. Chemical design of conjugated polymers with smaller exchange energies, desired namely as host materials for blue triplet emission from phosphorescent dyes in guest–host systems, relies on strategies for reducing the electron–hole wavefunction overlap. These include for instance localization of the occupied and unoccupied molecular orbitals on distinct spatial parts of the conjugated chains as in donor–acceptor copolymers or in heterocyclic structures with large contributions from n–π* excitations in the lowest singlet and triplet excited states.

Appendix: Theoretical Methodology

The ground-state geometries of all systems investigated have been optimized at the Hartree–Fock semiempirical AM1 level [38]. Except where otherwise noted, planarity was imposed on all structures in the simulations. This is a reasonable approximation in the case of PPV and PPE oligomers. Steric hindrance between hydrogen atoms leads to a twisted conformation for PPP oligomers in the gas phase; the torsion angle is, however, expected to be strongly reduced in the solid state due to packing effects. The fully planar conformations considered here are in fact more representative of ladder-type PPP chains. The influence of conformational relaxation on the energy of the lowest excited states has been explored in representative PPP oligomers. We have also explored geometric relaxation taking place in the excited states; in that case, the AM1 model was coupled to a configuration interaction formalism involving a limited number of molecular orbitals, as implemented in the AMPAC package [39].

These geometries were used as input for the calculation of vertical excitation energies, performed by combining the semiempirical intermediate neglect of differential overlap (INDO) [40] Hamiltonian to a

single configuration interaction (SCI) scheme. The Ohno–Klopman [41,42] potential, which best reproduces the position of triplet states, has been adopted to depict electron–electron interactions. For planar conformations, all π occupied and unoccupied molecular orbitals were included in the CI active space. In the case of twisted conformations, the active molecular orbitals were selected on the basis of their π character on the individual repeating units of the oligomers. The INDO/SCI calculations provide both singlet and triplet excitation energies on an equal footing. To characterize the spatial extent of the excited states, the two-particle hole–electron, $\psi(h_p, e_q)$, wavefunctions were also computed [43]:

$$\psi(h_p, e_q) = \sum_\alpha x_\alpha^{i \to j} C_{ip} C_{jq} \qquad (1)$$

where the summation runs over all electronic configurations involved in the excited-state wavefunction (the ground-state wavefunction corresponds to the Hartree–Fock determinant); $X_\alpha^{i \to j}$ is the CI expansion coefficient for the configuration α involving excitation from occupied molecular orbital (MO) i to unoccupied molecular j; C_{ip} is the linear combination of atomic orbitals (LCAO) coefficient for MO i on atomic site p.

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