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Singlet-Triplet Splitting of Geminate Electron-Hole Pairs in Conjugated Polymers

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The singlet-triplet splitting of geminate polaron pairs in a ladder-type conjugated polymer has been studied by the thermally stimulated luminescence technique. The energy gap separating the singlet and triplet states of the geminate pairs is measured to be in the range of 3–6 meV, depending on the polymer morphology. The results of correlated quantum-chemical calculations on a long ladder-type oligomer are fully consistent with the observed values of the geminate polaron pair singlet-triplet gap. Such low splitting values have important implications for the spin-dependent exciton formation in conjugated polymers.

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Organic electroluminescence has generated much interest in the past 15 years especially in view of device applications where organic molecular or polymeric materials constitute the active elements [1–3]. In π-conjugated organic molecules, the energy splitting between the lowest singlet (S_1) and triplet (T_1) states is large, typically ≥ 1 eV; this is a signature of strong exchange interaction and confinement of the excited electron-hole pair. In π-conjugated polymers, such as polyphenylenes, polyfluorenes, or polyphenylenevinylenes, the observed singlet-triplet (S_1–T_1) energy splitting is large as well, $\sim$0.7 eV [4–7]; there is also direct spectroscopic evidence that, in these materials, the elementary optical excitations are strongly confined excitons with electron-hole separations on the order of 0.5–1 nm [8,9]. We note that this value is comparable to the interchain separation and, thus, to the size of interchain polaron-pair (charge-transfer) excitations; these correspond to Coulombically bound electron-hole pairs occupying adjacent chains and play a key role in electroluminescence since they are the direct precursors of the lowest (neutral) singlet and triplet excitons.

In an organic light-emitting diode (LED), electroluminescence is generated by the recombination of electrons and holes injected from the electrodes; the overall recombination rate is controlled by the carrier concentration and the mutual Coulombic capture radius, as described by the Langevin theory of recombination. The recombination process in conjugated polymers is generally considered to involve two steps [10]: first, the formation of intermediate charge-transfer (CT) polaron pairs in either singlet or triplet state and, second, the decay of these CT states down to the lowest neutral exciton states. Thus, two factors are critical: (i) the singlet/triplet ratio of the intermediate CT polaron pairs, f_{ST}, which could evolve with time and (ii) the spin-dependent rate constants, k_S and k_T, for decay from the intermediate polaron pairs and formation of the lowest neutral singlet or triplet excitons. Although the issue remains somewhat controversial [11], a number of recent experimental [12–15] and theoretical studies [16–20] point to the existence of a chain-length dependence of the neutral exciton formation rates.

When k_S and k_T are both very fast, which quantum-chemical calculations indicate is the case in short conjugated chains at room temperature [20], the fraction S/T of singlet-to-triplet neutral excitons generated at the end of the recombination process essentially depends on f_{ST}; if conventional spin statistics applies, i.e., $f_{ST} = 1/3$ [21], only 25% of all recombination events lead to potentially emissive singlet states; however, f_{ST} could deviate from the 1:3 ratio in favor of triplets if the energy splitting between the singlet and triplet states of the CT polaron pairs, Δ, is $>kT$. In long conjugated chains, the same quantum-chemical calculations show that k_S remains very fast while k_T slows down markedly [20]. In that case, triplet polaron pairs during their (long) lifetime can possibly dissociate or intersystem cross and lead to new singlet polaron pairs; the latter can then quickly decay to the lowest neutral singlet exciton, thereby biasing spin statistics [20]. For this to occur, however, Δ must be $\leq kT$.

To the best of our knowledge, the critical piece of information that Δ represents is not available to date.

The existence of intermediate singlet ($PP^{(S)}$) and triplet ($PP^{(T)}$) geminate polaron (charge carrier) pairs was initially suggested to explain the effect of magnetic field on photoconductivity and photoluminescence [22,23] in conjugated polymers, although no quantitative estimate for the $PP^{(S)}/PP^{(T)}$ splitting was obtained. In this Letter, we present pertinent experimental data for a protypical conjugated polymer, ladder-type polyparaphenylene (MeLPPP), derived from thermally stimulated luminescence (TSL) studies combined with correlated quantum-chemical calculations. Our focus here is on the recently synthesized nanostructured MeLPPP films; in addition, in order to evaluate the impact of two different morphologies, we have also analyzed the $PP^{(S)}$-$PP^{(T)}$ splitting in mesoscopically homogeneous MeLPPP.

In order to prepare nanostructured MeLPPP, a chloroform solution of a MeLPPP polymer was miniemulsified in water by using sodium dodecylsulfate as the surfactant. After evaporation of chloroform, a stable aqueous dispersion of polymer nanoparticles with a typical size of about 150 nm was obtained. The details of synthesis of the aqueous polymer dispersions were described elsewhere [24]. Films of MeLPPP nanoparticles (nano-MeLPPP) were formed by casting the aqueous solution onto a quartz substrate and dried for several hours. TSL measurements of nano-MeLPPP films were carried over a temperature range from 4.2 to 350 K using an optical temperature regulating helium cryostat. The films were photoexcited by light from a high-pressure 500 W mercury lamp at 4.2 K. Upon switching off the excitation, the thermoluminescence was detected as a function of temperature with a cooled photomultiplier, which was immediately adjacent to a cryostat window and operated in photon-counting mode. Because of the weakness of the TSL signals, two glass cutoff filters were used to separate the singlet (fluorescence) and triplet (phosphorescence) components of the TSL emission. The experimental details were described elsewhere [25,26]. The afterglow decay kinetics were measured at long delay times ranging from 1 to ~10^3 s after switching off the excitation with the same TSL setup, but at a constant temperature of 4.2 K. The TSL data collected earlier for mesoscopically homogeneous films of MeLPPP [25] were also reanalyzed in the present context of $PP^{(S)}$-$PP^{(T)}$ splitting (we note that the spectra for delayed fluorescence and phosphorescence measured in mesoscopically homogeneous MeLPPP films at 4.2 K were included in Ref. [25]; the same spectra were also measured in nanostructured MeLPPP under the same conditions and are found to be nearly identical; they are therefore not reproduced here).

No delayed fluorescence is detected in the isothermal afterglow emission. Although the lifetime of triplet excitations is around 1 s in MeLPPP [5], a phosphorescence afterglow decaying in hyperbolic fashion can be detected up to 10^3 s; this indicates that at helium temperature optical excitations are generated via rather slow geminate recombinations of charge carriers, which eventually populate only the triplet states. Upon raising the temperature, the TSL emission can be detected through both filters, implying that the TSL spectrum contains both fluorescence and phosphorescence components and, therefore, that some thermal activation is required for the generation of singlets. Thermally stimulated fluorescence (TSF) and phosphorescence (TSPh) curves of nano-MeLPPP are plotted in Fig. 1 where they are also compared to the curves obtained for mesoscopically homogeneous MeLPPP. The fluorescence and phosphorescence glow curves have similar shapes, yet the TSF curves are shifted to higher temperatures with respect to the TSPh curves.

The data presented in Fig. 1 point out that a barrier exists for the formation of singlet excitations from geminate

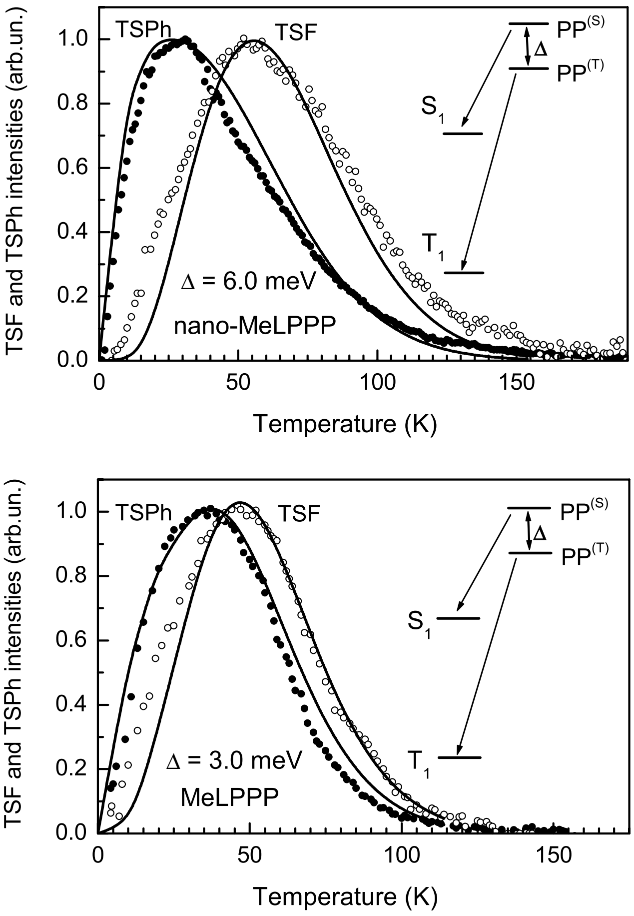

FIG. 1. Temperature dependences of the TSF and TSPh in (top) nano-MeLPPP and (bottom) mesoscopically homogeneous MeLPPP. The solid lines show the fit of the data by the hopping model of TSL [25,27]; the following set of parameters has been used in order to fit the data on both MeLPPP polymers: Gaussian DOS width $\sigma = 55$ meV, total density of hopping sites $N = 0.8 \times 10^{21}$ cm^{-3}, attempt-to-jump frequency $\nu = 10^{12}$ s^{-1}, and dielectric permittivity $\epsilon = 3$.

pairs while no additional activation is required for the triplet formation. These data also indicate that the additional barrier depends upon the morphology and/or molecular packing of the polymer. We argue that this barrier originates from the $PP^{(S)}$-$PP^{(T)}$ splitting in short-range geminate polaron pairs that are precursors for neutral singlet and triplet excitons. The crucial parameter of the model is then the exchange energy of an interchain geminate polaron pair. The data shown in Fig. 1 have been fitted in the framework of the hopping model of TSL [25,27] assuming the occurrence of an energy gap Δ between $PP^{(S)}$ and $PP^{(T)}$. The fits, illustrated by solid lines in Fig. 1, yield $\Delta = 6.0$ meV (48 cm^{-1}) for nano-MeLPPP; a Δ value of 3.0 meV (24 cm^{-1}) is obtained for mesoscopically homogeneous MeLPPP. Thus, this comparison indicates a larger $PP^{(S)}$-$PP^{(T)}$ gap in more densely packed nanostructured MeLPPP.

In order to back up these experimental findings, the electronic excitations in a model system consisting of two piled up seven-ring ladder-type phenylene oligomers have been modeled by means of correlated quantum-chemical calculations at the INDO-SCI (intermediate neglect of differential overlap–single configuration interaction) and INDO-CCSD (coupled cluster singles and doubles) levels [28]. Molecular mechanics calculations based on the universal force field [29] indicate that a face-to-face arrangement (where the chains are rotated by 180° around their longitudinal axes to reduce steric repulsion among alkyl side chains and maximize π-π interactions) is a favorable stacking configuration. The center-to-center interchain separation (d), while sensitive to the actual nature of the side chains, takes values in the range 3.5–5 Å [30]. Hence, we have explored the nature and energy of the singlet and triplet excited states in cofacial dimers for values of d spanning such a range.

Interchain versus intrachain singlet or triplet excitations can be unambiguously distinguished at the SCI level from the computed electron-hole wave functions; see Fig. 2. The lowest excited states, both in the singlet and triplet manifold, have a dominant *intrachain* character with dominant diagonal contributions as illustrated in Fig. 2(a); *interchain* excitations, dominated by off-diagonal shadings as shown in Fig. 2(b), occur at higher energy and are split by intermolecular exchange interactions. Figure 3 shows the evolution with interchain separation of the $PP^{(S)}$-$PP^{(T)}$ energy difference Δ as obtained from SCI and CCSD calculations. In both cases, a significant increase in Δ with decreasing intermolecular distances, especially pronounced for $d < \sim 4.1$ Å, is observed, which arises from the enhanced overlap of electron-hole wave functions. Since exchange interactions decay exponentially with distance the $PP^{(S)}$-$PP^{(T)}$ gap is negligible at longer distances.

The CCSD calculations yield larger Δ values than the SCI approach, a feature attributed to a more pronounced admixture of intrachain excitations to the interchain CCSD wave functions, which results from a better account of polarization effects when double excitations are included [31]. As d decreases, the energy difference between intrachain and interchain electronic excitations is reduced, giving rise to a more pronounced mixing of the corresponding wave functions especially at the CCSD level. This is corroborated by the relative increase with decreasing d of the long-axis polarized transition moment to the interchain species (intensity borrowing from the intrachain excitations). For d values between 3.8 and 4.8 Å, i.e., within a realistic range for ladder-type polymers, Δ is in the range $20 - 150$ cm^{-1} ($20 - 80$ cm^{-1}) at the CCSD (SCI) level, which compares favorably to the experimental values reported above ($24 - 48$ cm^{-1}). Thus, the larger exchange energy measured in nano-MeLPPP likely reflects an improved degree of intermolecular order.

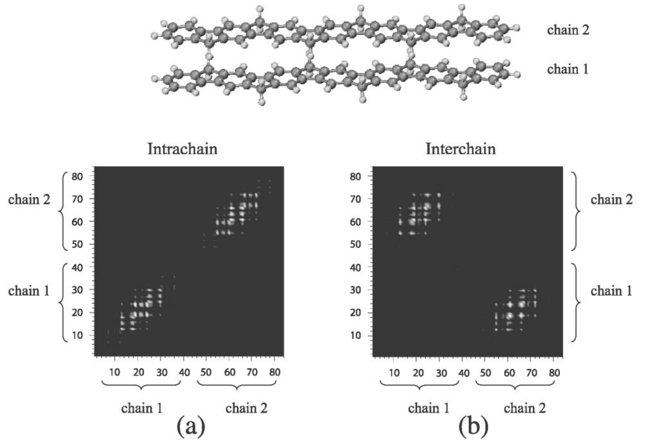

FIG. 2. Electron-hole SCI wave functions of the lowest intrachain (a) and interchain (b) excitation in a model seven-ring cofacial dimer (structure shown on top).

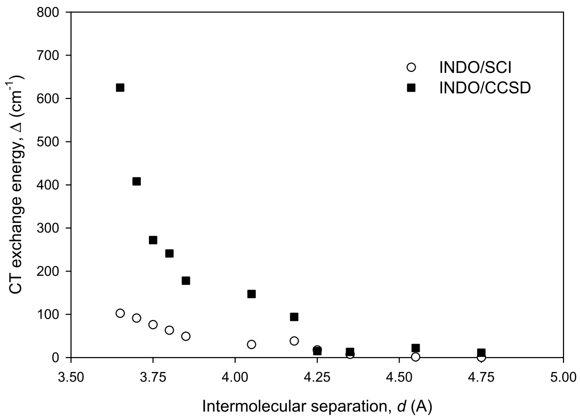

FIG. 3. Evolution with intermolecular separation, d, of the interchain electron-hole pair exchange energy, Δ, as obtained in a model seven-ring cofacial dimer at the INDO-SCI and INDO-CCSD levels.

The results of the quantum-chemical calculations are fully consistent with the experimental data and indicate that the exchange energy in polaron pairs is smaller than kT at room temperature ($\sim$200 cm^{-1}). This implies that in electronic devices at room temperature the initial ratio f_{ST} of polaron pairs in the singlet and triplet states follows spin statistics. We note, however, that at helium temperature a Δ gap of only a few meVs is sufficient to facilitate singlet-to-triplet transitions within polaron pairs; this explains the predominant phosphorescence contribution to the afterglow emission at 4.2 K seen in our measurements.

The results of the present study also indicate that the singlet-triplet branching can be strongly impacted by sample morphology. Since the exchange interaction exponentially increases with decreasing distance, one should expect a larger $PP^{(S)}$-$PP^{(T)}$ Δ gap in more densely packed materials. Even though such materials are expected to have higher values of carrier mobility, which is desirable for device applications, the increase in Δ could negatively influence the production of singlet excitons. This suggests that a compromise has to be found between charge carrier mobility and fraction of singlet excitons to achieve optimal polymer LED performance.

In conclusion, we have reported the first quantitative data on the energy splitting Δ separating the singlet and triplet states of the interchain polaron pairs, which are the precursors of the electroluminescent species in conjugated polymers. This splitting is both measured and calculated to be very small, lower than kT, and to depend on the polymer morphology. Our results support the following recombination scenario: when the triplet $PP^{(T)}$ to T_1 formation rate is slow, which appears to be the case in (long) polymer chains, the triplet polaron pairs at room temperature have the possibility to intersystem cross (or to dissociate) to the singlet $PP^{(S)}$ state; since the $PP^{(S)}$ to S_1 formation rate is fast, these pairs quickly decay to S_1. The occurrence of such processes can bias the spin statistics in favor of singlet neutral excitons, as has been measured in several conjugated polymers.

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