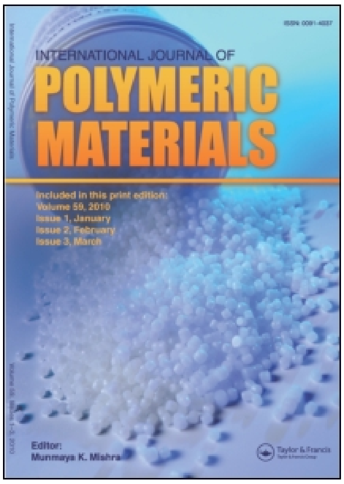

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Electroluminescence in Semiconducting Conjugated Polymers and Oligomers: A Quantum-chemical Perspective

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We discuss in this contribution the ability of quantum-chemical calculations to describe the essential aspects of one of the most promising applications of semiconducting conjugated polymers and oligomers, *i.e.*, their use as active layers in light-emitting diodes (LEDs). We present an overview of the results of recent theoretical studies that we have performed on oligomers representative of polyparaphenylenevinylene and polythiophene. We mostly deal with: (i) the modelling of the linear optical properties of the conjugated polymers involved in the emitting layer, taking into account the vibronic structure; (ii) the investigation of the relative locations of, and relaxation phenomena taking place in, the lowest singlet and triplet excited states; and (iii) a general discussion of the various terms contributing to the polaron-exciton binding energy.

Keywords: Electroluminescence; conjugated polymers; semiconductors; polyparaphenylenevinylene; polythiophene; quantum-chemical calculations

1. INTRODUCTION

In the search for new routes towards significant improvements in the performances of polymer- or oligomer-based LEDs [1 – 3], one important task is to provide a good understanding of the intrinsic geometric, electronic, and optical properties of the conjugated polymers that are involved in the devices. To do so, extensive theoretical and

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experimental investigations have addressed the properties of the corresponding conjugated oligomers. One main advantage of oligomer analogs over the parent polymers is that their well-defined chemical structure together with their improved solubility and processibility give access to detailed interpretations of the experimental measurements; moreover, they are particularly convenient when sophisticated theoretical modellings are to be performed. Quantum-chemistry calculations carried out on model molecules thus present a two-fold interest since they allow for a direct comparison with experimental data available for the conjugated oligomers and for an accurate description of the intrinsic properties of the polymers following extrapolation of the oligomer results to the scale of long chains. In this contribution, we illustrate that such calculations can prove useful in the context of light-emitting diodes by providing a deep insight into the basic phenomena taking place in the devices. We have chosen to focus our attention on oligophenylenevinylenes (hereafter denoted PPV*n*, where *n* represents the number of phenylene rings) and oligothiophenes (PT*n*), as well as on their derivatives.

We first show that the simulated absorption spectra of PPV oligomers compare very well with experimental data and allow us to describe the nature of the four absorption features observed in the spectrum of the corresponding polymer. We also pay particular attention to the evolution with chain length of the lowest energy feature corresponding to the $1B_u$ excited state, from which singlet polaron-excitons radiatively decay to give rise to luminescence; on the basis of well-resolved optical absorption spectra of PPV oligomers, we have set up a theoretical strategy to model the vibronic couplings and provide, on the basis of the fitting procedure, direct estimates of the extent of relaxation occurring in the $1B_u$ state. Then, dealing both with PPV and PT oligomers, we investigate the evolution with chain length of the relative locations of the lowest singlet excited state (S_1) and lowest triplet excited state (T_1); the latter plays an important role in the context of LEDs since this state can be reached both by intersystem crossing processes or by triplet recombination of the electron-hole pairs. We also discuss in the case of oligothiophenes the way the singlet-to-triplet intersystem crossing is affected by chain length; such an analysis provides valuable information for the design of new molecular architectures, for which such nonradiative decay routes, competing with light emission, could be avoided. The following part is related to a theoretical characterization of the geometry relaxation phenomena occurring in both the S_1 and T_1 states of PPV oligomers; our motivation is to gain a refined picture of the singlet and triplet polaron-excitons, responsible of the fluorescence and phosphorescence processes, respectively. We finally discuss the various terms that contribute to the polaron-exciton binding energy in electroluminescent conjugated polymers.

2. OPTICAL ABSORPTION SPECTRA OF PPV OLIGOMERS

We present in Figure 1 the simulated absorption spectrum of the five-ring PPV oligomer, calculated at the INDO/SCI level, together with the experimental spectrum of the polymer [4].

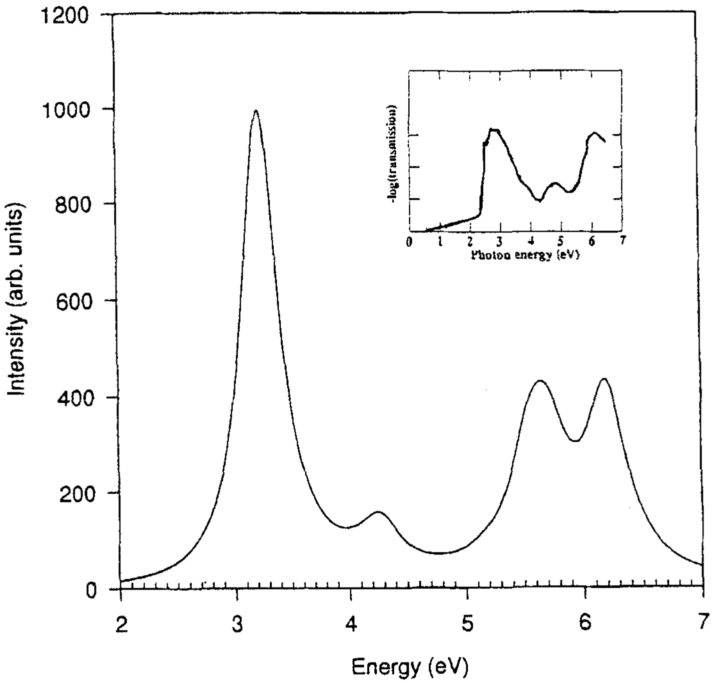

FIGURE 1 INDO/SCI-simulated optical absorption spectrum of the five-ring PPV oligomer. We show in the insert the experimental spectrum of the polymer.

In the polymer, three distinct absorption features appear around 3.0, 4.8 and 6.1 eV as well as a weak shoulder at 3.7 eV. Similarly, we observe that four absorption bands dominate the spectrum of the oligomer. It is therefore straightforward to establish a one-to-one correspondence between the two spectra in order to uncover the nature of the absorption peaks in the polymer; furthermore, we aim at distinguishing the roles of the delocalized and localized molecular orbitals (the latter are characterized by the existence of very weak LCAO coefficients on the para-carbon atoms of the phenylene rings and the carbons of the vinylene moieties).

Analysis of the CI expansion coefficients indicates that the lowest energy feature primarily originates from an electron transition between the HOMO and LUMO levels. The second peak results from the mixing of several configurations, each of them involving exclusively delocalized levels. The third band is depicted by $l \rightarrow d^*$ and $d \rightarrow l^*$ transitions (l and d denoting localized and delocalized levels, respectively) which are characterized by similar weight due to the existence of a quasi electron-hole symmetry in such systems. Finally, the highest absorption peak is described by the interaction of configurations associated to transitions between localized levels (within the phenylene rings). The discrepancy in the relative intensities of the absorption peaks as well as the existence of shifts in the transition energies when comparing the two spectra have to be mainly attributed to finite-size effects that are inherent to our calculations. However, we stress that the theoretical evolution with chain length (going from 3 to 5 phenylene rings) of the simulated spectra follows remarkably well the available experimental measurements [4] and is fully in agreement with the results of the model calculations of Rice and Gartstein [5].

We now focus our attention on the lowest energy singlet excited state (S_1) from which radiative decay takes place in light-emitting diodes. We display in Figure 2 well-resolved optical absorption spectra of phenylenevinylene oligomers containing from 2 to 5 rings together with the INDO/SCI simulated spectra for which we fit the amplitude of both the damping factor (that defines the bandwidths of the abosrption features) and the Huang-Rhys factor (that governs the relative intensities within the vibronic progression). From the comparison between theory and experiment, we can highlight the following aspects:

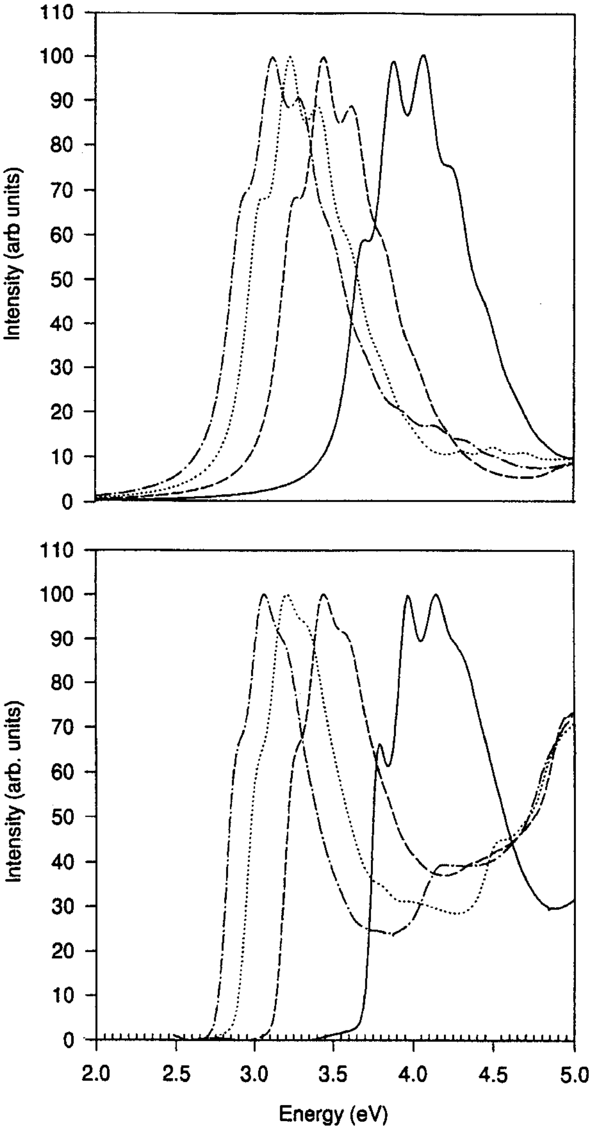

FIGURE 2 Experimental (lower part) and INDO/SCI-simulated (upper part) absorption spectra of the two- (solid line), three- (dashed line), four- (dotted line) and five-ring (dash-dotted line) PPV oligomers.

- The similarity in shape of the measured and simulated spectra validates the theoretical approach we have adopted.
- As for most conjugated oligomers [6, 7], both the experimental and theoretical data show a linear relationship between the 0–0 transition energy and chain length.
- The fitted values obtained for the Huang-Rhys factor are found to diminish as the chain grows (going from 1.95 for stilbene to 1.60 for the longer chains). This evolution is consistent with the experimental absorption spectrum of improved PPV showing a dominant intensity for the 0–0 transition [7]; such a behavior actually illustrates a progressive softening of the relaxation process occurring upon photoexcitation of electron-hole pairs.
- Direct estimates of the strength of relaxation in the $1B_u$ state can actually be obtained by expanding the relaxation energy into a sum of two contributions corresponding to the energy of an effective mode weighted by the Huang-Rhys factor related to this mode; this leads to a value on the order of 0.39 eV for stilbene and 0.34 eV for the other oligomers.

3. RELATIVE LOCATIONS OF THE S_1 AND T_1 STATES-INTERSYSTEM CROSSING PROCESS

We display in Figure 3 the evolution with chain length in oligothiophenes of the $S_0 \rightarrow S_1$ transition energy as well as the $S_0 \rightarrow T_1$ energy difference, as calculated at the INDO/MRD-CI level. Strikingly, we observe the $S_0 \rightarrow T_1$ energy difference to hardly evolve with chain length while there occurs a significant red shift of the lowest one-photon allowed excitation (shifts on the order of 0.2 eV and 1.4 eV, respectively, when going from the dimer to the hexamer). The weak evolution of the lowest triplet excitation energy actually reflects the strong confinement of the triplet exciton; this is further supported by Optically-Detected Magnetic Resonance (ODMR) measurements on polythiophene indicating that only a single thiophene unit is needed for a proper accommodation of the triplet defect [8].

The calculated $S_0 \rightarrow T_1$ energy differences compare well with available experimental data. Indeed, a weak and broad peak

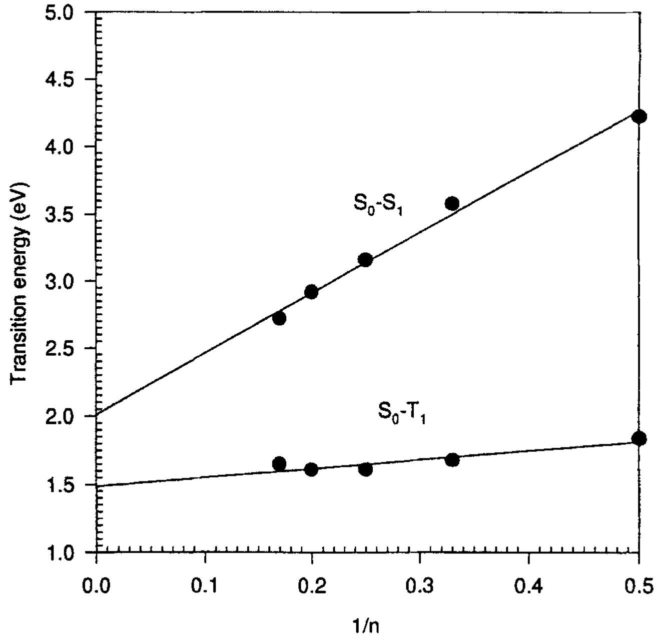

FIGURE 3 Evolution with the inverse number of thiophene units (1/*n*) of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow T_1$ excitation energies, as calculated at the INDO/MRD-CI level.

associated to this transition has been observed in the absorption spectrum of PT3 due to spin-orbit coupling induced by the existence of heavy atoms in the solvent; the experimental value reported at ~1.71 eV [9] is in excellent agreement with the 1.68 eV calculated result. Further experiments dealing with charge transfer between C_{60} and oligothiophenes ranging in size from 6 to 11 units have located the position of the T_1 state in these oligomers between 1.57 and 1.71 eV [10], *i.e.*, within an energy range similar to that obtained with the MRD-CI calculations. Finally, we mention that a phosphorescence signal has been detected around 1.5 eV in polythiophene [11]; the same value is obtained by extrapolating the theoretical data at the scale of an infinite polymer chain.

Fully similar conclusions can be drawn from the evolution with chain length of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow T_1$ excitations in oligo(phenylenevinylene)s [12]. Here also, the strong confinement of the triplet exciton is confirmed by ODMR data [8].

Recent time-resolved fluorescence measurements have shown a sharp increase in the fluorescence quantum-yield f_F of unsubstituted oligothiophenes when going from 2 to 7 units [13–15]. Such an evolution has been closely related to a decrease in the nonradiative decay rate k_{NR} since almost no change is observed for the radiative decay rate k_R. Furthermore, the main nonradiative process was found to originate from singlet-to-triplet intersystem crossing [14]. We have therefore tried to rationalize the evolution with chain size of the nonradiative decay rate in oligothiophenes. Note that our analysis was done under the reasonable assumption that the changes in k_{NR} are mainly driven by the energy difference between the singlet and triplet states involved in the crossing.

Although the S_1-T_1 energy differences are much too large to give rise to efficient crossing, our calculations indicate that a higher-lying triplet excited state, the T_4 state, is located within the same energy range as S_1, and is thus in all likelihood the essential triplet state to consider to better comprehend the intersystem crossing processes. Starting from bithiophene where the position of T_4 is below that of S_1, there occurs a progressive reversal in the ordering of these two states as the chain grows. The crossing between the two states takes place at a chain length corresponding to the trimer, as sketched in Figure 4 (where we observe the position of the T_4 state in the trimer to be largely overestimated due to the lack of account of spin-orbit interactions). The experimental trends can therefore be understood on the basis of these considerations. Indeed, the location of T_4 below S_1 in bithiophene makes the intersystem crossing a nonactivated and very efficient process that strongly inhibits the fluorescence. In contrast, f_F is expected to be substantially raised as the chain elongates due to the appearance of an increasing activation energy.

4. GEOMETRY RELAXATION PHENOMENA IN THE S_1 AND T_1 STATES OF OLIGOPHENYLENE VINYLENES

Analysis of the AM1/CI (semiempirical Hartree-Fock Austin Model 1 method coupled to configuration interaction scheme)–optimized

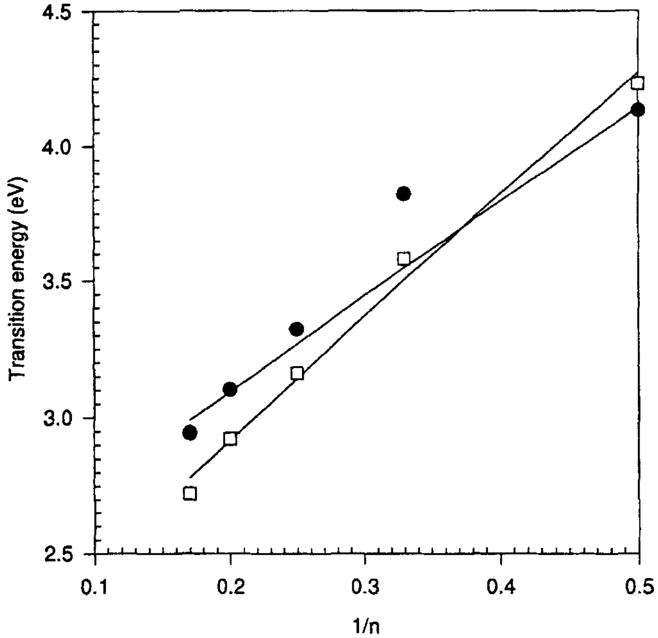

FIGURE 4 Evolution of the INDO/MRD-CI-calculated $S_0 \rightarrow S_1$ (open squares) and $S_0 \rightarrow T_4$ (full circles) transition energies as a function of the inverse number of thiophene rings.

geometry of the lowest singlet excited state in stilbene shows relatively weak deformations with respect to the ground state. The C — C bond-lengths in the phenylene rings are found to be almost unaffected (changes on the order of 0.01 Å) while a more significant change in the bond-length alternation takes place in the vinylene moieties (going from 0.11 Å in S_0 to 0.02 Å in S_1); these trends are in excellent agreement with the results of earlier Pariser–Parr–Pople calculations [16]. In contrast, a much more pronounced geometry relaxation occurs for the triplet polaron-exciton; indeed, the phenylene rings adopt a semiquinoid character while the single-double C — C bond pattern is reversed within the vinylene linkages. As a result, the relaxation energy associated to the triplet is calculated to be about twice as big as for the singlet (0.60 and 0.28 eV, respectively).

As the chain elongates, in the S_1 state, only the central portion of the molecule is affected by the relaxation process while the geometry of the external units is unchanged with respect to the ground state; the weak deformations extend over a spatial domain corresponding typically to three or four aromatic rings, *i.e.*, some 25–30 Å. As a result, a weak and similar relaxation energy on the order of 0.23 eV is calculated for the three- and four-ring oligomers. Note that these trends are consistent with the estimates provided on the basis of the fitting procedure of the experimental absorption spectra (on the order of 0.34 eV); the slight discrepancy between the two sets of values can be partly attributed to the fact that the experimental data do not originate from fully planar ground-state conformations, as assumed in the calculations.

The triplet exciton in the longer oligomers is characterized by local and strong deformations; the defect is calculated to extend over a single phenylene ring, in agreement with ODMR measurements [8]. Similar trends prevail for the oligothiophenes; however, the lattice distorsions that are calculated in the triplet state of the PPV oligomers are stronger, especially when considering the vinylene linkages.

5. ON THE NATURE OF THE EXCITON BINDING ENERGY

We now turn to a discussion of the issue related to the nature of the emitting species in the lowest excited state of luminescent conjugated polymers, with the help of theoretical calculations including both electron–phonon and electron–electron interactions. Specifically, we address the following propositions that have been reported in the literature: (i) free charge carriers are generated in the excited state [17] and emission is an interband process; (ii) emission originates from a tightly bound electron-hole pair with a binding energy larger than 1 eV [18]; (iii) emission is from the radiative decay of weakly bound polaron-exciton with a binding energy of a few tenths of an eV [19–21]. Note that the polaron-exciton terminology implies that lattice relaxations are associated to the photogenerated electron-hole pair.

In our opinion, any Hamiltonian used to characterize the nature of the photogenerated species has to incorporate electron–phonon contributions since these correspond to a basic feature of π-conjugated compounds. As mentioned above, a typical manifestation of lattice relaxations taking place in the excited states is the appearance of vibronic progressions in the experimental optical absorption spectra. It is worth stressing that the lowest energy transition (*i.e.*, the 0–0 transition) is to the relaxed geometry of the excited state.

In the framework of models considering rigid and fully delocalized bands, the excited-state relaxations (and thus the vibronic effects) are expected to decrease linearly with the inverse number of atoms in the chain; hence, they would be thought to be insignificant at the scale of long conjugated chains. However, the existence of a vibronic progression in the absorption spectra of conjugated macromolecules indicates that self-localization phenomena occur in the excited states.

On the other hand, given the ease of delocalization and polarization of π electrons, electron correlation is another major ingredient to be incorporated in a theoretical modelization. We have thus to consider the influence on the binding of photogenerated electron-hole pairs, that is due to electron–lattice coupling and to electron–electron interactions [22].

We have described above that an analysis of the *absorption spectra* of PPV oligomers indicates that the relaxation energy in the $1B_u$ excited state is on the order of 0.30 eV for the 3, 4 and 5-ring oligomers; it thus hardly evolves with increasing chain length. In contrast, we have established on the basis of experimental *photoluminescence spectra* reported for the same oligomers [23] that, in the case of emission, the total Huang-Rhys factor of the $1B_u$ excited state decreases as the chain grows; the evolution is linear as a function of inverse chain length, tending to 0.2 eV at the limit of long chains. These contradictory results for absorption and emission suggest that the absorption process is actually affected by conformational disorder; the latter is strongly reduced in the emission spectra due to migration of the polaron-excitons towards the most ordered conjugated segments. We emphasize that the relaxation energy estimates provided by the analysis of the photoluminescence spectra are in excellent agreement with direct geometry optimizations of the $1B_u$ excited state performed on the 2, 3, and 4-ring oligomers [24] within the AM1/CI formalism.

We now refer to recent experimental measurements carried out on luminescent conjugated polymers that have dealt with estimating of the polaron-exciton binding energy. Note that the binding energy is defined as the difference between the creation energy of two noninteracting polarons of opposite charge and the formation energy of a neutral polaron-exciton [22].

Internal photoemission experiments have been performed on polymers in a LED architecture; the measurements give access to the energy difference between the electron and hole injections and thus the energy gap for creation of two polarons of opposite charge; the data provide a value of 2.45 eV in the case of poly(2-methoxy-5-(2′-ethyl-hexyloxy) paraphenylene vinylene), MEH-PPV, taking into account image charge effects and extrapolating to zero photon energy [25]. Since the 0−0 transition of the polymer peaks at 2.25 eV [26], the binding of the electron-hole pair is estimated to be 0.2 eV (±0.1 eV). Similar experiments using internal field emission report binding energies of 0.2 ± 0.2 eV in the case of MEH-PPV and poly-2-decyloxy-paraphenylene, DO-PPP [26]. The recent fabrication of light electrochemical cells (LECs) has also enabled independent measurements of the energy gap to be done [27]; the emission process in such devices is indeed expected to occur for an applied voltage equal to the energy gap. The results collected for various luminescent polymers indicate that the turn-on voltage is always approximately identical to the measured optical gap; the LEC data can thus be consistent with the semiconductor model in which the exciton binding energy is at most a few times k_BT at room temperature. Such binding energy values might, however, constitute a lower limit, since thermally-assisted mechanisms could tend to slightly lower the emission threshold.

According to these important experimental measurements, we conclude that the most reasonable values of the binding energy of polaron-excitons in conjugated polymers lie in an energy range between a few kT's (0.1 eV) and at most 0.4 eV, the latter value corresponding to a number of earlier experimental estimates [19, 20]. These results further demonstrate that binding energies as high as 1 eV are not reasonable.

It is informative to note that Ultraviolet Photoelectron Spectroscopy (UPS) measurements performed on a PPV sample indicate that the valence band edge is located at 1.55 ± 0.10 eV below the Fermi energy [28]; assuming that the Fermi level is located in the middle of the gap, the energy gap corresponds to twice this value. Since UPS spectroscopy incorporates neither relaxation effects nor interactions between the departed electron and the remaining hole, we then subtract from this value twice the polaron relaxation energy (2×0.15 eV from our AM1 calculations [29]) and obtain a value of 2.80 eV for the creation energy of two polarons of opposite signs. Since the 0–0 transition of the same PPV sample, *i.e.*, the formation energy of a neutral polaron-exciton, is measured at 2.45 eV, the binding energy of the polaron-excitons is estimated to be on the order of 0.35 eV. Our estimate lies within the range given above; its uncertainty is, however, very difficult to assess, as is also the case in the other experimental measurements we refer to.

It is important to distinguish the contributions to the polaron-exciton binding energy arising from electron correlation effects and electron-lattice coupling. The results derived from both the analysis of the vibronic structures observed in photoluminescence spectra of long PPV oligomers and direct AM1/CI geometry optimizations [24], indicate that the relaxation energy in the lowest neutral excited state amounts to ~ 0.20 eV. The amplitude of the polaron relaxation energy cannot be evaluated in a simple way by experimental means; as mentioned above, AM1 calculations provide an estimate on the order of 0.15 eV for each polaron. The comparison of the relaxation energy of two polarons to that of a neutral polaron-exciton leads to the conclusion that the lattice contribution to the binding energy is very weak and could actually even be negative. It is worth stressing that such a conclusion would not be expected in the framework of one-electron models where the relaxation energy of a neutral polaron-exciton is found to be equivalent to that of a doubly charged bipolaron and is thus much larger than in a single polaron (up to some 0.5 eV [30]). On the other hand, very recent highly correlated Density Matrix Renormalization Group (DMRG) calculations performed at the Extended Hubbard level by Shuai and co-workers [31] conclusively demonstrate that the electron-electron contribution to the polaron-exciton binding energy is in the range from 0.1 eV up to at most 0.3 eV.

A most important result we have obtained is thus that *the small value of the polaron-exciton binding energy results from a cancellation of the electron–electron and electron–lattice contributions.* Such a behavior clearly demonstrates the need for correlation effects to be taken into account when describing the excited state wavefunctions. (Note that the fact that polarons and polaron-excitons are found to spread over 3–4 rings [24, 29], *i.e.*, over about 25 Å, does not prevent the first optical transition to evolve linearly with the inverse number of rings ($1/n$); the binding energy has indeed to be considered relative to the single-particle gap energy, which generally evolves as $1/n$.)

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