

## The Role of Intermolecular Interactions on the Optical and Charge-Transfer Properties of Conjugated Polymers

J. Cornil<sup>a,b</sup>, D.A. dos Santos<sup>a</sup>, R. Silbey<sup>b</sup>, J.L. Brédas<sup>a,\*</sup>

<sup>a</sup>Laboratory for Chemistry of Novel Materials, University of Mons-Hainaut,  
Place du Parc 20, B-7000 Mons (Belgium)

<sup>b</sup>Department of Chemistry, Massachusetts Institute of Technology,  
Cambridge, Massachusetts 02139 (USA)

### Abstract

We investigate by means of quantum-chemical calculations the influence of intermolecular interactions on the properties of conjugated chains. We first focus on the optical absorption and emission of clusters formed by identical poly(paraphenylene vinylene), PPV, oligomers; we address the role played by the relaxation effects in the lowest excited state as well as the number and relative orientations of the interacting units. Several strategies are suggested that can be developed to avoid a substantial decrease in luminescence quantum yield in the solid state. In a second part, we illustrate by means of a simple theoretical model that charge or energy transfer can take place at the interface between two different PPV derivatives, depending on the nature of the substituents grafted on the PPV backbone.

*Keywords:* Semi-empirical models and model calculations, poly(phenylene vinylene) and derivatives, opto-electronic devices, optical absorption and emission spectroscopy.

### 1. Introduction

The development of efficient emitting devices [1,2] and field-effect transistors [3,4] built on organic conjugated materials as active element has triggered attractive prospects in the field of displays [5]. Advantages of conjugated polymers and oligomers over their inorganic counterparts rely on their ease of synthesis, modulation of the properties upon derivatization of the backbone, and patterning. In the last decade, the emergence of sophisticated quantum-chemical approaches have allowed a better understanding of the basic mechanisms that take place in the devices. Such calculations traditionally focused on the intrinsic electronic properties of isolated conjugated chains and were thus based on the assumption that the influence of interchain interactions is of secondary importance. However, many recent experimental studies have unambiguously demonstrated that intermolecular interactions could lead to dramatic changes in absorption and emission properties [6–8]; the results also suggest that interchain species, other than the intrachain electron-hole pair (exciton) characteristic of isolated chains, are created upon photoexcitation in a condensed medium. A good understanding of these interchain effects is still lacking, mostly because the experimental data are highly sensitive to the nature and/or quality of the samples [9].

In this context, we have investigated by means of quantum-chemical calculations the way interchain coupling affects the electronic and optical properties; here, a special emphasis is given to poly(paraphenylene vinylene), PPV, and its derivatives. When studying clusters formed by identical chains, our primary goal is to shed light into the nature of the most stable photogenerated species and to provide guidelines aimed at avoiding a substantial decrease in fluorescence quantum yield in light emitting devices. We also consider binary systems formed by PPV backbones of different nature and illustrate that charge or energy transfer can take place at the interface between the two polymers depending on the nature of the attached substituents.

### 2. Theoretical Methodology

A detailed description of the theoretical approach followed in this study has been reported previously [10]. Briefly, we have optimized the ground-state geometry of the clusters by means of the semiempirical Hartree-Fock Austin Model 1 (AM1) method [11]; the latter is coupled to a Configuration Interaction (CI) scheme when determining the equilibrium geometry in the lowest excited state. Note that the relative locations of the interacting units is fixed in the calculations. On that basis, we compute the vertical transitions associated to the absorption and emission processes with the help of the semiempirical Hartree-Fock Intermediate Neglect of Differential Overlap (INDO) Hamiltonian, developed by Zerner *et al.* [12], combined to a Single Configuration Interaction (SCI) technique. In contrast to traditional excitonic theories, we calculate here the *total* wavefunction of the cluster, thus mixing explicitly intrachain

\*This work is partly supported by the Belgian Federal Government of Science Policy "Pôle d'Attraction Interuniversitaire en Chimie Supramoléculaire et Catalyse", the Belgian National Fund for Scientific Research (FNRS-FRFC), the Commission of the European Union (support under Brite-Euram Contract BRPR-CT97-0469 'OSCA') and an IBM Academic Joint Study. JC is an FNRS research fellow. The work at MIT was partly supported by a National Science Foundation grant to the Center for Materials Science. We acknowledge stimulating discussions with Prof. A.J. Heeger, Prof. R.H. Friend, and Dr. J.J.M. Halls.

and charge-transfer excited states in the description of the optical properties. The choice of an SCI approach is validated by the fact that we here only deal with excited states primarily described by singly excited configurations.

### 3. Results and discussion

#### 3.1. Identical chains in interaction

We first consider cofacial dimers formed by two PPV oligomers superimposed on top of another one. We display in Figure 1 the INDO/SCI-calculated lowest two optical transitions of a dimer constituted by two stilbene molecules, with the interchain distance  $R$  varied between 3.5 and 30 Å. In the weak coupling regime ( $R$  larger than the size of molecule,  $\sim 8$  Å), the molecular orbitals are localized on a single unit. The nature of the lowest two excited states results from the interaction of the two intrachain transition dipole moments and can be effectively described by the point-dipole model [13]. At short distances (around 4 Å), the molecular levels are found to be delocalized over the two interacting chains, thus reflecting a strong coupling regime. In all cases, the entire oscillator strength is concentrated in the second excited state, which is blue-shifted with respect to the energy of the  $1B_u$  excited state of the isolated stilbene molecule [14], in agreement with experimental data [15]. In contrast, the lowest excited state corresponds to a forbidden optical transition due to the selection rules. Interestingly, we calculate that, for a given interchain distance, the energy splitting between the lowest two excited states decreases as a function of chain length [10]; this behavior is consistent with experimental evidence showing that highly delocalized conjugated chains do not undergo the concentration quenching typically encountered with organic dyes [2].

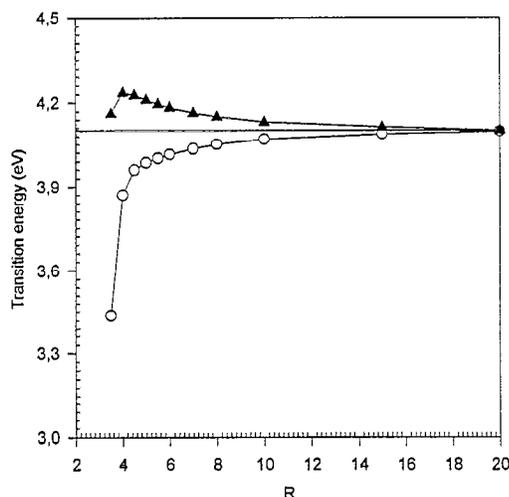


Fig. 1. INDO/SCI-calculated transition energies of the lowest two optical transitions of a cofacial dimer formed by two stilbene molecules as a function of the interchain distance  $R$ . The horizontal line refers to the energy of the  $1B_u$  excited state of the isolated molecule.

When taking into account the geometry relaxation effects in the lowest excited state, AM1/CI calculations performed on a cofacial dimer formed by two stilbene molecules show that the

geometry deformations mostly affect a single unit; this result is valid for the whole range of interchain distances we have considered. The geometry changes are very close to those calculated for the intrachain exciton in the  $1B_u$  excited state of the stilbene molecule. The calculations thus indicate that the most stable photogenerated species has a mostly intrachain character, which is driven by the Coulomb attraction between the electron and the hole. The self-localization of the exciton is further illustrated by a wavefunction analysis [16] of the lowest excited state of a cofacial dimer formed by two five-ring PPV oligomers separated by 4 Å; this analysis indicates that, when the hole is fixed on the center of chain I, the largest probability is to find the electron on the same chain, see Figure 2. The probability for the electron to be transferred on chain II increases when the interchain distance is reduced, as shown in the inset. We emphasize that charge-transfer excited states, where the hole and the electron located on two different chains, are calculated to appear at higher energies.

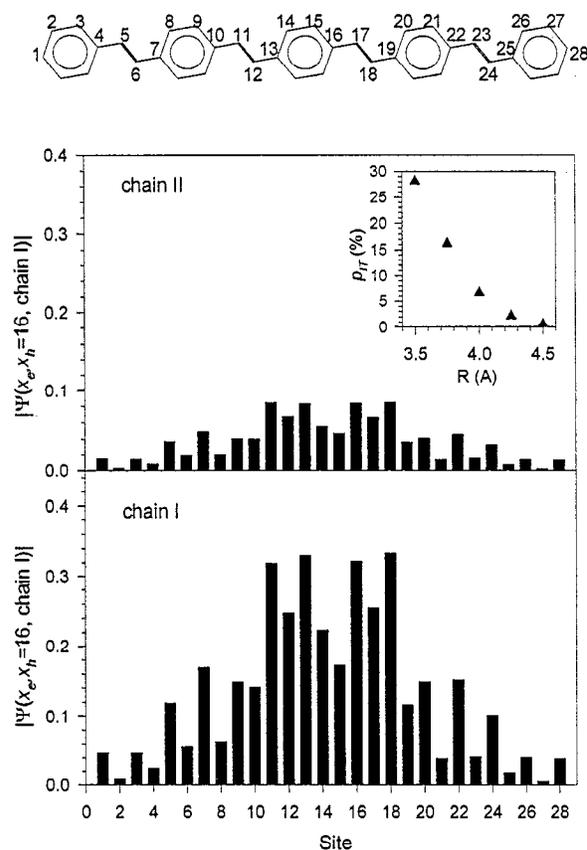


Fig. 2. INDO/SCI simulation of the first singlet excited state wavefunction in a cofacial dimer formed by two five-ring PPV oligomers,  $|\psi(x_e, x_h=16, \text{chain I})|$ , assuming an intermolecular distance of 4 Å.  $|\psi(x_e, x_h=16, \text{chain I})|$  represents the probability amplitude to find an electron in a given site  $x_e$  assuming the hole is centered on the site 16 of one chain of the dimer, which is denoted as chain I (the other chain being referred to as chain II). The site labelling is represented in the top panel. The inset shows the evolution of the probability to create an interchain exciton,  $p_{II}$ , as a function of intermolecular distance  $R$ . The  $R$  values are given in Å.

Due to the relaxation effects in the lowest excited state, the symmetry constraints previously described are relaxed; a luminescence signal, which is red-shifted with respect to that of the isolated molecule is predicted. When the interchain distance is lowered, the calculations further indicate that the amplitude of the red shift increases and that of the transition moment between the ground state and the lowest excited state is reduced. The weak optical coupling prevailing at short distances rationalizes the significant increase in radiative lifetime observed in recent experimental studies [7,17].

We have also investigated the properties of clusters formed by more than two units and have found that the main conclusions derived from the dimer picture hold true. The excitonic band built in clusters formed by several hexathienyl molecules in their crystalline structure has been recently characterized; the reliability of the INDO/SCI approach is confirmed by the remarkable agreement observed between the experimental and theoretical estimates of the Davydov splitting in the hexathienyl crystal (0.31 eV versus 0.35 eV) [18].

Finally, we have characterized the influence of the relative orientations of the interacting units on the calculated properties, in order to suggest supramolecular architectures that would allow for a significant optical coupling between the ground state and the lowest excited state in the emission process. The INDO/SCI results establish that a strong coupling can be achieved in configurations where there occurs a finite angle between the directions of the long chain axes [10]; this suggests that positional disorder is not detrimental for the device efficiency, as early recognized [19].

### 3.2. Different chains in interaction

We illustrate in this Section that a charge-transfer excited state or an intrachain excited state can be the lowest in energy when two different chains interact; in the first case, a photoinduced charge transfer occurs at the interface between the two materials while an energy transfer towards the chain with the lowest optical transition takes place in the second case. In this context, we model here the properties of two homogeneous blends of PPV chains recently investigated by the Cambridge group [20]. Photovoltaic and photoluminescence measurements have indeed provided firm evidence that the mixing of MEH-PPV and CN-PPV leads to photoinduced charge transfer processes at the interface between the two polymers, whereas blends of DMOS-PPV and CN-PPV show energy transfer towards the CN-PPV chains [20]; the chemical structure of these PPV derivatives are displayed in Figure 3.

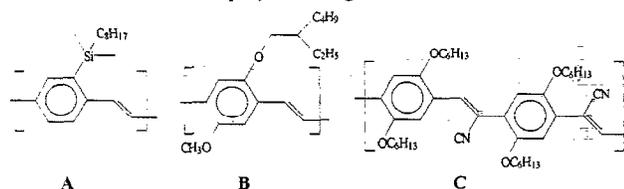


Fig. 3. Chemical structure of: A) DMOS-PPV; B) MEH-PPV; and C) CN-PPV.

The basis of the model is to locate in the two blends the relative position of the lowest *intrachain* excited state of each derivative with respect to that of the lowest *interchain* excited state. In this study, we depict the properties of DMOS-PPV by a

five-ring unsubstituted PPV oligomer and those of MEH-PPV and CN-PPV by corresponding five-ring oligomers in which the long alkyl chains are replaced by methyl groups. The lowest intrachain transition of these oligomers is dominantly described by an excitation between the HOMO and LUMO levels while the lowest interchain excited state corresponds to an excitation between the HOMO of one chain and the LUMO of the other chain. As a result, the relative positions of the three excited states of interest in a given blend can be inferred from theoretical estimates of the HOMO and LUMO energies of the two constituents.

In order to provide a suitable description of energy versus charge transfer, a key parameter to be evaluated is the amount of energy required to transform an intrachain exciton into an interchain exciton (also referred to as polaron pair or charge-transfer exciton in the literature). In this context, INDO/SCI calculations performed on two five-ring unsubstituted PPV oligomers separated by 4 Å in a cofacial conformation indicate that the difference between the average energy of the lowest two intrachain excited states and the energy of the lowest charge-transfer excited state is 0.75 eV (note that an average value is considered because the energy match between the frontier levels giving rise to the splitting of the lowest two excited states disappears when two chains of different nature interact); similar estimates are obtained when changing the interchain separation, the chain length and the number of chains in interaction.

Another feature to be taken into account is that the energy required for the formation of the interchain exciton is partly compensated by solid-state polarization effects that stabilize species with a pronounced charge-transfer character [21]. It is not straightforward to directly estimate the strength of the polarization effects by means of quantum-chemical calculations. We will show below that polarization energies in a range between 0.3 and 0.6 eV allow us to rationalize the experimental data obtained by the Cambridge group. We emphasize that such values: (1) lead to estimates of the exciton binding energy in the range 0.15 and 0.45 eV (*i.e.*, 0.75 – [0.6 or 0.3]), in very good agreement with most of the experimental values reported so far [22]; (2) correspond to the difference between the INDO/SCI-calculated and experimental energies of the lowest charge-transfer excited states in the hexathienyl crystal [23]; (3) are smaller than the typical decrease in ionization potential and increase in electron affinity of small organic conjugated molecules when going from gas phase to the molecular crystal (typically on the order of 1–2 eV) [24]; this is due to the small separation between the electron and the hole found here in the charge-transfer exciton. In the following, we adopt a value of 0.35 eV for the polarization effects, thus assuming that an amount of  $\sim (0.75 - 0.35) = 0.40$  eV is required in the two blends to transform the lowest intrachain exciton into a charge-transfer exciton.

Figure 4 gives for the two blends investigated experimentally by the Cambridge group the relative locations of the HOMO and LUMO levels of the two constituents as well as the relative energies of the intrachain versus interchain excited states. In the CN-PPV/DMOS-PPV blend, we calculate the lowest optical transition of CN-PPV to be red shifted by 0.38 eV with respect to that of DMOS-PPV, as a result of the substitution effects leading to an asymmetric stabilization of the HOMO and LUMO levels by 0.17 and 0.55 eV, respectively [25]. Assuming for instance that the DMOS-PPV chain is initially photoexcited, the transfer of an electron from the HOMO level of DMOS-PPV

to the LUMO level of CN-PPV would save 0.55 eV; to this value, we have to subtract the 0.4 eV needed for the creation of the charge-transfer exciton. Therefore, the lowest charge-transfer excited state lies 0.15 eV below the lowest intrachain excited state of DMOS-PPV, but 0.23 eV above that of CN-PPV. The lowest excited state is thus the intrachain CN-PPV excited state. Thus, we conclude that an energy transfer towards the CN-PPV chains is expected to take place in the DMOS-PPV/CN-PPV blend, as clearly supported by the experimental data [20].

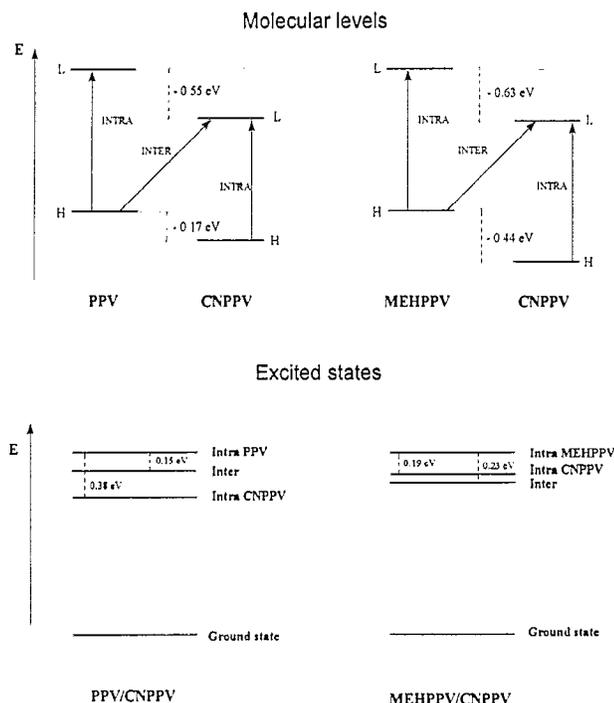


Fig. 4. Energy diagram of the INDO-calculated energies of the HOMO and LUMO levels (top) and ordering of the lowest intrachain (INTRA) versus interchain (INTER) excited states (bottom) in the CN-PPV/DMOS-PPV and MEH-PPV/CN-PPV blends.

Applying the same model to the MEH-PPV/CN-PPV blend, we calculate the lowest intrachain excited state of CN-PPV to be red-shifted by 0.19 eV and the lowest charge-transfer excited state by 0.23 eV (*i.e.*, 0.63–0.40 eV) with respect to the lowest intrachain excited state of MEH-PPV. In this case, a photoinduced charge-transfer between the two chains is thus expected whatever the derivative initially photoexcited; this is fully consistent with the experimental observations. Note that the choice of a polarization energy larger than 0.6 eV would make the charge-transfer state the lowest in energy in the two blends while values smaller than 0.3 eV would give rise to energy transfer between the chains in both cases, in contrast to the experimental measurements. This thus supports the range of polarization energies previously considered.

Despite the fact that the relative location of the frontier levels in the two blends looks very similar (see Figure 4), our model illustrates that a simple modulation of the substituents grafted on the conjugated backbone allows for charge or energy transfer to take place at the interface between the two polymers. This also demonstrates that subtle changes in the molecular

topology of PPV chains can make blends acting as materials of choice for use in photodiodes where charge transfer processes need to prevail, or in light-emitting devices where energy transfer processes take place. The simple model we have developed is consistent with the experimental data and provides a good insight into the nature of the main parameters governing the occurrence of charge or energy transfer between two conjugated chains. We believe that charge-transfer processes induced for instance upon photo-oxidation can be understood on the basis of similar considerations.

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