

# Excited-State Electronic Structure of Conjugated Oligomers and Polymers: A Quantum-Chemical Approach to Optical Phenomena

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## Introduction

Twenty years after the discovery by Heeger, MacDiarmid, Shirakawa, and co-workers<sup>1</sup> that an organic conjugated polymer can be “doped” (i.e., in chemical terminology, oxidized or reduced) to metallic-like electrical conductivity,<sup>2</sup> the field of conjugated oligomers and polymers has enjoyed a tremendous development, amply illustrated in the present issue of *Accounts of Chemical Research*. What once was a mere exotic curiosity has now turned into the market place. The interest goes all the way from making

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conducting transparent plastics<sup>3</sup> to exploiting the nonlinear (both second-order and third-order) optical response<sup>4</sup> and the semiconducting properties, for instance in thin-film field-effect transistors,<sup>5</sup> light-emitting diodes,<sup>6</sup> solid-state lasers,<sup>7</sup> and photovoltaic devices.<sup>8</sup>

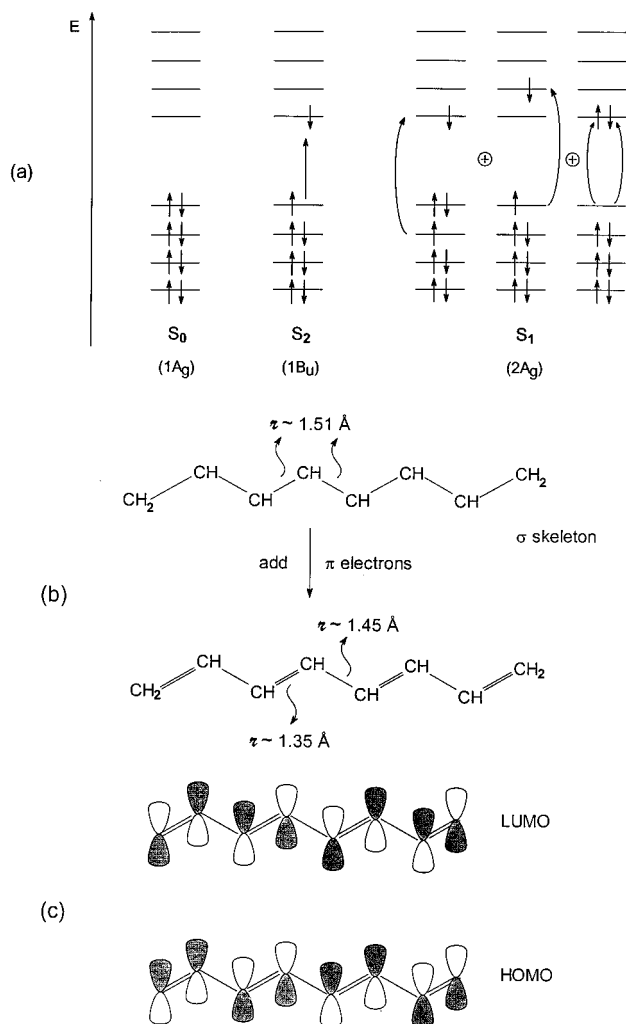
Since, in this specific class of polymers, small variations in chemical structure play an essential role and the properties of interest directly depend on the electronic structure, quantum-chemical approaches,<sup>9</sup> which take the chemical nature fully into account, have provided a tremendous input to the field. This has helped in forging a fundamental understanding of the electronic and optical characteristics of the conjugated materials and in guiding the experimental efforts toward novel compounds with enhanced characteristics.

It is the main purpose of our contribution to illustrate the usefulness of quantum-chemical methods (as we have exploited them in the Mons group over the past 10 years) in the field of conjugated oligomers and polymers, with a focus on luminescence phenomena. We do not wish to dwell on the theoretical methodologies that have been designed (these are detailed elsewhere<sup>9,10</sup>) but rather on the concepts. In the first section, we recall the basic electronic-structure ingredients of conjugated systems, which make their chemistry and physics so rich and fascinating. We then discuss the nature of the lowest excited states that play a key role in absorption, emission, transport, or nonlinear optical processes. As quantum-chemical calculations had long been restricted to single chains, interchain interactions had often been neglected; their influence, which by now is realized to be significant, is described in the last section.

## A Primer on the Electronic Structure of $\pi$ -Conjugated Oligomers and Polymers

By  $\pi$ -conjugated system, it is meant a (macro)molecule along the backbone of which there occurs a continuous path of carbon atoms or heteroatoms, each carrying a  $\pi$  atomic orbital. When the backbone is fully planar, there exists a strict distinction between  $\pi$  orbitals (antisymmetric with respect to the backbone plane) and  $\sigma$  orbitals (symmetric). The smallest conjugated molecule is ethylene,  $\text{CH}_2=\text{CH}_2$ . Among its occupied valence molecular orbitals (MOs), there are one  $\sigma$  “C–C” MO, four  $\sigma$  “C–H” MOs, and one  $\pi$  MO; the latter is formed by the bonding combination of the two  $\pi$  atomic orbitals and constitutes the highest occupied MO (HOMO). The antibonding combination of the  $\pi$  atomic orbitals leads to the lowest unoccupied MO (LUMO).

The determination of the electronic structure of conjugated systems might, at first glance, be considered as an easy task. Indeed, every chemist remembers that the first and most simple quantum-chemical method he/she has been introduced to, the one-electron Hückel technique, is mainly designed for conjugated molecules. However, the properties that are nowadays eagerly sought



**FIGURE 1.** Schematic illustration, in the case of octatetraene  $\text{CH}_2=\text{CH}=\text{CH}=\text{CH}=\text{CH}=\text{CH}=\text{CH}_2$ , of (a) the main electronic configurations contributing to the ground state  $S_0$  and the lowest singlet excited states  $S_1$  and  $S_2$ , (b) the “dimerization” of the geometric structure due to the uneven distribution of the  $\pi$  electrons over the bonds, and (c) the bonding–antibonding pattern of the HOMO and LUMO levels.

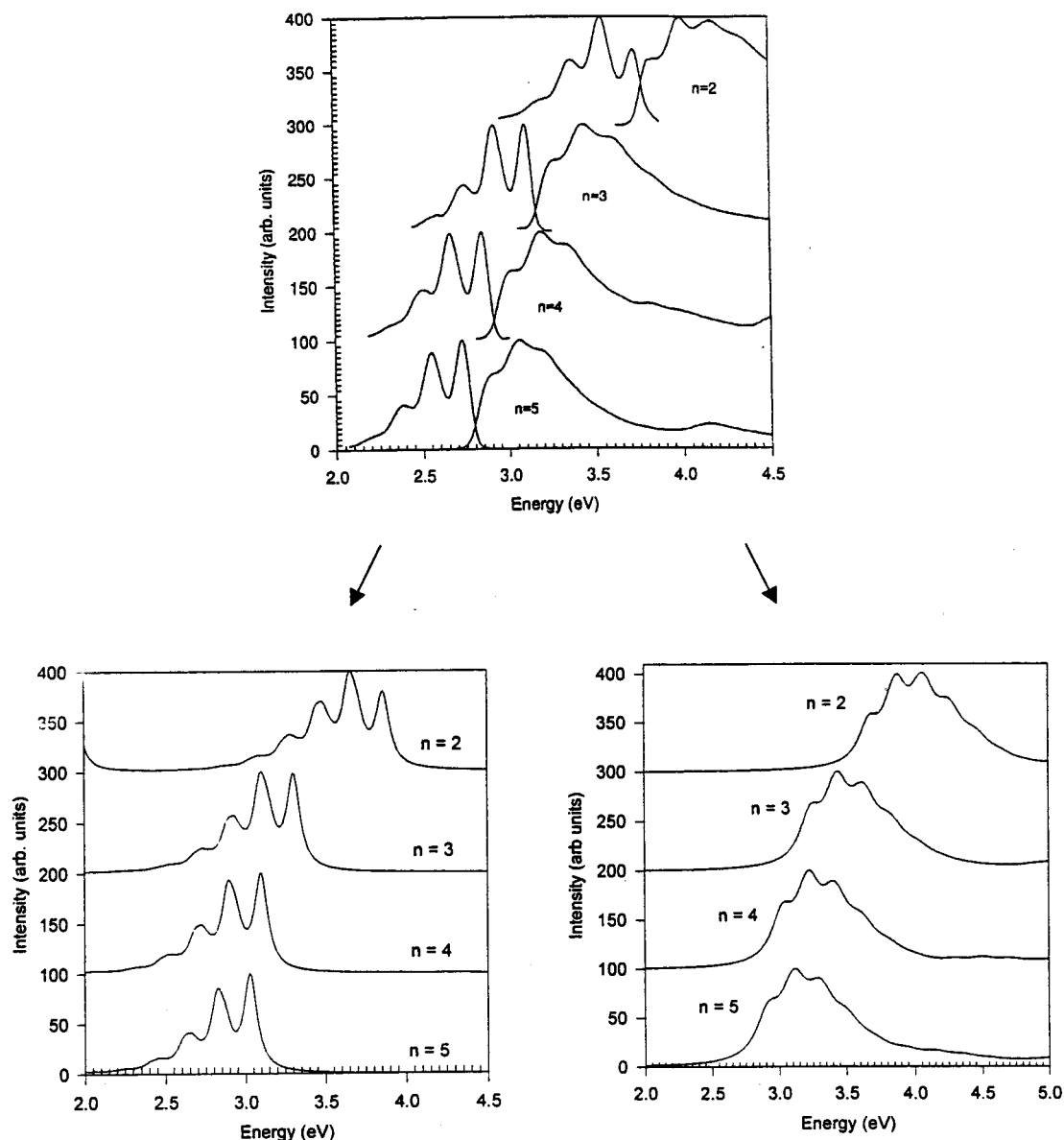
after (e.g., luminescence, electron–hole separation, nonlinear optical response) require a proper description of electronic excited states and interchain interactions, for which the role of many-body effects is large. In this context, the theoretical treatment of  $\pi$ -conjugated systems often becomes very elaborate because of the need (i) to incorporate electron correlation effects and (ii) to take account of the strong connection between, and mutual influence of, the electronic and geometric structures.

That electron correlation effects are important can be seen from an analysis of the ordering of the lowest singlet excited states in polyenes and polyacetylene.<sup>11</sup> Take the simple example of octatetraene, Figure 1. A one-electron (e.g., Hückel or Hartree–Fock) treatment produces eight  $\pi$  MOs whose symmetries alternate between “gerade” (g) and “ungerade” (u) and energies increase with the number of nodes in the wave function.<sup>12</sup> The eight  $\pi$  electrons distribute among the eight  $\pi$  MOs; each of their possible repartitions defines a so-called electronic configuration

whose individual wave function can be cast in the form of one Slater determinant. The lowest energetic configuration corresponds to the situation where the  $\pi$  electrons occupy two by two the four lowest  $\pi$  MOs and defines the singlet ground-state  $S_0$  (of  $A_g$  symmetry). At the one-electron level, the lowest (one-photon allowed) excited state (of  $B_u$  symmetry) is described by promotion of a single electron from the HOMO to the LUMO; any (one-photon forbidden)  $A_g$  excited state lies higher in energy because it requires promotion of a single electron from the HOMO to the LUMO + 1 or the HOMO – 1 to the LUMO or promotion of two electrons from the HOMO to the LUMO, and these processes nominally cost a larger energy (see Figure 1a).

However, an entirely different picture emerges when electron correlation is switched on. Various methods have been developed to take account of electron correlation effects;<sup>13</sup> for instance, in the often-exploited configuration interaction (CI) approach, each state is cast into a linear combination of electronic configurations (the wave function is then described by a linear combination of the corresponding Slater determinants). In polyenes, it so happens that the singly excited HOMO to LUMO + 1 and HOMO – 1 to LUMO configurations and the doubly excited HOMO to LUMO configuration (illustrated in Figure 1a) strongly mix and result in the  $2A_g$  state being located *below* the  $1B_u$  state; in other words, in polyenes (at least those longer than butadiene), the lowest excited singlet state,  $S_1$ , is one-photon forbidden vs the ground state.<sup>11</sup> The consequence is that polyenes and polyacetylene do not luminesce. Indeed, according to Kasha’s rule, luminescence takes place from the lowest excited state;<sup>14</sup> in order to observe strong fluorescence, a large one-photon coupling between  $S_0$  and  $S_1$  is thus required.<sup>15</sup>

A major feature that is specific of conjugated compounds is the interconnection between electronic structure and geometric structure. This connection has been beautifully exemplified in the field of conducting polymers with the emergence of concepts such as solitons, polarons, and bipolarons.<sup>16–17</sup> Consider again octatetraene, Figure 1b, and suppose that, in a first step, only the  $\sigma$  backbone is taken into account. The geometry would then be such that all carbon–carbon bond lengths are roughly the same and equal to ca.  $1.51 \text{ \AA}$  (the typical single bond length between two  $\text{sp}^2$  carbons). When the  $\pi$  electrons are thrown in, the main aspect is that they distribute *unevenly* over the bonds and in such a way that alternating larger and smaller  $\pi$  bond densities appear when starting from one end of the molecule; this results in alternating (physicists would say “dimerized”) double-like carbon–carbon bonds (ca.  $1.35 \text{ \AA}$  long) and single-like bonds (ca.  $1.45 \text{ \AA}$  long). A notable feature is that this geometry is reflected into the bonding–antibonding pattern of the HOMO wave function while the LUMO wave function displays the exactly opposite bonding–antibonding pattern; see Figure 1c. It can then be easily understood that, in the  $1B_u$  excited state (which mainly involves promotion of one electron from the HOMO to the LUMO), the  $\pi$ -bond densities are strongly modified; as a consequence,



**FIGURE 2.** Experimental absorption and cw photoluminescence spectra (top) at 77 K of PPV oligomers containing from two to five rings (PPV $_n$ ,  $n = 2\text{--}5$ ).<sup>21b</sup> The intermediate neglect of differential overlap/single configuration interaction (INDO/SCI) simulated absorption (bottom right) and photoluminescence (bottom left) spectra of these PPV oligomers are also displayed.

the equilibrium geometry in the  $1B_u$  state is markedly different from that in the ground state and is characterized by a significant reduction in C–C bond alternation. All other  $\pi$  excited states also have equilibrium geometries determined by their  $\pi$ -bond density distributions. Note also that, as the molecules become longer, the geometry relaxations no longer affect the whole chain but become localized (in the  $1B_u$  state of long polyenes, the optimal relaxation is calculated to extend over 20–25 Å<sup>18</sup>).

Another manifestation of the twinning between the geometric and electronic structures is the dependence of the ordering of the lowest singlet excited states on the effective degree of bond-length alternation,  $\delta$ , along the backbone.<sup>19</sup> As  $\delta$  increases, e.g., when switching from a purely polyenic backbone as in polyacetylene, to a mixed aromatic–polyenic backbone as in poly(*p*-phenylene-vinylene), PPV, or to an aromatic backbone as in poly(*p*-phenylene), PPP, and poly(2,5-thienylene), PTh, the  $2A_g$

state becomes destabilized vs the  $1B_u$  state, up to the point that  $1B_u$  becomes the lowest singlet  $S_1$  state.<sup>19</sup> As a result, for instance PPV and its derivatives can strongly luminesce and are prime candidates for incorporation as emissive layers in polymer-based light-emitting diodes;<sup>6</sup> this is the reason we focus on such polymers in the next section.

### Nature of the Lowest Singlet Excited States

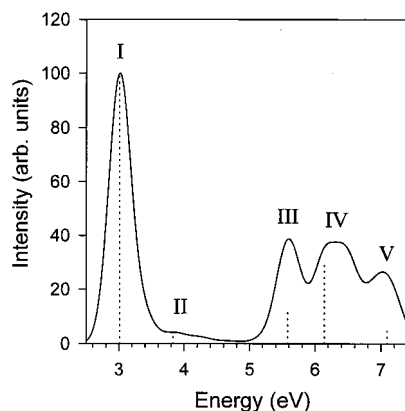
It is useful to analyze first the nature of the lowest excited state,  $S_1$ , since it rules the emission properties that can be exploited in light-emitting diodes, LEDs. In the case of PPV, this issue has been debated hotly in the literature among proponents of  $S_1$  being either the true band gap (i.e., corresponding to separated, free electron and hole) or an exciton (correlated electron–hole pair) with binding energies ranging from as little as 0.1 eV up to as large as 1 eV.<sup>20</sup>

A first remarkable feature is that the optical spectra of PPV or oligomers and their derivatives present clear signs of strong vibronic coupling. A very good theoretical simulation of the absorption and emission spectra of oligomers containing from two to five rings is obtained (Figure 2) by considering the coupling of the  $S_0$  to  $S_1$  or  $S_1$  to  $S_0$  electronic transition with two Raman modes (at 0.16 and 0.21 eV) corresponding to the C–C bond stretching and phenylene breathing modes, respectively.<sup>21</sup> From the evolution of the vibronic progression, the relaxation energy in the long chains can be estimated to be on the order of 0.15–0.2 eV.<sup>21</sup> The very presence of a vibronic progression in the polymers indicates that the electronic excitation produces a *localized* geometry relaxation around it (which extends over 20 Å<sup>21</sup>) and as such can hardly be related to a pure band gap transition.

In all cases we have studied (oligophenylenevinylenes, oligothiénylenes, and their derivatives<sup>22–23</sup>), it is found that the lowest  $B_u$ -type excited state has a dominant *intra-chain* excitonic character. This is good news in terms of the luminescence properties: the  $S_1 \rightarrow S_0$  transition being polarized mostly along the chain axis, the presence of the electron and the hole on the same chain will maximize the probability of light emission. On the other hand, the first excited state with *interchain* charge-transfer character and possibly leading to electron–hole (charge) separation is located a few tenths of an electronvolt above it and typically has a weak oscillator strength from the ground state. We will address this issue further in the section dealing with interchain interactions.

It is also of interest to try to understand the nature of upper lying excited states that have a strong coupling with the ground state. The main purpose in doing so is not only to be able to rationalize the shape of the optical absorption spectra in the visible and near-UV but also to correlate that information with the photocurrent action spectra that have been measured for instance in the case of PPV and poly(2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylenevinylene), MEH–PPV. From the frequency dispersion of the short-circuit photocurrent (recorded in air and corrected for the incident photon flux), the Cambridge group has shown<sup>24</sup> that the following occurs: (i) a one-to-one correspondence between the absorption features and the photocurrent peaks and (ii) a large increase in the photocurrent around the third absorption band, which cannot be related to changes in the absorption coefficient.

To understand the origin of the large photocurrent measured at high photon energies, the absorption spectrum of an isolated PPV oligomer containing 11 rings has been theoretically simulated as shown in Figure 3. The wave functions of the excited states located in each of the absorption bands were then evaluated, assuming that the hole is located near the middle of the oligomer backbone (we stress that the incorporation of interchain interactions or the consideration of the full correlation between the motions of the electron and the hole in the excited states does not modify the results discussed below). The excited-state wave functions are sketched in Figure 4; note that there is actually a manifold of similar excited states

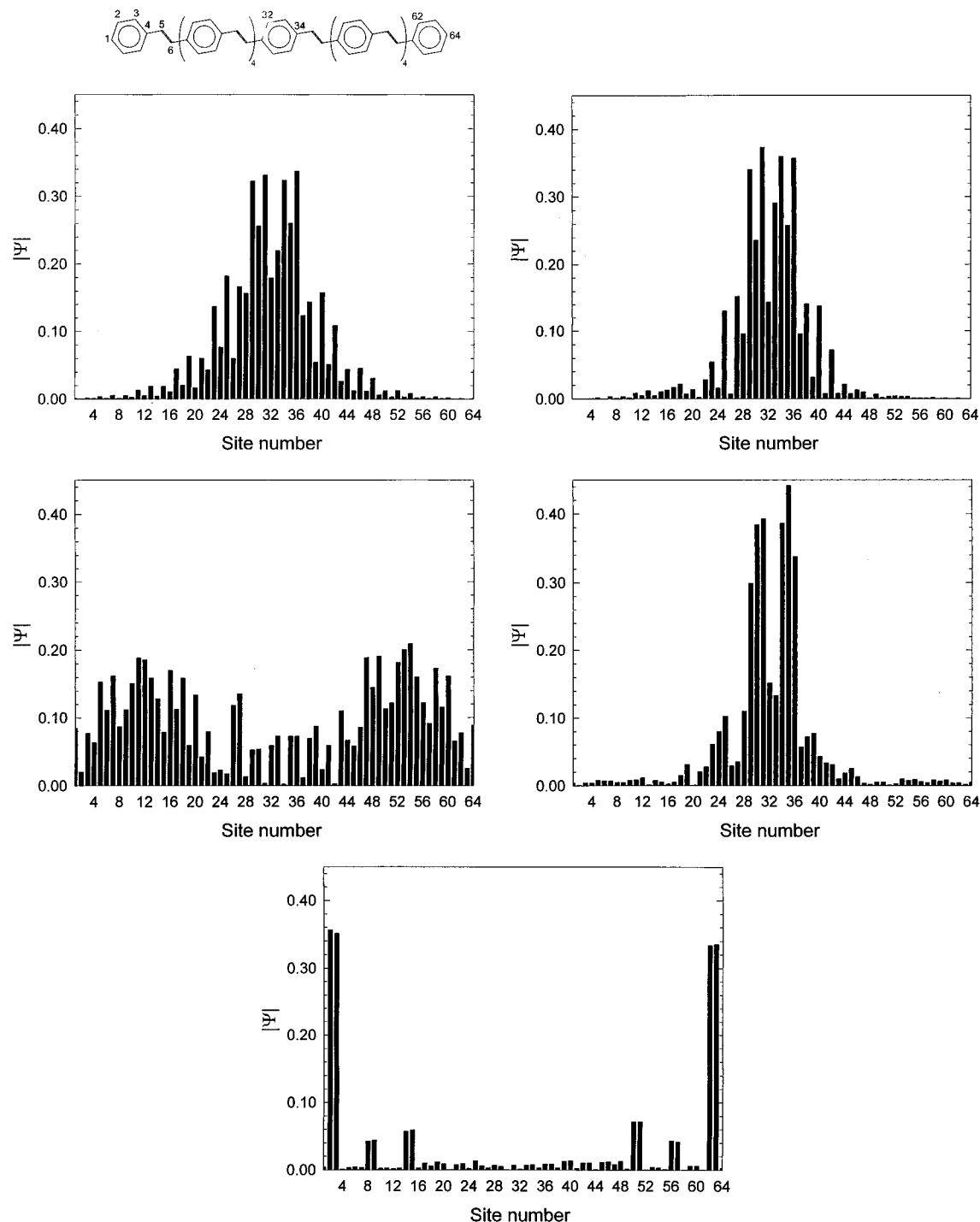


**FIGURE 3.** INDO/SCI simulated linear absorption spectrum of the 11-ring PPV model oligomer. The vertical dotted lines represent the oscillator strength of the excited states for which the wave functions have been computed (see Figure 4).

contributing to the total intensity of bands III, IV, and V in Figure 4, but it suffices to discuss the most intense feature for each band.

Two types of excited states can be clearly distinguished in Figure 4. On one hand, excited states with Gaussian-like electron distributions, centered on the hole position and extending over a few repeat units, occur; this is observed for states involved in the first, second, and fourth absorption bands (note that the center of the Gaussian is not necessarily on the site where the hole is located due to the nature of the molecular orbitals contributing to the description of the excited states). There, the photogenerated electron and hole are significantly bound by Coulomb attraction (these states are mainly polarized along a direction parallel to the chain axis<sup>25,26</sup>). It is interesting to point out that, from these results, the coherence length of the exciton in the lowest excited state (peak I) can be estimated to be on the order of five phenylene rings (ca. 30 Å), as confirmed by the results of calculations based on the coupled electronic oscillator (CEO) representation<sup>27</sup> (thus, the delocalization of the electronic wave function of the exciton is calculated to be larger than the width of the corresponding lattice relaxation, on the order of 20 Å, as mentioned above); this is a typical feature in conjugated chains. A detailed analysis of the configuration interaction (CI) expansion of these excited states reveals that they originate from excitations among the *same* type of molecular orbitals, i.e., either between delocalized levels, as is the case for peaks I and II, or between localized levels, peak IV (these localized levels are characterized by nodes on the para carbon atoms of the phenylene rings and hence confined within the aromatic cycles<sup>28</sup>).

On the other hand, in the third and fifth absorption peaks, the oscillator strength is provided by charge-transfer states, for which there is a significant probability of finding the electron and the hole separated by a few phenylene rings. Such states are polarized mostly perpendicularly to the long chain axis and are described at the CI level by a mixing of excitations taking place from an occupied delocalized level to an unoccupied localized level or vice versa. Picosecond time-resolved measure-



**FIGURE 4.** INDO/SCI simulation of the absolute value of excited-state wave functions  $|\psi(x_e, x_h=34)|$  calculated for the PPV undecamer as a function of carbon site for a fixed position of the hole at site 34 for excitations into the first (a), second (b), third (c), fourth (d), and fifth (e) absorption peaks. The site labeling is shown at the top of part a.

ments have shown that the decay of high-lying excited states is extremely fast and the emission is essentially from the lowest excited state within 1 ps;<sup>29–30</sup> therefore, the probability of charge transfer is intimately related to the ability of the electron and hole to separate at short times. Under these conditions, the charge-transfer character observed in the absorption bands III and V is a favorable element for a fast dissociation of the exciton (this dissociation, however, remains an *extrinsic* phenomenon since it is believed to be linked to the presence of

impurities; the external agents could for instance be oxygen molecules giving rise to photooxidation of the samples and the appearance of carbonyl groups along the conjugated chains,<sup>31</sup> water molecules,<sup>32</sup> or triplet oxygen<sup>33</sup> forming van der Waals complexes with the chains). Thus, via elaborate excited-state wave function analyses, it becomes possible to distinguish excited states where the electron and the hole are significantly bound by Coulomb attraction from those where the two carriers are loose due to efficient charge separation. These charge-transfer states

can be related to the large photocurrent yields observed experimentally at high energies.<sup>24</sup>

These results also bear significance in the context of another issue. The question has indeed often been raised as to whether the electronic structure of conjugated oligomers and polymers is better described via a molecular picture or a band picture. The intricate mixing between localized and delocalized levels and the alternation between excitonic and charge-transfer states make the answer clear. Both the molecular and band pictures need to be simultaneously incorporated.<sup>24</sup>

## Impact of Interchain Interactions

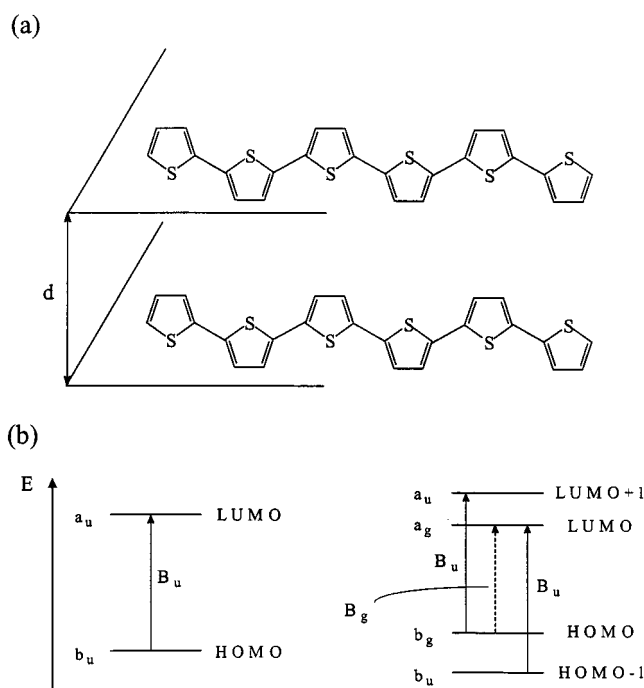
Up until recently, only a few quantum-chemical investigations had been devoted to the understanding of interchain interaction effects in  $\pi$ -conjugated systems. There were many reasons behind this situation: (i) the intrinsic difficulty in properly evaluating these interactions; indeed, while intrachain bonding has a covalent nature, interchain bonding relates to van der Waals dispersion forces whose description, by essence, requires the accurate handling of electron correlation; (ii) the common belief that in most instances the main electronic properties are governed by what happens on a single chain; and (iii) the poor knowledge of the chain packing since, with few exceptions, conjugated polymers have little degree of crystallinity. Note that, in the cases where interchain interactions were known to be important, for instance for the transport properties that obviously depend on interchain hopping, mostly phenomenological models had been developed.

However, a number of recent findings have forced quantum chemists interested in conjugated materials to go beyond the single-chain approach.

(1) In the case of photoluminescence, a number of experimental studies have highlighted the influence of interchain interactions when going from dilute solutions to the solid state<sup>34–39</sup> and brought into light somewhat contradictory results: (i) the appearance of a significant increase in radiative lifetime without any substantial loss in quantum efficiency;<sup>36</sup> (ii) a lack of correlation between the dynamics of the luminescence and that of fast photoinduced absorptions, a feature which is not observed for isolated chains;<sup>34,39</sup> and (iii) in some cases, a significant decrease in fluorescence quantum yield.<sup>35</sup>

(2) The discovery of charge transfer phenomena that critically depend on charge separation of the photoexcited electron–hole pair over chains of different nature has attracted much attention in the context of photovoltaic applications; this is the case for instance in conjugated polymer/fullerene systems or blends of various PPV derivatives.<sup>8</sup>

(3) A better knowledge of the way chains pack in ordered phases has been obtained in the cases of sexithienyl, a PTh oligomer used as the semiconducting layer in organic field-effect transistors,<sup>40</sup> as well as for some PPV<sup>41</sup> and PPP<sup>42</sup> oligomer derivatives; purification and



**FIGURE 5.** (a) Structure of the Th6 cofacial dimer. (b) Sketch of the one-electron levels for the Th6 isolated chain (left) and a cofacial dimer in the case of strong interaction (right).

crystallization of the sexithienyl oligomer has resulted in a dramatic increase in carrier mobility, up to  $10^{-1}$   $\text{cm}^2/\text{Vs}$ .<sup>43</sup>

The possibility to rely on an X-ray diffraction structure for sexithienyl, the six-ring oligomer of thiophene (hereafter denoted Th6), and the importance of this compound in potential applications make it appropriate to discuss the influence of interchain interactions by taking it as an example. The concepts discussed below are, however, fully applicable to other interacting conjugated chains.

To lay down the basic ideas, our approach to describe the influence of interchain interactions on the optical response of the Th6 single crystal starts with a simple two-chain model; we first consider a cofacial arrangement of the two sexithienyl chains, separated by an interchain distance  $d$  (Figure 5). Note that, like the isolated Th6 chain itself, such a cofacial dimer belongs to the  $C_{2h}$  symmetry point group; to differentiate between the molecular and dimer excited states, we use the labels “mo” (for molecular) and “di” (for dimer).

It is useful to examine the following two limiting cases in terms of interchain separations. For short interchain distances, i.e.,  $d$  much shorter than the length of the molecule, interaction between the conjugated chains leads to a splitting of the one-electron HOMO and LUMO levels of the isolated molecule into gerade and ungerade molecular orbitals that are fully delocalized over the whole complex (Figure 5b). At this stage, it is interesting to emphasize that the splitting calculated for the HOMO level is larger than that for the LUMO level; this reflects a different extent of the overlap between the molecular orbitals, which is directly related to the different number of nodal surfaces in the HOMO and LUMO wave func-

tions. If we extrapolate to a one-dimensional stack of such interacting conjugated molecules, the stack valence band is therefore expected to be wider than the conduction band. This result is consistent with the fact that, in conjugated polymers or oligomers, holes usually possess a larger mobility than electrons.<sup>44</sup>

At the correlated level, the  $1B_u^{mo}$  excited state of the isolated compound is split into two delocalized electronic states with different symmetries (see Figure 5): (i) the lowest excited state (described mainly by the promotion of an electron from the dimer HOMO to LUMO) has  $B_g$  symmetry ( $1B_g^{di}$ ) and thus no coupling with the ground state; (ii) most of the oscillator strength is concentrated in the upper excited state, with  $B_u$  symmetry ( $1B_u^{di}$ ), which results from the constructive combination of the dimer HOMO to LUMO + 1 and HOMO - 1 to LUMO excitations (the destructive combination of such configurations leads to another  $B_u$  excited state ( $2B_u^{di}$ ) with weak absorption cross-section but strong charge transfer (CT) character). Note that when the distance between the molecules becomes very small (typically  $d < 4 \text{ \AA}$ ), electronic excitations with different characters start mixing efficiently; this leads to a transfer of oscillator strength from the  $1B_u^{di}$  state to CT excited states. Therefore, in the regime of strong interactions, the excited-state analysis of a stacked dimer indicates (i) an almost complete quenching of the luminescence and (ii) the possibility of a significant electroabsorption signal (together with a raise in photocurrent) associated with low-lying states with mixed Frenkel exciton/charge-transfer exciton nature.

In the limit of weak interactions, that is, when the distance between the conjugated units is large with respect to the length of an isolated chain, the wave functions of the dimer excited states can be expressed to a first approximation as a linear combination of products of isolated-chain wave functions, in accordance with Kasha's model.<sup>45</sup> This situation prevails in dilute solution, where the photophysical properties of the isolated chains are retained; in this limiting case, luminescence is not quenched since the excited species remains on a single chain and the transfer rate between the units is slow.<sup>45,46</sup>

In the crystal, the sexithienyl molecules pack in a herringbone fashion,<sup>40</sup> see Figure 6, with rather short intermolecular contacts (on the order of 3.5–5 Å) and four unequivalent molecules in the unit cell. The interaction forces in the Th6 crystal are in the medium to strong regime; this is confirmed by (i) the much lower luminescence quantum yield measured in sexithienyl films and crystals with respect to solution<sup>47</sup> and (ii) the observation in Th6 films of an intense electroabsorption signal associated with low-lying charge-transfer excited states (close in energy to the lowest optically allowed state).<sup>48</sup> Therefore, a simple point-dipole model based on isolated-chain wave functions<sup>45</sup> is *not* appropriate to describe the photophysical properties of Th6 in the solid state (at least on a quantitative basis). The intermolecular interactions taking place within the Th6 layers ( $bc$  plane in Figure 6) largely dominate over the interlayer interactions (due to much smaller interchain distances within the layers, 3.5–

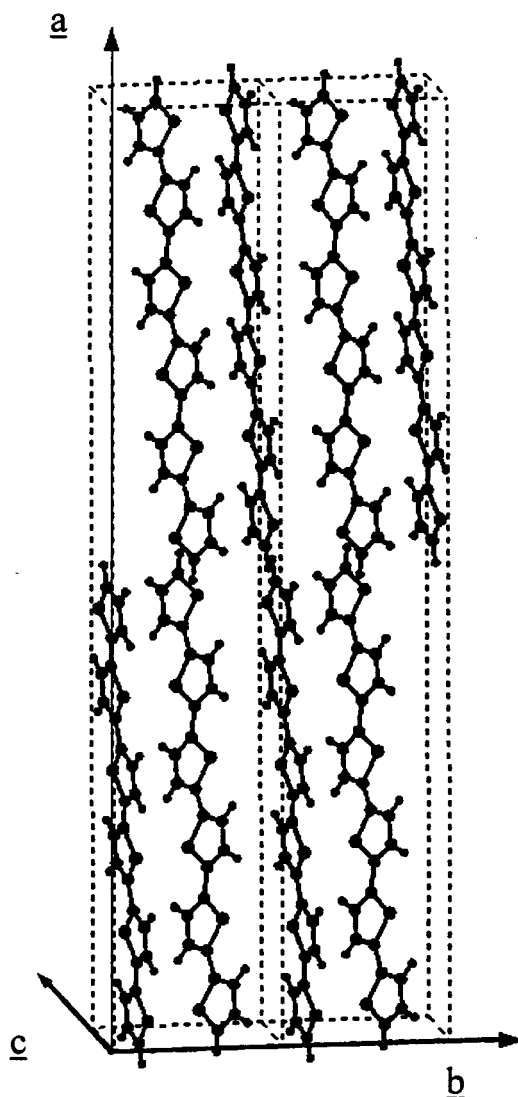
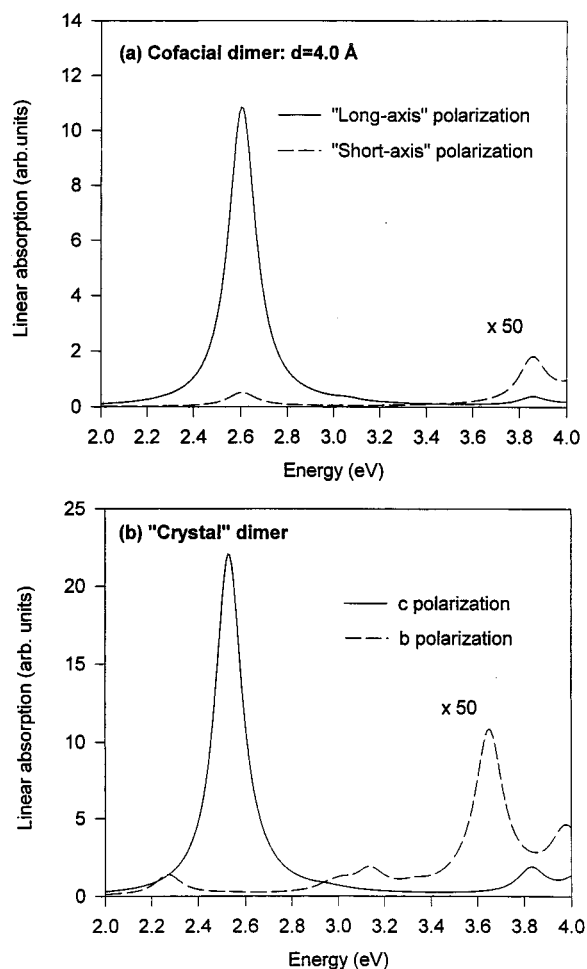


FIGURE 6. Structure of the Th6 single-crystal unit cell (as adapted from ref 40).

4.5 Å, than between the layers, ca. 20 Å). In the following, the focus is therefore on clusters built by considering Th6 chains lying within the same  $bc$  layer (note that there are two unequivalent molecules within a  $bc$  layer and thus two so-called Davydov components<sup>14</sup>); for the sake of clarity, lower case symbols are used for the symmetry of crystal states).

We now consider what we refer to as a crystal dimer, since its geometry is taken from the X-ray structure of the Th6 single crystal.<sup>40</sup> In this crystal dimer, the conjugated molecules are arranged in a herringbone configuration, with a distance of about 4.5 Å between the chain axes. The lowest two excited states (which result from the splitting of the  $S_1$  state of the isolated chain and correspond to the Davydov components) are found not to be confined to a single Th6 unit and acquire a weak charge-transfer character; conversely, CT excited states located just above the upper Davydov component gain some optical absorption intensity with respect to the situation prevailing in the case of weak interchain coupling.



**FIGURE 7.** INDO/SCI simulation of the polarized absorption spectra of (i) a cofacial dimer with an interchain separation of 4.0 Å and (ii) the "crystal dimer", whose geometry is taken from the X-ray crystal structure<sup>40</sup> (intralayer dimer). Note that absorption along the short axis of the molecule [*b* axis of the crystal] has been magnified by a factor of 50.

In Figure 7, the simulated absorption spectrum of the crystal dimer is compared to the corresponding spectrum calculated for a cofacial dimer with  $d = 4.0$  Å. In both cases, the intense peak around 2.55 eV (corresponding to the high-lying Davydov component) is characterized by a strong dichroic ratio, with predominant absorption in the *ac* plane of the crystal, i.e., along the long axis of the molecule; there is also a very weak long-axis polarized absorption due to CT excited states around 3.0 eV. In contrast, the absorption band at 3.6–3.8 eV is polarized along the short axis of the molecule, i.e., in the *bc* plane of the crystal. On going from cofacial-like to herringbone-like arrangement of the sexithienyl units, the lowest excited state (with  $B_g$  symmetry in the cofacial dimer and  $a_u$  symmetry in the crystal) becomes weakly allowed along *b* and leads to a weak absorption feature around 2.25 eV. The Davydov splitting calculated for the crystal dimer is close to that obtained by considering the  $d = 4.0$  Å cofacial dimer case ( $\sim 0.25$  eV vs  $\sim 0.3$  eV); this illustrates that the interchain interactions taking place within the layers are on the strong side.

We next turn to larger clusters, where only interactions within a single Th6 *bc* layer are involved. When the number of Th6 molecules considered in the cluster grows, the Davydov splitting, defined as the difference between the optically allowed  $a_u$  (*b*-polarized) and  $b_u$  (*ac*-polarized) transitions, increases and saturates toward 0.35 eV for about six molecules; this is in excellent agreement with the 0.31 eV experimental estimate.<sup>49</sup> At the same time, the upper, strongly allowed, Davydov component moves nearer the bottom of the CT band. In the crystal, the application of a static electric field therefore leads to a pronounced mixing of the intrachain and CT excitons and, as a consequence, to important deviations in the shape of the electroabsorption spectrum with respect to the first derivative of the optical absorption.<sup>48</sup>

Finally, three points are worth stressing.

(i) The Davydov splitting is maximum (and most detrimental to the luminescence properties) when the long axes of adjacent conjugated chains are parallel to one another, which is nearly the case in the herringbone structure.<sup>46</sup>

(ii) The Davydov splitting decreases and its lower-lying component starts acquiring significant oscillator strength as soon as an angle appears between the long axes of adjacent chains and/or the chains become longer: this is good news for luminescence in well-ordered conjugated polymers.<sup>46</sup>

(iii) In the case of identical chains, the lowest CT state always appears a few tenths of 1 eV above the lowest singlet excited state. In the context of photovoltaic applications, it is essential that the lowest CT state becomes  $S_1$ ; this can occur when chains of different chemical nature are mixed, for instance between MEH-PPV and a cyano-substituted PPV chain or between buckminsterfullerene and conjugated polymers.<sup>8</sup>

## Synopsis

In this Account, we have conveyed that quantum-chemical calculations can now address in a realistic way the nature of the lowest-lying excited states and the optical properties of conjugated polymer and oligomer chains of large size. Moreover, it has become possible to investigate in depth the impact of interchain interactions, well beyond the approximation of the point-dipole approach and Kasha's model. We are confident that these advances will open the way to the calculation of other important materials properties. For instance, the quantum-chemical investigation of the interactions taking place between chains of different chemical nature should allow one to define the basic features leading to electron-hole separation in the lowest-lying excited state(s) and the design of photovoltaic devices. The better grasp on interchain interactions should also result in the quantum-chemical determination of electron and hole mobilities within well-ordered structures (at least on a semiquantitative basis), thereby providing an access to transport properties.

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