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Charge- and energy-transfer processes at polymer/polymer interfaces: A joint experimental and theoretical study

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When an exciton approaches the interface between two conjugated polymers, either energy or charge transfer can take place. We present a detailed experimental investigation of these processes in various binary polymer systems. The results are interpreted in the context of quantum-chemical calculations that provide estimates of the relative energies of intrachain versus interchain excited states in pairs of various PPV-related chains. In particular, we show that charge-transfer occurs at the interface between MEH-PPV and a cyano-substituted PPV derivative, whereas energy transfer takes place at the interface of PPV with the same cyano-substituted polymer. [S0163-1829(99)08031-5]

I. INTRODUCTION

There is growing evidence that the main photogenerated species in conjugated polymers are intrachain excitons, which correspond to electron-hole pairs bound by the Coulomb interaction. Polymer/polymer interfaces play an important role in organic electronic devices that use polymers in multilayer or mixture configurations; it is the behavior of excitons when they encounter such an interface that make these systems function efficiently as light-emitting devices or cells for solar energy conversion or light detection. When an exciton located on a conjugated chain reaches the interface with a second polymer, one of the following processes can occur: (i) the exciton is transferred to the second material, where it may decay radiatively (then giving luminescence characteristic of the second polymer) or nonradiatively; (ii) the exciton dissociates by transfer of a single charge to the second material, leaving behind an opposite charge in the first material; or (iii) the exciton remains in the first material where it decays radiatively (then giving luminescence characteristic of the first polymer) or nonradiatively.

Early work on molecular semiconductors has demonstrated that the separation of oppositely charged photogenerated carriers is efficient at the interface between certain materials having different ionization potentials and electron affinities. The effect was first reported in the early 1950s; organic dyes adsorbed on the surface of inorganic semiconductors were shown to sensitise this material, giving an additional photoresponse in the spectral range associated with the inorganic photoconductor.[1] Gol'dman and Akimov sensitised AgI with a variety of dyes,[2] and Nelson observed that the photoconductivity of CdS in the red and near infrared was enhanced by sensitisation with cyanine dyes;[3] it was argued that the conduction band of the dye lies above that of CdS, such that electrons photoexcited in the organic compound are transferred to CdS. Interest was renewed in the 1980s when Tang combined two molecular semiconductors in a photovoltaic cell and observed a strong-photovoltaic effect.[4] Tang proposed that the high-local field at the heterojunction interface favors the dissociation of excitons that diffuse towards it. Recently, conjugated polymers have been combined with molecular electron acceptors, such as C_{60}, to make efficient photovoltaic cells.[5,6]

Work carried out independently in Cambridge and Santa

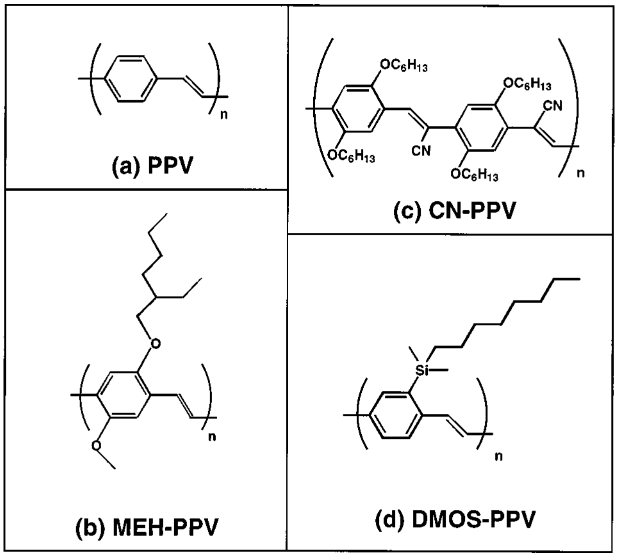

FIG. 1. Chemical structures of (a) PPV, (b) CN-PPV, (c) MEH-PPV, and (d) DMOS-PPV.

Barbara has demonstrated that efficient polymer photovoltaic cells can be fabricated from blends of poly[2-methoxy-5-(2′-ethyl-hexyloxy)-*p*-phenylenevinylene], MEH-PPV, with a cyano-substituted PPV derivative, poly (2,5,2′,5′-tetrahexyloxy-7,8′-dicyano-di-*p*-phenylenevinylene), CN-PPV;[7,8] the polymer structures are depicted in Fig. 1. The enhanced response of these composite cells is attributed to the efficient dissociation of excitons at the distributed interfaces between the two polymers. It is considered that dissociation is caused by transfer of the electron to CN-PPV (which has the higher electron affinity) or of the hole to the MEH-PPV (which has the lower ionization potential).

Interfaces between different molecular materials have also been exploited to drive energy transfer. In the process of photosynthesis, light is harvested and energy is channeled to the reaction center by a system of dyes with overlapping emission and absorption bands, which are organised in a way that maximizes the interactions and encourages directional energy transfer. The same cascading effect governs the operation of red-green-blue organic full color displays based on color conversion techniques.[9,10] Efficient polymer light-emitting diodes (LED's) have also been made by combining CN-PPV with PPV in a double layer structure.[11] The high efficiency is attributed to the recombination of electrons (which accumulate in the CN-PPV layer) with holes (which accumulate in the PPV layer) across the interface. Luminescence from such an LED structure is orange, indicative of radiative decay from CN-PPV; excitons formed in PPV appear thus to be transferred to the lowerband gap CN-PPV.

There is, thus, evidence that charge transfer occurs in an MEH-PPV/CN-PPV composite whereas energy transfer takes place in a PPV/CN-PPV blend. These examples demonstrate how a small change in the substitution pattern (and therefore in the energies of the frontier levels) of one chain in a polymer/polymer system can lead to an abrupt change in the behavior of an exciton at the interface between them. In this paper, we characterize in more detail, on the basis of experimental and theoretical considerations, both of these polymer combinations. In addition, we include measurements using a silyl-substituted polymer, DMOS-PPV, a soluble derivative of PPV, which has electronic properties very similar to those of PPV and can be used in blends with CN-PPV.

In the second section of this paper we review experimental evidence for charge and energy transfer in the three polymer/polymer systems that are investigated. In the third section, we use the relative energies of the frontier levels, calculated at a quantum-chemical level for each component of the composites, to illustrate that charge or energy transfer can take place at the interface between the two chains; in this model, we highlight the role played by the polarization effects, which are highly significant in these dielectric materials.

II. EXPERIMENTAL INVESTIGATIONS

A. Experimental method

Evidence for charge and energy transfer was obtained from photovoltaic and photoluminescence measurements. Photovoltaic cells were fabricated by spin coating the polymer system (which consisted of one or more polymers in a layered or blended structure) onto ITO-coated glass substrates,[12–15] which act as the hole collecting electrodes. The top electron-collecting contacts (aluminum or magnesium) were subsequently deposited over the polymer layer by thermal evaporation; the contacts create an electric field in the polymer matrix when the contacts are connected together in an external circuit. Cells were fabricated in a nitrogen-filled glovebox and characterized under vacuum. The cells were illuminated through the glass substrate using a xenon-arc lamp coupled to a single-grating monochromator; the light absorbed in a photocell generates excitons, which produce positive and negative charges upon dissociation. These charges relax to form oppositely charged polarons and move under the influence of the internal electrode field to the appropriate contacts; the charges are then collected and a photocurrent is measured, here with a Keithley 617 electrometer.

Thin polymer films for optical measurements were fabricated by spin coating ''pure'' or blended polymers in solution onto quartz substrates. Absorption spectra were measured using a Perkin-Elmer lambda-9 spectrophotometer. Photoluminescence efficiency measurements were made using the integrating sphere technique, which is described in detail elsewhere.[16] The films were excited with an argon ion laser and a charge-coupled device array spectrometer (Oriel instaspec IV) coupled to the integrating sphere analyzed the emitted light.

B. Experimental results

Charge transfer at the MEH-PPV/CN-PPV interface

MEH-PPV and CN-PPV have similar band gaps (around 2.1 eV with $\lambda_{\max}$ around 2.5 eV) and are both soluble in chloroform. The electron withdrawing cyano groups attached to the backbone of CN-PPV increase its ionization potential and electron affinity by approximately 0.5 eV relative to MEH-PPV;[17] this has been confirmed in a study by Fahlman *et al.*[18] and is supported by the results of quantum-chemical calculations.[19] Polymer blend films were fabricated by spin

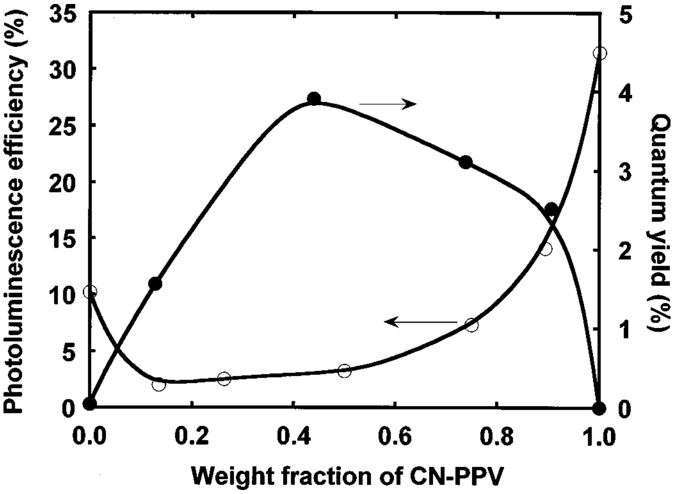

FIG. 2. Dependence of the photoluminescence and photocurrent on composition in MEH-PPV/CN-PPV systems. The open circles show the absolute photoluminescence efficiencies of thin films of the composite, which were excited by an argon-ion laser at 488 nm. The filled circles show the quantum yields of photovoltaic cells made using the MEH-PPV/CN-PPV composite as the active layer, sandwiched between electrodes of Al and ITO. The cells were excited with monochromatic illumination at 500 nm through the ITO contacts.

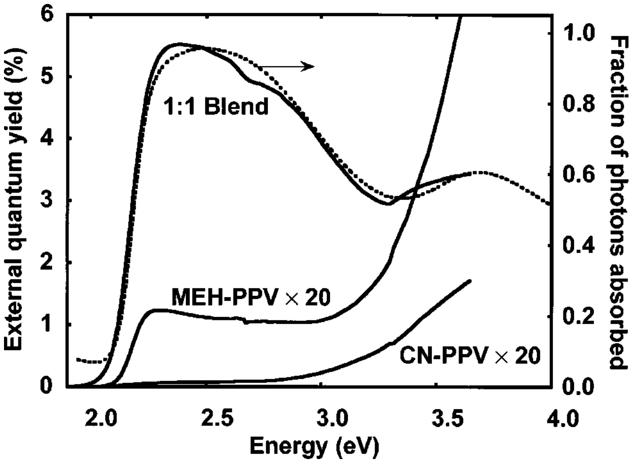

FIG. 3. Short-circuit photocurrent quantum yield plotted as a function of incident photon energy for three ITO/polymer/Al diodes; the polymers were CN-PPV (thickness of ~1000 Å), MEH-PPV (700 Å) and a 1:1 MEH-PPV/CN-PPV blend (800 Å). The quantum yields of the two homopolymer devices have each been scaled by a factor of 20. Shown for comparison is the proportion of light absorbed for two passes through the blend film, calculated as 1−transmission (dotted line). The absorption spectra of the two homopolymers are similar to that of the blend, and, for sake of clarity, are not shown here.

coating from a chloroform-based solution containing both MEH-PPV and CN-PPV. Transmission and scanning tunneling electron microscopy revealed the formation of an interpenetrating network of the two polymer phases within the plane of the film.[7]

Figure 2 (open circles) shows the absolute photoluminescence efficiencies of five blends of different composition, along with those of the ''pure'' homopolymers. Values of 10% and 32% are obtained for MEH-PPV and CN-PPV, respectively, whereas the luminescence in the blends is efficiently quenched to a level of 2% to 5% for mixtures containing 10% to 60% of CN-PPV. This significant though incomplete quenching is consistent with the scale of phase separation and exciton diffusion range, which have been shown to be both of order 10 nm.[7]

Further evidence for the dissociation of excitons in the blend driven by charge transfer, comes from the characterization of polymer blend photovoltaic cells. Figure 2 (filled circles) plots the external quantum efficiency (ratio of electrons out to photons in) of four polymer blend photocells of different composition along with that of cells made from the ''pure'' polymers. The composite photodiodes have efficiencies in the range 1.5% to 4% (we have measured efficiencies up to 7% in devices of this type), whereas devices based on ''pure'' MEH-PPV and CN-PPV were considerably less efficient, with values of 0.05% and 0.004%, respectively.

Figure 3 shows the photocurrent action spectrum of photovoltaic cells with active layers of CN-PPV, MEH-PPV, and a blend of the two, respectively. The photocurrent data for the two homopolymer cells has been scaled by a factor of 20 so that it can be compared more easily with the photoresponse of the composite device. The action spectrum of the MEH-PPV device exhibits a peak at the onset of absorption in the polymer and a minimum where the absorption is highest. This indicates that the photocurrent arises from excitation of the polymer close to the back metal contact. The CN-PPV cell (as well as the MEH-PPV cell at higher photon energies) shows a response that increases steeply with increasing excitation energy; this has been recently rationalized by a joint experimental and theoretical analysis of the nature of the excited states in PPV and derivatives.[20] By contrast, the photoresponse of the blend photocell follows the absorption spectrum of the composite film, indicating that charge generation occurs throughout the bulk of the device and thus providing firm evidence for charge transfer at the distributed MEH-PPV/CN-PPV interfaces.

Energy transfer at PPV/CN-PPV and DMOS-PPV/CN-PPV interfaces

The efficiency of PPV-based light-emitting diodes is limited by the relative difficulty of electron injection from a stable metal into the polymer layer; this arises from the low-electron affinity of PPV, which makes the barrier to electron injection large compared to the barrier for hole injection. Efficient electroluminescent operation requires a balanced electron and hole injection rate. Improvements in efficiency can be obtained by employing low-work function metals such as calcium,[21] although their reactive nature makes these devices deteriorate rapidly in air. An alternative approach is to use a chemically modified derivative of PPV with a higher electron affinity; by making a double-layer LED with CN-PPV inserted between the PPV layer and the electron-injecting electrode, electron injection into the polymer is enhanced.[11] Electrons accumulate at the interface between PPV and CN-PPV, and subsequently recombine with holes located in the PPV layer. A stable aluminum contact can then be used without sacrificing device efficiency. The high efficiency of these double-layer LED's and their orange emission are evidence for the high probability of exciton formation in CN-PPV at the PPV/CN-PPV interface.

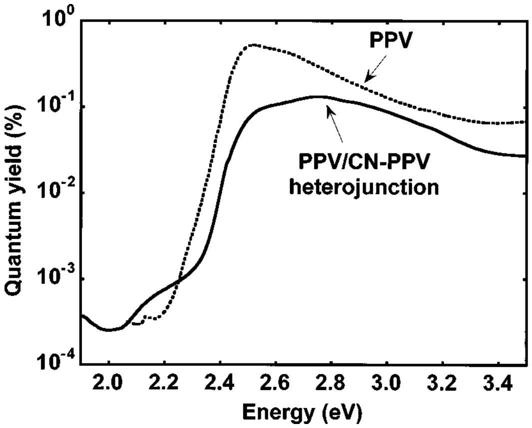

FIG. 4. Short-circuit photocurrent action spectrum of an ITO/PPV(550 Å)/CN-PPV(1250 Å)/Mg cell (dotted line); the cell is illuminated through the ITO/glass substrate. The action spectrum of an ITO/PPV(600 Å)/Mg diode is shown by a dotted line for comparison.

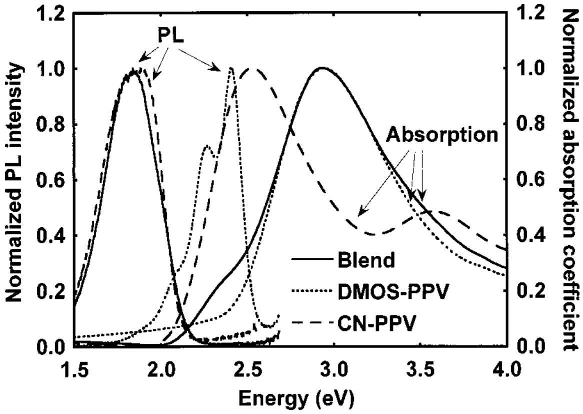

FIG. 5. Absorption and photoluminescence spectra of thin spin-cast films of DMOS-PPV (dotted lines), CN-PPV (dashed lines), and a 2:1 blend by weight of DMOS-PPV with CN-PPV (solid line).

Double-layer PPV/CN-PPV photovoltaic devices (identical in structure to the polymer LED's described above) were fabricated and characterized; the action spectrum of the double-layer cell (solid line) and that of a cell fabricated from PPV alone (dotted line) are shown in Fig. 4. It is evident that the double-layer cell is less efficient than the single-layer cell (except below the bandgap of PPV where excitation of the CN-PPV chains contributes to the photocurrent), indicating that efficient exciton dissociation driven by charge transfer does not occur at the interface. Indeed, the extra layer appears to suppress the photocurrent. This is in total contrast with work carried out on photovoltaic cells using for example, the electron acceptor C_{60} in a double-layer structure with PPV.[6] Photovoltaic quantum yields of up to 9% are obtained in devices of this type; this efficiency is some ten times higher than in single-layer PPV cells.

PPV is intractable and has to be prepared via a soluble precursor route, making its use in composites difficult; the precursor dissolves in methanol, whereas CN-PPV is soluble in chloroform and is expected to be damaged by the high temperatures involved in the thermal conversion process. Investigations of excitonic behavior at the interface of PPV with other polymers can only therefore be done in double-layer structures. In order to better compare the characteristics of MEH-PPV/CN-PPV and PPV/CN-PPV systems, it is desirable to investigate the properties of a blend of PPV with CN-PPV; in a composite, interfacial effects are more significant owing to the large number of distributed interfaces throughout the bulk of the blend. In order to achieve this, we have used the polymer DMOS-PPV as a substitute for PPV (see Fig. 1). DMOS-PPV has silicon atoms inserted between the benzene rings of the main chain and the solubilising alkyl chains. These atoms strongly reduce the interaction between the main chain and the side chains, with the result that the electronic properties of DMOS-PPV are very similar to those of PPV. DMOS-PPV is soluble in chloroform and can therefore be blended with CN-PPV.

DMOS-PPV was synthesized by Hwang *et al.*, who used it for fabrication of green LED's (Ref. 22) and demonstrated that its photoluminescence efficiency is as high as 60%,[23] over twice that reported for PPV.[24] The energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of DMOS-PPV have been shown by cyclic voltammetry to be similar to those of PPV;[25] this is also supported by our quantum-chemical calculations performed at the semiempirical Hartree-Fock intermediate neglect of differential overlap (INDO) level. The absorption edge of the silyl-substituted polymer is slightly blueshifted with respect to that of PPV; this is attributed to the steric effect of the bulky dimethyloctylsilyl side group.

Solutions of DMOS-PPV and CN-PPV in chloroform were mixed together to make a polymer blend solution with a composition of 2:1 by weight. The absorption spectra of thin spin-cast films of DMOS-PPV, CN-PPV, and the blend are shown in Fig. 5. The absorption spectrum of the blend corresponds to a simple superposition of features from the absorption spectra of the two homopolymers, thus indicating that there is no ground state charge-transfer interaction between the two polymers.

The absolute photoluminescence quantum yields of the thin-film samples are measured using the integrating sphere technique. The samples are excited with an argon ion laser at a wavelength of 457.9 nm (2.71 eV). The absolute quantum yields of DMOS-PPV and CN-PPV samples are 63 and 33%, respectively while 37% is measured for the blend. In contrast to the case of MEH-PPV/CN-PPV blends, the luminescence in the DMOS-PPV/CN-PPV blend is not efficiently quenched. We have thus strong evidence that exciton dissociation driven by electron transfer to CN-PPV does not occur in this system.

Photoluminescence spectra of thin films of the two homopolymers and of the blend, excited at 457.9 nm (2.71 eV) with an argon ion laser, are illustrated in Fig. 5. The luminescence spectrum of the DMOS-PPV is similar to that of PPV, though with more pronounced vibronic structure. There are well-resolved peaks at 2.4 and 2.25 eV, and a shoulder at 2.1 eV; these correspond to the 0-0, 0-1, and 0-2 vibronic satellites associated with the $(S_1 \rightarrow S_0)$ electronic transition. The photoluminescence spectrum of the composite film is virtually identical to that of the CN-PPV sample, with no trace of fluorescence from DMOS-PPV.

These results imply that excitons in DMOS-PPV are transferred (presumably by a Förster transfer process) to the lower band-gap CN-PPV chains where they decay radiatively. Despite the fact that the absolute fluorescence quantum yield and absorption cross section of DMOS-PPV is higher than that of CN-PPV, we note a complete absence of luminescence from DMOS-PPV. This implies that the energy transfer process is extremely efficient and, therefore, that phase separation exists on a scale smaller than the exciton diffusion range.

The blend solution was also used to fabricate ITO/polymer/Al photovoltaic cells. The composite photodiodes were found to have very low-quantum yields compared to the MEH-PPV/CN-PPV counterparts; at around 2.5 eV, the quantum yield of the DMOS-PPV/CN-PPV blend device was about 0.001%, compared to the maximum value of over 5% obtained with the MEH-PPV/CN-PPV composite. Moreover, the photocurrent action spectrum closely resembles that of a CN-PPV single-layer photocell, which exhibits a poor response at low energies and a rapidly increasing photocurrent at higher energies. These results indicate that excitons created in DMOS-PPV are transferred by an energy-transfer process to CN-PPV regions where they are ionized (giving rise to the observed photocurrent) or decay radiatively.

From the evidence recorded above, we conclude that excitons created in PPV or its close relative DMOS-PPV are transferred by energy transfer to CN-PPV, provided that they can diffuse towards the interface between the two materials.

III. THEORETICAL INVESTIGATIONS

The main goal of the theoretical section is to define a simple model on the basis of which the conditions leading to charge or energy transfer between two different PPV derivatives could be determined as a function of the nature of the substituents grafted on the PPV backbone. Recent correlated quantum-chemical calculations performed on clusters formed by *identical* PPV oligomers have demonstrated that in the lowest excited state the electron-hole pair has a largely dominant intrachain character;[26–28] thus, in such clusters, when the hole is centered on a given chain, there is a very high probability of finding the electron on the same chain (Frenkel-type exciton).[27] On the other hand, charge-transfer excited states for which there is a high probability of finding the electron and the hole on separate chains are calculated to be higher in energy [such charge-transfer (CT) excitons correspond to interchain excitons or have also been referred to as polaron-pairs[27,28]].

In order to provide a good description of energy transfer versus charge transfer, the amount of energy required to transform the lowest intrachain exciton into an interchain exciton is an important parameter to assess. A reasonable estimate for this parameter can be obtained by considering two five-ring PPV oligomers. As in our previous works[26,27] the calculations were carried out at the correlated semiempirical quantum-chemical level with the INDO Hamiltonian combined with a single configuration interaction scheme (INDO/SCI).[29]

The interaction between the two PPV chains gives rise to a significant splitting of the lowest excited state (S_1) of the isolated chain; that this splitting can be large results from the identical energy location of the highest occupied molecular orbital (HOMO) levels and the lowest unoccupied molecular orbital (LUMO) levels of the two chains (we recall that S_1 is predominantly determined by a HOMO to LUMO transition) (Ref. 30). For face-to-face PPV chains separated by 4 Å, the splitting of the isolated chain S_1 state into the interacting chains S_1 and S_2 states amounts to 0.25 eV; the S_1 and S_2 split states both have an *intrachain* exciton character. The first *charge-transfer* exciton is calculated to be 0.88 eV [0.63 eV] above S_1 [S_2]. On average, the energy difference between the lowest interchain exciton and the lowest intrachain excitons is thus on the order of $[(0.88+0.63)/2]\approx 0.75\,\text{eV}$. Very similar values are calculated: (i) for different interchain separations (0.75 and 0.83 eV for two five-ring oligomers separated by 3.75 and 3.5 Å, respectively); (ii) for different chain lengths (0.68 and 0.81 eV for two three-ring and seven-ring PPV oligomers separated by 4 Å, respectively); or (iii) for a greater number of chains in interaction.

An essential feature to point out at this stage is that the splitting between S_1 and S_2 is drastically reduced as soon as the two chains have a different chemical nature due, for instance, to different substitutions on the two chains. Indeed, a significant stabilization [destabilisation] of the HOMO/LUMO frontier levels occurs in the presence of π-acceptor [π-donor] substituents. As a result, the energy match between the HOMO levels and between the LUMO levels on the two chains disappears. Thus, the average difference of 0.75 eV between the lowest intrachain exciton and the lowest interchain exciton is a meaningful value that we will use below when considering chains of different nature.

It is also important to address the influence of the polarization effects induced by the surrounding medium. Polarization effects are expected to stabilize the energies of the interchain excited states more significantly than the lowest intrachain excited state, since interchain excitons have a more pronounced charge-transfer character. It is not straightforward to determine directly the changes in magnitude of the polarization effects when going from the lowest intrachain exciton to the lowest interchain exciton by means of quantum-chemical calculation. However, the experimental results given in Sec. II as well as the comparison between recent experimental and theoretical data on sexithienyl single crystals,[31] can help us in obtaining an indirect estimate.

In sexithienyl, our INDO/SCI calculations carried out on a cluster of interacting oligomers disposed as in the crystalline structure, have provided a remarkable reproduction of the optical absorption features associated with the intrachain excited states, such as the magnitude of the Davydov splitting.[31] The lowest interchain exciton is calculated to be some 0.2 eV above the upper Davydov component;[32] the electroabsorption data, however, locates this state very close in energy to the upper Davydov component.[33] It can thus be concluded that in the sexithienyl single crystal, the polarization effects stabilize the lowest interchain exciton state by about 0.2 eV with respect to the lowest intrachain exciton states. Such a small polarization is consistent with the fact that the average separation between the electron and the hole is not significantly larger in the interchain than in the intrachain exciton. A somewhat larger polarization can, however, be expected in the presence of polar substituents such as alkoxy or cyano groups. Since the analysis we present below puts a 0.6-eV upper limit for the polarization effects, we have chosen a working value of 0.4 eV for the DMOS-PPV/

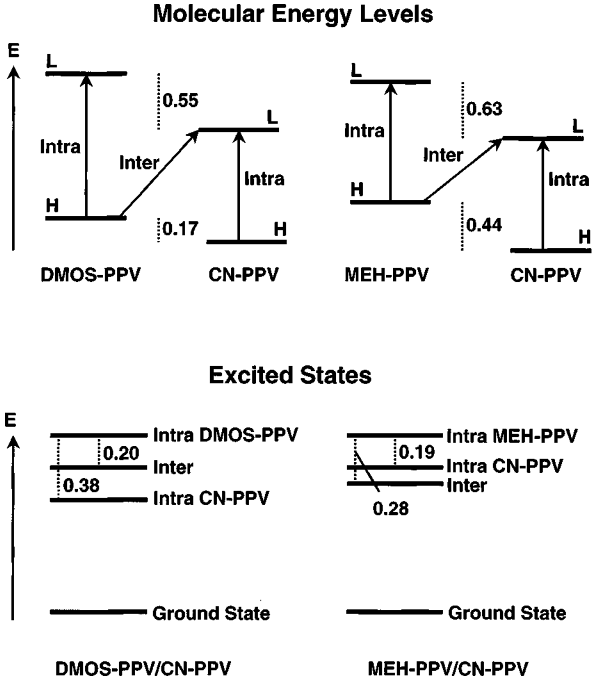

FIG. 6. Sketch of the energy diagram of the INDO-calculated relative positions of the HOMO and LUMO levels (top) and ordering of the lowest intrachain (intra) versus interchain (inter) excited states (bottom) in CN-PPV/DMOS-PPV and CN-PPV/MEH-PPV.

CN-PPV and MEH-PPV/CN-PPV systems, i.e., intermediate between 0.2 and 0.6 eV. The energy penalty to go from an intrachain exciton to an interchain exciton can thus be estimated to be on the order of [0.75−0.40=] 0.35 eV; that this estimate is reasonable is supported by the fact that it is of the order of the exciton binding energy in PPV as well as its derivatives.[34]

Keeping these elements in mind, we can now address the major issue that arises when considering DMOS-PPV/CN-PPV and MEH-PPV/CN-PPV blends, which is to know whether the lowest excitation is localized on one component or corresponds to charge transfer from one to the other component. To do so, we compare the calculated electronic properties on one hand of DMOS-PPV and CN-PPV and on the other hand of MEH-PPV and CN-PPV (note that in all cases, the alkoxy groups are modelled in the calculations by methoxy groups).

The results are illustrated in Fig. 6 where we plot a comparison of the INDO one-electron frontier energy levels (top) and the estimated ordering of the excited states (bottom) for each pair of compounds. We note that the one-electron approach is relevant here because the lowest intrachain transition of each chain is predominantly described by an excitation between the HOMO and LUMO levels on a single chain.[19] In contrast, the lowest interchain transition is essentially depicted by an excitation between the highest occupied level lying on one chain and the lowest unoccupied level located on the other chain. For instance, the redshift of the lowest excited state in going from DMOS-PPV to CN-PPV is estimated to be 0.38 eV from the difference in the HOMO-LUMO transition energies of the two chains; this result is in very good agreement with the value of 0.32 eV obtained from INDO/SCI calculations and with the experimental data showing a redshift on the order of 0.3-0.4 eV between the two polymers.[11] In going from DMOS-PPV to CN-PPV, the stabilization of the LUMO level by 0.55 eV, which is induced by the cyano groups, significantly lowers the energy of the lowest charge-transfer excited state. However, this stabilization is compensated by the energy required to transform the intrachain exciton into an interchain exciton, which we have estimated above to be [0.75−0.40=] 0.35 eV. Therefore, we calculate the lowest charge-transfer excited state in the DMOS-PPV/CN-PPV blend to be located 0.20 eV below the lowest excited state of PPV, and hence 0.18 eV above the lowest intrachain transition of CN-PPV. The rather large separation between the latter two states thus mostly results from the large difference in the bandgaps of the two polymers. In the DMOS-PPV/CN-PPV blend, a gain in polarization energy on the order or larger than 0.6 eV would be required to make the charge-transfer excited state the lowest in energy. Since the experimental measurements clearly indicate that energy transfer takes place at the interface between DMOS-PPV and CN-PPV, it is reasonable to conclude on the basis of our model, that the change in magnitude of the polarization effects when going from an intrachain exciton to an interchain exciton is lower than 0.6 eV.

In the case of the CN-PPV/MEH-PPV pair, analysis of the one-electron structure reveals that the lowest optical transition of CN-PPV is redshifted by only 0.19 eV with respect to that of MEH-PPV (this result is consistent with the correlated INDO/SCI calculations and the experimental data giving similar band gaps for MEH-PPV and CN-PPV). The LUMO level of CN-PPV is 0.63 eV lower than that of MEH-PPV due to the strong acceptor character of the cyano groups. However, this stabilization of the lowest charge-transfer excited state by 0.63 eV with respect to the intrachain transition of MEH-PPV must once again be compensated by the energy required to separate the electron and the hole (0.35 eV). As a result, the lowest charge-transfer excited state in the MEH-PPV/CN-PPV blend is estimated to be ca. 0.28 eV below the lowest intrachain transition of MEH-PPV, and hence some 0.10 eV below the lowest excited state of CN-PPV.

It is worth stressing that the charge-transfer excited state could not be the lowest in energy in the MEH-PPV/CN-PPV pair without an explicit account of the increased polarization energy in going from intrachain to interchain exciton. In the framework of our model, our calculations indicate that a choice of amplitude for the polarization energies between 0.3 and 0.6 eV brings agreement with the experimental data, i.e., it makes the charge-transfer excited state the lowest in energy in CN-PPV/MEH-PPV blend while the intrachain exciton on CN-PPV is the lowest excitation in the DMOS-PPV/CN-PPV blend.

IV. CONCLUSION

We have shown that charge or energy transfer can take place between two different PPV derivatives depending on the nature of the substituents grafted on the conjugated backbone. In the case of CN-PPV/MEH-PPV blends, photoluminescence and photocurrent measurements clearly demonstrate that charge transfer occurs at the interface between the two polymers, which can thus be used for the fabrication of efficient photovoltaic cells. In contrast, similar measurements performed on CN-PPV/PPV and CN-PPV/DMOS-PPV systems indicate that energy transfer toward the CN-PPV chains take place; as a result, high-luminescence quantum yield is obtained in LED's based on a double layer or a blend of these two polymers.

The two different behaviors are rationalized by a theoretical model based on estimates, at a quantum-chemical level, of the relative positions of intrachain versus interchain excited states in the binary systems. The theoretical calculations provide a clear insight into the physics of such processes and illustrate the important role played by polarization effects. When compared to the experimental data, the theoretical results set an upper limit of 0.6 eV for the changes in the magnitude of the polarization effects when going from an intrachain exciton to an interchain exciton.

The calculations underline that the difference in band-gap energy between the two partners is a critical parameter governing charge vs energy transfer at their interface. A large band-gap difference (as in CN-PPV/PPV) favors energy transfer toward the low band-gap partner (here, CN-PPV) while a small bandgap difference (as in MEH-PPV/CN-PPV) opens the way for charge transfer. Finally, we emphasize that the widely used approach of simply looking at the relative positions of the HOMO and LUMO levels of the two partners, is inappropriate to determine which type of transfer process can occur. The mere examination of the top of Fig. 6 would indeed lead one to believe that in both cases charge transfer would be favored, with the electron on CN-PPV and the hole on PPV or MEH-PPV.

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